

8 Magnetic and related properties of silicates and phosphates

8.1 Silicates

8.1.1 Orthosilicates

(See subvolume III/27I1)

8.1.2 Sorosilicates

(See subvolume III/27I2)

8.1.3 Cyclosilicates

(See subvolume III/27I3)

8.1.4 Inosilicates

8.1.4.1 Pyroxenes, pyroxenoids and silicates with related compositions

8.1.4.1.1 Crystal structures. Lattice parameters

Pyroxenes are chain silicates with the general formula $\{M2\}[M1](T2)O_6$. The structure of ideal pyroxene will be given below. Here, we analyse the main structures in which pyroxenes crystallize. The coordination polyhedra in all pyroxene structures include four-coordinated tetrahedra that contain the T cations and five- to eight-coordinated polyhedra that contain the M cations. There are five principal structure types which belong either to the orthorhombic or the monoclinic crystal system. The orthorhombic types crystallize in space groups Pbca or Pbcn. Monoclinic pyroxenes are called **clinopyroxenes**. Their space groups are C2/c, P2₁/c and P2/n depending on their chemical composition and genetic history. In the principal structure types there are two types of M sites labeled M1 and M2. In space groups C2/c and Pbcn these sites occur in special positions on twofold axes of rotation parallel to *b*, whereas in the Pbca and P2₁/c structures they occupy general position [81C1]. In the space group P2/n, reported for omphacites – Table 1 – there are four symmetrically distinct M sites, each of which occupies a special position on a twofold axis of rotation parallel to *b*. The T cations occupy general positions in all five space groups. There is only one symmetrically distinct T site in the C2/c and Pbcn structures, whereas there are two in the other three space groups. In the Pbcn and P2₁/c pyroxene structures, the more extended chain with the smaller tetrahedra is referred to as the A chain, whereas the more kinked chain with larger tetrahedra is referred to as the B chain. Except for the P2/n pyroxenes, there is only one type of tetrahedra within a given tetrahedral layer and adjacent tetrahedra along the chain are related by a *c*-glide. The P2/n pyroxene structure has only one type of chain, but adjacent tetrahedra within each chain are not equivalent [87P1]. The M2 polyhedra are five- to eight-coordinated depending on their occupancy by cations [97B1]. This site is eight-coordinated when it contains Ca or Na, but is approximately six-coordinated when containing the smaller Mn²⁺, Fe²⁺, Mg²⁺ or Li⁺ cations [87P1]. The six-coordinated M1 site is occupied by Mg²⁺, Fe²⁺, Fe³⁺, Al³⁺, Ti⁴⁺, etc. The four-coordinated T site is preferentially occupied by Si and to a minor amount also by Al³⁺, Fe³⁺, Ti⁴⁺ and others. A flow chart which gives a diagrammatic representation of the site allocation of the principal cations was presented [88M3]. However, because the distribution of cations among the M1, M2 and T

sites, in a given pyroxene, is partly a function of temperature, the accurate site occupancy must be obtained by structure determination.

The structure of pyroxenes can be described in terms of alternating tetrahedral and octahedral layers that lie parallel to the (100)-plane. Within the tetrahedral layer each T tetrahedra shares two corners with adjacent tetrahedra to form infinite chains parallel to the *c*-axis – Fig. 1 [81C1]. The base of each tetrahedron lies approximately in the (100)-plane and the repeat unit of each chain consists of two tetrahedra with the formula $(\text{TO}_3)^{2-}$. The coordination polyhedra of M cations share edges to form either laterally continuous sheets or wide bands polyhedra that are almost parallel to the *c*-axis within the (100)-plane. The structure types reported for most pyroxenes (C2/c, P2₁/c, Pbc and Pbcn) differ mainly in the manner in which the octahedral and tetrahedral layers are linked. The only other important reported space group is P2/n, which results from ordering of alternate M2 and M1 cations along *c* for omphacite pyroxenes [87P1]. In addition to pyroxenes with space group P2/n also space groups such as C2, P2 and P2₁ca have been reported, but, in general, such occurrences are limited. These space groups are all subgroups of either C2/c or Pbc [72B2, 74M2, 74O2, 81C1].

As above mentioned, the pyroxene structures differ mainly in the manner in which the octahedral and tetrahedral layers are linked. As result, the basic coordinations of both anions and cations vary only slightly [81C1]. Each symmetrically distinct T cation is coordinated by one O1, one O2 and two O3 oxygen atoms – Fig. 1a. The O1 anions are referred as apical oxygen atoms and the O3 anions as bridging oxygen atoms because they shared between adjacent tetrahedra in the chains. The M1 cation is coordinated by four O1 and two O2 anions that have a fairly regular octahedron configuration. The coordination of M2 varies from 5 to 8 and depends on the size of cation occupying the site. In the C2/c pyroxenes the O1 oxygen atom is coordinated by two M1, one M2 and one T cation; O2 by one M1, one M2 and one T cation and O3 by two M2 and two T cations in the Ca and Na series and by one M2 and two T cations in the Li series. In terms of classical Pauling bond strengths, O1 is approximately charge-balanced, O2 is highly underbonded and O3 is highly overbonded. The apparent charge unbalance is largely eliminated by variations in cation-oxygen bond distances [68C1, 69C1, 74F1, 77H2].

The topological differences between the four principal structure-types of pyroxenes can be evidenced by the I-beam diagrams [70T1, 73P1]. These depict the pyroxene structures as tetrahedral-octahedral-tetrahedral units whose infinite dimensions lie parallel to *c* – Fig. 2. The correspondence between the I-beam diagrams and the pyroxene-type structure of C2/c type is shown in Fig. 1b. In each I-beam two tetrahedral units point inward and are cross-linked by octahedrally-coordinated cations. The symbols within the I-beam units provide information on the symmetry and orientation of individual coordination polyhedra. The A and B tetrahedral layers refer to chains that are kinked by different amounts and/or those whose tetrahedra are distorted differently [81C1]. The absence of this notation indicates that the chains in adjacent layers within one I-beam unit are symmetrically equivalent and are related to twofold axes of rotation parallel to *b*. Two possible relationships between the tetrahedral chain and the adjacent octahedral strip were evidenced and referred to them as **S** and **O**-rotations. The completely rotated (i.e. O3-O3-O3 angle is 120°), **O** and **S**-configurations are based on close-packed arrangement of oxygen atoms with a tetrahedral to octahedral edge ratio of 1:1 – Fig. 3. Cubic close-packing of oxygen atoms produces a tetrahedral-octahedral configuration referred as an **O**-rotation, whereas hexagonal close packing produces an **S**-rotation [70T1]. In an **O**-rotation, the basal triangular face of the tetrahedra (approximately parallel *bc*) have an orientation opposite to the triangular faces of the octahedral strip to which they are linked through apical O1 oxygen atoms. In an **S**-rotation, the triangular faces of the octahedra and tetrahedra, that are joined through O1, have the same orientation [81C1]. The completely rotated **O** and **S** configurations represent the geometric extremes produced by rotating tetrahedra in the chains in opposite directions about imaginary lines passing through oxygen O1 and perpendicular to the (100) layer. Fully extended chains (O3-O3-O3 angle 180°) – Fig. 3c – are only possible in an ideal structure with a tetrahedral to octahedral edge ratio of $\sqrt{3} : 2$. In the structures of real pyroxenes, the tetrahedral chains approach and achieve full extension (180°), but they are never kinked by an amount as extreme as 120° [81C1]. The positive (+) and negative (–) symbols in the octahedral layers refer to the “skew”, “tilt” or direction of stagger of the layer with respect to a right-handed set of crystallographic axis. Within a single layer each octahedron has a pair of triangular faces that lie approximately parallel to (100). The apices of the upper and lower face of each pair are oriented in an opposite sense, but all triangular faces on one side of an octahedral layer point in the same direction – Figs. 1a and 3. A plus (+) or minus (–) skew is defined by the direction that the lower triangular face of the octahedron (in the *bc*-plane) takes relative to the *c*-axis. If the lower triangular face points in the direction + *c*, then the skew is said to be positive (+). If the lower triangular face points in the direction – *c*, then

the skew is negative (–) – Fig. 2. For the ideal structures with the ratio of tetrahedral to octahedral edge 1:1, there are only certain ways that the chains with **O** and **S**-rotations can be combined [70T1]. Geometrical modes for an ideal, completely-rotated pyroxene structure are shown in Fig. 4. In C2/c-type structure with octahedral stacking sequence +, +, +,, the tetrahedral chains may have **O**-rotations or all **S**-rotations but cannot have both. The reason for this is that in space group C2/c, the tetrahedral chains above and below the octahedral strip are symmetry equivalent and are related by a twofold axis parallel to **b**. The P2₁/c pyroxenes show an octahedral stacking sequence +, +, +, as in the C2/c structures, but having several significant differences [73P1]. The twofold symmetry axes that were present in the C2/c structure are absent in the P2₁/c structure. Thus, the two tetrahedral chains (A and B) can have different rotational aspects (both **O** and **S**-rotations). The A chains which have the **S**-rotations are not as kinked as the B chains which have **O**-rotations. The octahedral stacking sequence in Pbca pyroxene is +, +, –, –, +, +, and there are two symmetrically distinct tetrahedral chains, A and B. As mentioned above, the A chains are related by 2₁ axes parallel to **c** while the B chains are related by 2₁ axes parallel to **b**. For Pbcn pyroxene, the octahedral stacking sequence is +, –, +, –, and there is only one symmetrically distinct chain with **O**-rotation. In real Pbcn and Pbca pyroxene structures, linkage between adjacent octahedral and tetrahedral layers is achieved largely by extension or straightening of the A tetrahedral chains relative to B chains and by distortion of the cation polyhedra.

The P and N symbols between the I-beam describe the structural configuration around the M2 site [76S1] – Fig. 5. They refer to the relative orientations of triangular faces parallel to (100) of octahedra and tetrahedra that are joined laterally through O2 oxygen atoms. In an N configuration the basal triangles of the lateral tetrahedral chain point in a direction opposite to that of the octahedral faces to which they are joined through O2 atoms. In a P configuration the triangular faces of the tetrahedra and octahedra joined through O2 are similarly oriented. The N-P symbols describe thus the relative orientations between an octahedral layer and the tetrahedral chains above and below it [81C1]. They also provide information on the number of shared edges and size of the M2 polyhedron. The complete symbol for each M2 site includes two letters and a dot, which represents the position of the M2 cation. Each N indicates an edge shared between the M2 octahedron and a tetrahedron. The M2

N

octahedron in those structures with a • configuration is relatively small because it shares two edges with

N

P

tetrahedra. The • configuration produces the largest (most open) M2 coordination polyhedron and appears to be

P

the most stable arrangement because the polyhedron edges are shared.

The differences between the four main structures may be analyzed – Fig. 2. The monoclinic C2/c pyroxene structure has octahedral stacking sequence (+c/3)(+c/3)(+c/3)... and all **O** (or all **S**) rotations of the tetrahedral chains. There is only one type of chain, and those in adjacent tetrahedral layers are related by a twofold axis of rotation parallel to **b**. In this ideal model the tetrahedra and M2 octahedra share no edges. The orthorhombic Pbca structure has octahedral stacking sequence (+c/3)(+c/3)(–c/3)(–c/3)(+c/3)(+c/3)... which produces zero displacement parallel to **c** for each four octahedral layers. The M2 octahedron shares one edge with adjoining tetrahedra. The monoclinic P2₁/c structure has octahedral stacking sequence (+c/3)(+c/3)(+c/3)... It contains symmetrically distinct chains in adjacent tetrahedral layers: the A chain is **S**-rotated and the B chain is **O**-rotated. The M2 octahedron shares one edge with a tetrahedron as in the Pbca structure. The orthorhombic space group Pbcn has the stacking sequence (+c/3)(–c/3)(+c/3)(+c/3)(–c/3)... and one type of tetrahedral chain which is **O**-rotated. The M2 octahedron shares two edges with adjacent tetrahedra.

The stacking arrangements and possible space groups for pyroxenes were also examined by [79P1, 80L2]. In [79P1] a new classification was presented in which pyroxene structures were described in terms of various stacking sequences of layer-like subunits, the smallest of which are termed oxygen (O) layers. In [80L2] the [70T1] model for pyroxenes was further examined.

We mentioned already that the main topological features of pyroxenes can be described by the stacking sequences of the octahedral and tetrahedral layers. Only transformations involving symmetry changes between C2/c and P2₁/c and between Pbcn and P2₁cn have been observed that do not change these stacking sequences. The mechanism for stacking changes is not completely understood, but it clearly requires extensive changes in the M1-O and M2-O bonded interactions [75C2, 84S4, 85Y1, 91K1]. In [84S4] the importance of bonding to the M2 atom was recognized. The distribution of bonds associated with the M2 sites in various well-ordered

pyroxenes was further studied [03D2] by using a topological analysis of the electron density in the manner proposed by [98B3]. Parallel chains of edge-sharing M1O_6 groups and corner-sharing SiO_4 groups are the common skeletal components of pyroxene structures. One of the major differences between pyroxene structures is the bond distribution involving the M2 atom. It is always bonded to four O atoms ($2 \times \text{O1} + 2 \times \text{O2}$), that are also bonded to M1. However, the M2 atom can have up to four more bonds with neighbouring bridging O3 atoms. The existence and distribution of these bonds is a function of temperature, pressure and chemistry and correlates to some extent with the space group of a particular structure. Each M2 atom is bonded also to zero, one, two or four bridging O3 atoms. Each of the symmetries displayed by pyroxenes have their own bonding systematics and each pyroxene-to-pyroxene phase transition involves a change in bonding to M2. As a function of temperature and pressure, the bonding changes appear as a well-defined sequence of steps that can be related to the degree of distortion from the ideal closest packing of anions. It was proposed that the condition at which an individual phase transition occurs is related to M2-Si repulsion through a shared edge [03D2]. Thus, the bonding analysis should provide a qualitative method to interpret the behavior of all pyroxene structures over T , p and composition.

Ideal pyroxenes are hypothetical structures based on ideal closest-packed arrangements of O anions. They are modeled after observed pyroxene structures and have the general formula $\text{M}_2\text{M}_1\text{T}_2\text{O}_6$, where M2 and M1 represent octahedrally-coordinated cations and T represents tetrahedrally-coordinated cations. Two of the defining structural elements in ideal pyroxenes are chains of edge-sharing octahedra and corner-sharing tetrahedra that run parallel to c . These chains can be constructed by placing cations in the interstitial voids between closest-packed monolayers of anions stacked along a^* . The cation sites, in a given chain, are related to each other by a c -glide perpendicular to b . This is the only symmetry element common to all possible ideal pyroxene structures. The arrangements of anions in these ideal structures can be described as stacking sequences of closest-packed monolayers, denoted A, B and C in the traditional way. As example, the anion arrangement in ideal $\text{P}_2\text{1cn}$ protopyroxene can be described as $\text{A}^0\text{B}^1\text{A}^0\text{C}^1$, with octahedrally-coordinated (O) cations between AB and AC and tetrahedrally-coordinated (T) cations between BA and CA. An algorithm has been created to construct all possible ideal pyroxenes based on closest-packing stacking sequences of length 12 or less [03T1]. There are 81 ideal pyroxenes, based on stacking sequences of length 12 or less, yet commonly observed pyroxene topologies are based on only five different ideal pyroxenes. A pyroxene with a fixed composition may assume more than one of these topologies, depending on pressure and temperature. The only significant structural parameters that vary between ideal pyroxenes are M1-T and M2-T distances. It was shown that the repulsive forces between these pairs of cations distinguishes the energetics of the ideal pyroxenes and may be important in determining the topologies of observed pyroxenes [03T1].

The **pyroxenoids** are a family of silicate minerals with general formula MSiO_3 (where M can represent Na^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Al^{3+}) in which SiO_4 tetrahedra are corner-shared to form chains within the crystal structure. The corner-sharing occurs in one direction only, such that single chains are formed, the only structural differences between the various members of the pyroxenoid family being in the repeat pattern, and hence the periodicity of the basic unit of the single $(\text{SiO}_3)_\infty$ chain [75O2, 77T2, 80J1].

The five structures of silicates in the pyroxenoid group are shown schematically in Fig. 6a [80A1]. The simplest is the pyroxene configuration where SiO_4 tetrahedra are linked in a zig-zag fashion to produce a straight chain with a 5 Å repeat unit, containing two tetrahedra. The more complex structures can be considered as consisting of strips of the zig-zag chains, these strips being linked to one another by additional tetrahedra rotated by some 30° with respect to those of the pyroxene strip. Where the zig-zag strips are eight tetrahedra in length, ferrosilite III [66B1] results. Where the zig-zag strips are respectively six, four and two tetrahedra in length, pyroxmangite [59L1], rhodonite [59L2] and wollastonite [56M1] occurs. As in pyroxenes, the pyroxenoids consist of alternating tetrahedral and octahedral layers. The octahedral layers contain five- to eight-coordinated divalent cations, whose coordination polyhedra share edges to form continuous bands that run parallel to the tetrahedral chains.

The pyroxenoid structure can be analyzed considering linear arrays consisting of m and n regular-octahedra showing stacking vectors \mathbf{t} and $\bar{\mathbf{t}}$ – Fig. 6b [77T2]. The array n can be stacked on the m band by one of the above stacking vectors $(\mathbf{t}, \bar{\mathbf{t}})$, the location being denoted by n or \bar{n} respectively. The two sets of arrays – Fig. 6b – may be thus symbolized by mn and $m\bar{n}$, respectively. For example, if an infinite number of m are stacked one after another, based on stacking vector \mathbf{t} , an infinite, m octahedra wide band is obtained. This band may be denoted by $mmm\dots$ or m_∞ . The wollastonite band can be looked as consisting of triplet octahedra having

stacking vector t . This band may be described by $3333\dots$, or 3_K , for a stack of K triplets or 3_∞ for the infinite case. In case of pyroxene, pairs of octahedra are stacked alternatively based on t or \bar{t} . The band is hence denoted by $\bar{2}2\bar{2}2\bar{2}2\dots$ or $(\bar{2}2)_K$ for K repetition. The notations of octahedral bands in ferrosilite III, pyroxmangite and rhodonite – Fig. 6a – may be expressed by $\bar{3}322(\bar{2}2)_2$; $\bar{3}322(\bar{2}2)$ and $\bar{3}322$, respectively. In the pyroxenoids series each triplet of tetrahedra (P, Q, R) occurs on the same octahedron – Fig. 6a.

The obvious relationships between these various structures have been formalized [72L2]. Although a structural classification was made on the basis of the silicate chain, in [72L2] was suggested that the octahedral ribbons, to which two corners of every SiO_4 are bonded, are the main factor in influencing which particular chain repeat is adopted. A misfit between SiO_4 tetrahedra and MO_6 octahedra will occur unless average dimensions of octahedral and tetrahedral cations lie within a limited range. Outside the range, any misfit can to some extent be accommodated by distortions, particularly of the $(\text{SiO}_3)_\infty$ chains, but if the misfit becomes large a change in structural configuration will be required. Thus, in pyroxenoids, there is a progressively breaking of the basic, zig-zag pyroxene chain and consequently insertions of extra tetrahedra, as the size of the octahedral cations becomes greater. This cumulates in the wollastonite structure – Fig. 6a – where only pairs of the original chain remain, and any further increase in octahedral cation size necessitates an abandonment of the chain configuration and an adoption of a ring structure [80J1].

Both, in pyroxene and pyroxenoids, stacking faults and polytypic modifications have been observed [75I1, 75J1, 76J1]. The heat treated pyroxenoids indicate that their chain configurations can be varied [61D1, 79A1].

The physical properties of silicate minerals from pyroxene groups VIIID01 and VIIID02 [91N1] as well as of pyroxenoids or other synthetic and natural silicates having compositions close to those $(\text{MM}')\text{SiO}_3$ are now presented. The basic sequence of compositions given by [67B5, 88M3] will be generally followed, completed by other silicates as above mentioned. The main groups of silicates analyzed in this chapter are listed in Table 1.

I. (Mg,Fe) silicates

Enstatite, $\text{Mg}_2\text{Si}_2\text{O}_6$

Enstatite (En), $\text{Mg}_2\text{Si}_2\text{O}_6$, is a common mineral phase in many igneous and metamorphic rocks and the main phase in some low-voltage insulators, refractory and tough glass ceramics [91E1, 96M2]. Several $\text{Mg}_2\text{Si}_2\text{O}_6$ polymorphs have been evidenced from both natural and synthetic samples. **Orthoenstatite** (OEn) having space group Pbca is by far the most abundant. **Low clinoenstatite** (LCEn) having space group $\text{P}2_1/\text{c}$ is rare in terrestrial rocks, being found in meteorites, in unusual volcanic rocks [80K1] and as fine intergrowths in OEn of igneous metamorphic rocks [75B2]. **High-pressure clinoenstatite** (HPCEn) having space group $\text{C}2/\text{c}$ [92A1, 99R2, 01U1] is a non-quenchable high-pressure polymorph. **Protoenstatite** (PEn) having space group Pbcn [02J1] and high-temperature **clinoenstatite** (HTCEn) with space group $\text{C}2/\text{c}$ [93S3] have been reported as high-temperature (1 atm) polymorphs of $\text{Mg}_2\text{Si}_2\text{O}_6$, the latter being non-quenchable. A novel phase transition in orthoenstatite was reported [04J1]. It was suggested that the displacive phase transition would lead to a previously unreported **pyroxene structure with Cmca symmetry**. An isosymmetric phase transition from OEn to a new high-temperature orthorhombic phase was also reported [04M2].

The crystal structures of the enstatite polymorphs were studied: orthoenstatite [69M1, 69S1, 77H2, 82S1, 84O1, 86G3]; protoenstatite [52A1, 59S1, 63B1, 69S1, 71S3, 75C1, 82M5, 84M3, 95Y2], low clinoenstatite [60M1, 78T1]; high-temperature clinoenstatite [64B2, 69S4, 71S1, 82M5, 90G2, 91S2, 93S3, 95I3]; high-pressure clinoenstatite [90P1, 92A1, 94A1, 97H3, 99Y1].

A description of the crystal structures of Pbcn , Pbca , $\text{P}2_1/\text{c}$ and $\text{C}2/\text{c}$ polymorphs of enstatite was reported [81C1], as already mentioned. All enstatite structures can be regarded as different stacking sequences of alternating $[\text{SiO}_4]$ tetrahedral and $[\text{MO}_6]$ octahedral layers along a . In enstatites, the $[\text{SiO}_4]$ tetrahedra share corners to form single chains parallel to $[001]$. Of the two crystallographically distinct $[\text{MgO}_6]$ octahedra, M1 is smaller and nearly regular and M2 larger, more distorted. The lattice sites and thermal parameters for some enstatite structures are given in Table 2. Lattice parameters of representative silicates are listed in Table 3. The structure differences among the enstatite polymorphs primarily lie in the orientation of the M1 octahedra within the octahedral layers as viewed down the b -axis. In PEn, they point alternatively in opposite directions and in OEn they alternate every two layers. Such stacking sequences account for the common occurrence of (100) stacking faults in natural crystals characterized by the diffuse scattering parallel to a^* as observed by X-ray, electron and neutron diffraction studies [63B1, 69S1, 74S2, 82P1, 90S1, 91B1]. The stacking faults and mixed

layer sequences have been also observed directly by TEM [73K2, 75I1, 85R2, 85V1, 87N1]. The structure of protoenstatite (Pbcn) consists of two SiO_4 tetrahedra (A and B) [86G3]. Each forms a distinct chain, the c -axes by sharing oxygen atoms O3. Of the two tetrahedra, B is larger and as a consequence, the A chains are more extended than the B chains. In both chains, the bridging Si-O3 bonds are the longest of the three types (Si-O1, Si-O2, Si-O3) and vary the most. The Mg1 octahedra form the backbone of a zig-zag double octahedral strip of $[\text{MgO}_6]$ extended along the c -axis – Fig. 7. These octahedra are fairly regular. The Mg2 octahedra, which link the two tetrahedra-octahedra-tetrahedra (T-O-T) strip together, are highly distorted with two unusually long bonds. The inequality of two Mg2-O3 bonds from each other is in contrast with the situation found in HTCEn (C2/c) phase [74S1] where these two bands are equal. The variation observed in Si-O bond lengths within the silicate tetrahedra are caused by the differences in the primary coordination of the oxygen atoms and the proximity of magnesium ions to the silicon cations. The latter effect is most pronounced for bridging bonds of tetrahedron A. The smallest O-Si-O angle is the result of edge-sharing by the M2 octahedron and the A tetrahedron.

The high-temperature (1 atm) phase relations of $\text{Mg}_2\text{Si}_2\text{O}_6$ pyroxene polymorphs are generally uncertain. In [93S3] was shown by high-temperature TEM analyses that OEn transforms to HTCEn above $\approx 1200^\circ\text{C}$ at 1 atm, finding no evidence for PEn. Several reports concluded that at 1 atm PEn is the only stable phase between $\approx 1000^\circ\text{C}$ and the incongruent melting point of 1557°C [64B3, 82M5, 90S1, 91B1, 92B3, 99T1, 02J1]. These results were supported by molecular dynamics simulations [92M1] and lattice dynamical calculations [98C3, 00C3] which suggest that OEn transforms to PEn, not to HTCEn, at high temperatures. Some studies indicate that both HTCEn and PEn have a high-temperature stability field [95I3]. Intermediate phases have been described near the transition [90S2]. The temperatures reported for the transition of OEn to high-temperature phases ranges from 950°C [71S3] to 1230°C [93S3]. The different results on the stabilization of the enstatite polymorphs have been explained by variations in sample chemistry, grain size, thermal history, microstructures as well as by the difficulty of accurately identifying polymorphs by XRD [62S1, 63B1, 83S2]. The transition has been reported to be sluggish and partially reconstructive, requiring the breakage of Mg-O bonds [74S2]. In [04J1], by single crystal Brillouin scattering measurements on natural OEn, by increasing or decreasing temperature, a transition temperature in the range $1090(10) \leq T_c \leq 1175(10)^\circ\text{C}$ was shown and pronounced acoustic mode softening is evident above 900°C . No evidence for other transitions up to 1350°C was shown. The results were interpreted in terms of elastic softening ahead of a displacive phase transition. Before the displacive transition can occur, however, the elastic softening appears to trigger the observed reconstructive transition to the more stable PEn (or HTCEn) structure. It was suggested that the displacive phase transition would lead to a pyroxene structure having Cmca symmetry [04J1].

The C2/c – $\text{P}2_1/\text{c}$ transition in clinoenstatite and pigeonite occurs by rotations of tetrahedra within the pyroxene chains, to give a change in the coordination around the M2 cation site. There are close structural similarities between Pbca and $\text{P}2_1/\text{c}$ structures, in that the former is effectively alternating (100) twins of the latter on a unit-cell scale [91B1, 04J1]. The pattern of non-linear variations of tetrahedral chain rotation angles with temperature in the $\text{P}2_1/\text{c}$ structure, which gives rise to the change in coordination at the M2 site [72B1, 74S1, 84P1, 97A2, 02C1], is also displayed by orthopyroxenes [73G1, 76S1, 84S4, 95Y1, 95Y2]. In $\text{P}2_1/\text{c}$ structures, the rotation angles of the A and B chains converge, becoming identical in C2/c structures. The difference in rotation angles thus reflects the variation of the order parameter for the C2/c – $\text{P}2_1/\text{c}$ transition. The same convergence occurs in Pbca structures [95Y1] and the difference in chain angles also has the characteristic evolution of the order parameter [04J1]. Thus, it was proposed that the difference in chain angles would be the order parameter for the transition Cmca – Pbca [04J1]. By analogy with the structural relationship between $\text{P}2_1/\text{c}$ and Pbca pyroxenes, a Cmca pyroxene might be a unit-cell-scale twinned version of C2/c pyroxene containing only one symmetrically distinct tetrahedral chain.

As mentioned above, an isosymmetric phase transition from orthoenstatite to a new high-temperature orthorhombic phase of enstatite was observed at about 1230 K in molecular dynamics (MD) simulations for $\text{Mg}_2\text{Si}_2\text{O}_6$ [04M2]. Two high-temperature XRD studies [82M5, 95Y1] seem be relevant for the above mentioned proposal. At 1273 K, when increasing the duration of heating, the coexistence of orthoenstatite and protoenstatite was shown [82M5]. After four hours, the orthoenstatite reflections disappeared and a new type of reflections with shorter $d(001)$ spacing appeared. Based on lengthening of the c -dimension, it was suggested that the silicate chains are stretched like those in protoenstatite but the structural scheme is maintained as a whole and this structure is in transitional state between orthoenstatite and protoenstatite. In [95Y1] orthopyroxene $(\text{Mg}_{0.75}\text{Fe}_{0.25})_2\text{Si}_2\text{O}_6$ was studied and it was shown that the expansion rate of a and c parameters sharply increases

from 1200 to 1300 K without a discontinuity and that the difference of the kinking angles between A and B chains varies smoothly from 296 K to 1300 K, similar to the behavior expected in a second order phase transition. They suggested a transitional state between orthopyroxene and protoenstatite while protoenstatite has no stability field in the compositional range of the studied pyroxene. In [04M2], by using MD simulation, the isosymmetrical structural phase transition was observed. Orthoenstatite below and above the transition temperature $T_c \cong 1270$ K were referred as the **low-temperature orthoenstatite (LTOEn)** and **high-temperature orthoenstatite (HTOEn)**. From 300 K to 1220 K, all the cell parameters gradually increase with temperature. Around 1230 K, however, the a and c parameters and volume increase steeply, whereas b slightly decreases. The angles α , β and γ do not show any significant changes from 90° . These features seem to indicate that a first order transition occurs from LTOEn to HTOEn. This new phase, as OEn, has space group Pbca [04M2]. The transition is characterized by the switching of bonds between Mg atoms at the M2 sites and the coordinated O3 atoms.

There are numerous studies on the transition to different polymorphs of enstatite, but not all data are agreement, as already mentioned. There are many p - T phase diagrams for $\text{Mg}_2\text{Si}_2\text{O}_6$ pyroxenes [85I1, 87S1, 89I2, 90P1, 90P3, 94A1]. In Fig. 8 the data reported by [90P1] are plotted. In [00C3] the free energy and the relative stability of enstatite polymorphs were analysed theoretically. The calculated phase diagram is in qualitative agreement with experimental data.

Protoenstatite was reported to be a stable phase above $\cong 1273$ K at atmospheric pressure, and below that temperature, the orthoenstatite was considered to be stable [63B1, 64B2, 72K1, 74S2, 74S3]. The stability field of LCEn was studied [64S1, 65B1]. These authors reported that LCEn is stable at temperatures below $\cong 900$ K. The deformation experiments of OEn showed that shear stress affects the OEn – LCEn inversion boundary, suggesting the possibility that LCEn has no stability field under hydrostatic conditions [67R1, 68M4, 70C1, 71R1]. The authors of [72G2] succeeded in crystallizing LCEn below 839 K, which suggested that LCEn is the stable low-temperature form, although the possibility of metastable crystallization does not appear to be considered. The phase transition of LCEn to OEn has been determined at low pressures [72G2] and up to 4 GPa [65B1]. These studies give relative steep p - T slopes of 0.022 [72G2] and 0.0385 [65B1] GPa/K. Thus, the low-pressure experiments can be inferred to produce LCEn with space group $P2_1/c$ [60M1]. Then, at pressures $p > 5$ GPa, the phase boundary between LCEn and OEn was constrained to much higher temperature, and gives flat slopes of 0.0044 [77Y1] and 0.0031 [90P1] GPa/K. The HCEn – OEn phase boundary was expressed by the relation p [GPa] = 0.00454 T [K] + 1.673 [01U1]. The LCEn – OEn boundary was not as well constrained, but the data suggested that the invariant point where all three MgSiO_3 phases coexist is at 6.6 GPa and 820°C [01U1].

The PEn – LCEn inversion was described as essentially instantaneous, diffusionless, oriented, athermal, stress inducible and reversible, showing thus features of martensitic phase transformation. No shape deformation has, however, been observed in temperature induced transformation [69S1]. The transformation has a large negative volume change on cooling [88K3]. A change $\Delta V/V$ from 2 % at 910 K to 3 % at RT was observed [90S1]. The temperature of transition is greatly influenced by the crystallite size [62S1] and may be low as 500 K for 40 nm grains [89M4]. Theoretical considerations of the transformations of PEn to OEn, similar to those of the transformation of LCEn to OEn suggest that a variety of translational faults may occur in the resulting OEn [82P1]. Several translational faults are also expected from OEn crystallizing from melt or by recrystallization. So, depending on the density of the different faults, the diffraction patterns may be even more complex in these cases than for OEn inverted from LCEn. Mistakes in stacking sequences, indicating an isolated fault and the coexistence of various stacking disorders, resulting from the phase transition of the high-temperature phase PEn to LCEn, have been observed [93W1]. They consist of a sequential arrangement of some kind of SiO_3 tetrahedral chains with identical and opposite skews, respectively. These stacking faults possibly are formed during the early stage of nucleation of clinoenstatite on cooling. As a result, the new polytypes with repeat periods of 1.35 and 2.25 nm, respectively, perpendicular to the (100)-plane, were introduced by varying the stacking sequences in clinoenstatite matrix.

The OEn transforms directly to PEn at $\cong 1360$ K according to [74S2, 95Y2], whereas in [93S3] a direct transformation of OEn to HTCEn at $\cong 1473$ K was observed. According to [74S2] the transformation of PEn to coexisting OEn is much more sluggish and needs slow cooling rates to produce ordered OEn from PEn. Prolonged annealing between 900 K and 1200 K produces OEn via a slow LCEn – OEn inversion. In [90S1] the evolution with temperature of the crystal structure of a natural enstatite was studied in situ by ND. The

transformation behaviour is rapid for PEn – LCEn and sluggish for PEn – OEn inversion. The latter proceeds in two steps: OEn starts to grow slowly below 1180 K on cooling, whereas the main transformation takes place below 800 K simultaneously with the PEn – LCEn inversion. The athermal martensitic character was confirmed for the PEn – LCEn inversion. The diffuse background in the powder diagrams was related to stacking faults which irreversibly create during the transformation and affect the degree of order. In [91B1], for a natural enstatite, was also shown that the PEn to OEn/LCEn inversion is most probably triggered by preformed single stacking faults acting as nuclei and completed by a subsequent rapid growth process compatible with the martensitic nature of the transformation. New stacking faults were created during the transformation. The formation of “out-of-phase” OEn was shown. Single layer faults and PEn-type faults can be ruled out. The transformation mechanism suggested by [69S1] was confirmed. The origin of the transformation is not an elastic shear instability [91B1]. A transient increase of the elastic constant c_{55} was interpreted as a secondary effect caused by elastic strains in the process of the transformation. According to [80B2] the OEn structure may be understood formally as microtwinned LCEn on an unit cell scale.

The HTCEn (C2/c) to LCEn (P2₁/c) phase transition revealed to possess the characteristics of a first-order transition, due to the coexistence of both phases separated by the sharp interfaces and the nucleation-growth process [91S2]. The diffusionless and time independent reaction suggests that the transition occurs athermal, martensitically. The small or even negative thermal hysteresis and interface motion are in agreement with the above assumption.

The temperature dependences of the lattice parameters and of the volume at the transition, from OEn to PEn, are shown in Fig. 9 [95Y2]. At $T_0 = 1360$ K, the orthoenstatite (Pbca) transformed to protoenstatite (Pbcn). The discontinuous increase in c and the decrease in b , due to the ortho- to protoenstatite transformation, were associated with the drastic unkinking of the silicate chains, whereas the abrupt increase in a results from the large expansion of the M2-O distances along a , coupled with the increase in the out-of-plane tilting of the silicate tetrahedra. Stacking faults form in orthoenstatite prior to the phase transition, as well as in protoenstatite between 1360...1400 K. With increasing temperature the silicate B chain in orthoenstatite straightens faster than the A chain as the configurations of the SiA and SiB tetrahedra tend to become similar. At T_0 , the A and B chains with the O3-O3-O3 angles of 163.0° and 149.5°, respectively, in orthoenstatite, attain an identical angle of 168.4° in protoenstatite. The configuration of the silicate chain in protoenstatite resembles that of the A chain in orthoenstatite. The ortho- to protoenstatite transition does not affect the configuration of the M1 octahedron significantly, but results in a decrease of the mean M2-O bond distance by 0.043 Å and highly distorted M2 octahedron in PEn [99Y2].

Several mechanisms were proposed to analyze the ortho- to protoenstatite transition [61B1, 69S1, 70C1, 74S2, 75C2, 79P1, 83S2] and reviewed by [69S3, 79P1, 83S2, 87L1, 95Y2]. In the model of [61B1], the silicate chains and the M cations are displaced in the same directions by $(2/3)c$ and $(1/3)c$, respectively. In the model of [69S1, 70C1], the M cations are displaced as those in the [61B1] model, but the silicate chains are displaced in the opposite direction by $c/3$. In both models, the M1 and M2 cations in OEn are assumed to move to the corresponding positions in PEn. In [74S2] the models developed by [69S1, 70C1] were modified by assuming that the M1 and M2 cations are displaced in the same direction as the silicate chains and their positions are interchanged during the phase transition. In [95Y2], by using the unit-cell dimensions of PEn and the fractional coordinates of two M cations in OEn and PEn at T_0 , the total displacement calculated for the M cations based on models [61B1, 69S1, 70C1] was 3.821 Å, whereas in the model of [74S2] it was 3.215 Å. If only the displacements of the M cations were considered, the [74S2] model is apparently energetically more favorable.

Hydrostatic high-pressure experiments using a multi-anvil cell high-pressure apparatus have shown that clinoenstatite has a stability field under high pressures and high temperatures [77Y1, 90P1, 91K1]. Subsequent high-pressure in situ single crystal X-ray diffraction, at RT, using a diamond anvil cell have shown that LCEn (P2₁/c) transform between 6.98 GPa and 7.93 GPa, upon compression to non-quenchable HPCEn with space group C2/c [92A1]. The HPCEn-phase was also reported at pressures above 5 GPa, at RT, by Raman studies [92C2] and the single crystal compression study of FeSiO₃ [94H2]. The different dp/dT slopes were attributed to different experimental conditions [91K1]. According to [91K1], the HPCEn can be stabilized by either hydrostatic pressure or differential stress and the latter tends to shift the transformation boundary defined under hydrostatic condition to low pressures. Similar phase relations with a low pressure P2₁/c and HPCEn were determined for samples containing Mn²⁺, Cr³⁺, Al³⁺, etc [92A1, 98A4, 00A2, 01U1]. According to [99S1] the transition LCEn – HPCEn is accompanied by a volume reduction of 2.5 %. The β -angle of the C2/c phase ranges

from 101.4° to 101.7° showing almost no variation with p and T and is about 8° smaller than that of the HTCEn phase. This confirms the suggestion [94H2] that the two clinoenstatite phases differ at high p and T .

The HPCEn occurs below 15 GPa at 1000°C and decomposes to modified spinel and stishovite at higher pressure. In [88K1] CEn was also observed as first liquidus phase in the $\text{MgSiO}_3 - \text{Mg}_2\text{SiO}_4$ system at 20 GPa and 2200°C. A phase diagram for MgSiO_3 was proposed [94A1] based on some of the above cited data and additional experimental constraints [86K2, 92W2, 95L3, 97W3].

The lattice parameters of some enstatite polymorphs are listed in Table 3.

The elastic properties of MgSiO_3 orthopyroxenes were studied [93W2, 94A1, 94H1, 95Z1, 02A1]. The compression experiments revealed that K'_0 has an anomalously high value [94A1]. This high K'_0 value is also consistent with the simultaneous high-pressure and temperature measurements of MgSiO_3 orthopyroxene [95Z1]. In [94H1] was shown that this high value of K'_0 is caused by the initial rapid compression of the long M2-O3 bond within the structure, together with the rotation of the chains of essentially rigid SiO_4 tetrahedra. The elastic properties of some enstatite polymorphs are listed in Table 4.

Molecular dynamics (MD) simulations, as function of increasing pressure, starting from the Earth's upper mantle phase of enstatite MgSiO_3 , reveals successive phase transitions, first to a new novel intermediate phase and then to the lower mantle perovskite phase [00C2]. While the silicate units are in tetrahedral coordination in the enstatite phase, they are five-coordinated in the new intermediate phase and the octahedral coordination in the lower mantle perovskite phase. The local structure of the five-coordinated polyhedra in the simulated phase of MgSiO_3 is comparable to that observed in five-coordinated phase of CaSi_2O_5 [96A1]. Molecular dynamics calculations have been used to determine the crystal structures of MgSiO_3 (enstatite, clinoenstatite, garnet, ilmenite, perovskite) by using an interatomic potential model which is composed of pairwise additive Coulomb, Van der Waals and repulsive interactions [96M3]. The MD simulations were quite satisfactory in reproducing the experimentally determined values.

Computer modeling of MgSiO_3 was performed. Computational techniques based on nearest-neighbour interactions were employed to predict structural parameters [78I1, 84M2]. Lattice dynamical calculations using empirical potentials provided estimate of elastic properties [87M2, 88C1] as well as defect energies [86W1] and ion immigration paths [88M2].

Thermal expansivities are listed in Table 5.

For crystal structure of pyroxenes see also [63D1, 64P1, 71D3, 74K2, 74M2, 74W1, 75W2, 76G2, 76L2, 78I1, 79I1, 80B3, 81C2, 82O3, 86M1, 87T1, 89O1, 91Y1, 92S6, 93K1, 95A1] and for pyroxenoids [61D1, 79A1, 81S1].

For elastic properties see also [80R1, 87H4, 98C4].

MgSiO_3 perovskite

The (Mg, Fe) SiO_3 perovskite phase was correlated with the 650 km mantle seismic discontinuity [76A2, 77L3, 79Y1]. The MgSiO_3 perovskite was also synthesized at 30 GPa and 1000°C in a diamond anvil press coupled with laser heating [75L2]. X-ray studies were made [74L1, 78I1, 78Y1, 80M1, 82Y1]. The crystal structure of MgSiO_3 perovskite, at RT, belongs to the orthorhombic system with space group Pbnm. This deviates significantly from the ideal cubic perovskite structure through the tilting of the regular SiO_6 octahedra and the large distortion of the MgO_{12} dodecahedron [83S3]. X-ray diffraction studies [87H6] on a single crystal synthesized by [86I1] show that the structure is fundamentally obtained by substituting Mg for Ca and Si for Ti in the perovskite structure (space group Pbnm). Both MgO_{12} and SiO_6 polyhedra occur in the structure and each polyhedron shares all edges with the others. SiO_6 octahedra share all corners. Mg and Si atoms are assumed to be completely ordered. The Si atom is located at the center of the SiO_6 octahedron and is in the center of symmetry. The small variations in Si-O distances and O-Si-O angles (88.5°...91.5°) show that the SiO_6 octahedron is much more regular than those of ilmenite-type MgSiO_3 (see below). The position of the Mg atom deviates from the center of the MgO_{12} polyhedron – Table 2. Geometrically, the deviation results in a wide range of Mg-O distances (2.014...3.120 Å) and O-Mg-O angles (52.19°...70.89°). An ideal value of the O-Mg-O angle is 60° for a regular MgO_{12} polyhedron. The variations of O-O distances in the MgO_{12} polyhedra is the same as those in the SiO_6 octahedra because both polyhedra share all of their edges with each other. The average value of the nearest-neighbour O-O distances in the structure is within ± 0.04 Å and for the second-nearest-neighbour O-O distances are ± 0.8 Å. These features contrast with oxygen arrangements in ilmenite-type MgSiO_3 in which the

first-nearest-neighbour O-O distances show a wide range of values. The small range of nearest-neighbour O-O distances and the large range of the second-nearest neighbours is due to a rotation and tilting of rigid, nearly regular, SiO_6 octahedra in the structure – Fig. 10. The rotation around the O-Si-O bond, along the *c*-axis is about 11.2° and the angle of tilt, measured against *c*, which is equivalent to the rotation around the *b*-axis is about 16.7° . The rotation and tilting greatly distort the MgO_{12} polyhedra and result in a structure that somewhat resembles the rigid and nearly regular SiO_4 tetrahedral framework of silicate under ambient pressure.

The effect of pressure on the perovskite structure was analyzed [78Y1, 79O4, 82Y1, 87K3, 90R3]. The SiO_6 octahedra were tilted as effect of pressure [87K3]. The polyhedral bulk moduli of SiO_6 and MgO_8 are 3.8 Mbar and 1.9 Mbar, respectively (see also Subvol. III/27I 1).

The possible phase transitions of MgSiO_3 perovskite were studied [92H1]. Attempts to produce samples for X-ray diffraction under mantle pressures have met with difficulty [87H4, 90R3, 91M1]. However, there has been evidence for an orthorhombic-tetragonal-cubic series of transitions from observations of twinning in the orthorhombic phase after quenching from high temperatures [92W1]. In [99S1] was shown that the orthorhombic perovskite transforms to a cubic structure at 82(3) GPa and temperatures above 1180 K. In Fig. 10b is shown a view down the axis of the ideal cubic and orthorhombic perovskite structures [00W1]. The difference between the two structures is due to the change of roughly eight-coordinated sites. The evolution of the structure may be analyzed comparatively with that of CaSiO_3 which crystallizes in a cubic lattice at RT. The radius of Mg^{2+} is somewhat smaller than that of Ca^{2+} , and to make cubic perovskite stable, the Mg-O bond distance needs to decrease and the electron clouds of Mg^{2+} and O^{2-} need to overlap much more. Accordingly, this can decrease the space of MgO_8 site. As result, MgSiO_3 should deviate from the cubic symmetry and exists with an orthorhombic structure. When increasing the temperature, thermal expansion enlarges the MgO_8 site to almost the same as that of Ca^{2+} occupancy, and the structure transforms to the cubic one.

The dissociation reaction: MgSiO_3 (perovskite) \leftrightarrow MgO (periclase) + SiO_2 high pressure, was studied at 82(3) GPa by in situ heating to temperatures between 300 and 1780(5) K [98S1]. The orthorhombic perovskite changed to a pseudo-cubic phase between 1280...1485 K followed by a breakdown to the oxide mixture which was observed to grow at temperatures between 1600...1700 K. Orthorhombic perovskite was recovered upon cooling at 1140 K [98S1]. MgSiO_3 orthorhombic perovskite shows a crystalline to amorphous transition near ambient pressure, when decompressed from their high-pressure stability field and heated up to $\cong 150^\circ\text{C}$ [92D2, 95H1]. This transition has been theoretically analyzed and it was concluded that amorphisation is initiated by a thermally activated step involving a soft polar optic mode in the perovskite phase at the Brillouin zone center [95H1].

The density-functional simulation was used to calculate structural properties of MgSiO_3 perovskite [96W3]. The observed orthorhombic phase (Pbnm) and two hypothetical high-temperature phases, cubic (Pm3m) and tetragonal (I4/mcm), were considered. The melting temperature of MgSiO_3 perovskite at high pressures was studied by using an empirical melting equation combined with the assumption of a boundary phase existing at the melting point [00W1]. This study indicates that MgSiO_3 perovskite has a cubic structure near the melting boundary and that the melting temperature is in general agreement with experimental data [98Z1].

The thermal expansion coefficient of orthorhombic MgSiO_3 perovskite between 298...381 K is $2.2(8) \cdot 10^{-5} \text{ K}^{-1}$ [89R2] – Table 5. Above 400 K, the single crystal becomes so multiply twinned that the cell parameters can no longer be determined. From 77...298 K the thermal expansion coefficient is $1.45(9) \cdot 10^{-5} \text{ K}^{-1}$. The thermal expansion is anisotropic; the *a*-axis shows the most expansion in this temperature range ($\alpha_a = 8.4(9) \cdot 10^{-5} \text{ K}^{-1}$) followed by *c* ($\alpha_c = 5.9(5) \cdot 10^{-6} \text{ K}^{-1}$) and then *b*, which shows no significant change in this temperature range. In addition, the distortion (i.e. the tilting of the SiO_6 octahedra) decreases with increasing temperature. Predictions of thermal expansion coefficients obtained in the $77 \text{ K} < T < 298 \text{ K}$ temperature range from quasi-harmonic theoretical models are presented in Table 5. In [89C3] was pointed out that there is significant error in their earlier calculation [87C2] because of the occurrence of a number of unphysical imaginary frequencies in the PIB model. Calculations were done by [89H3] to remove the effect of these unstable modes on thermodynamic properties of MgSiO_3 perovskite. The SSMEG models [87H4], show the better agreement with experimental data [89R2]. In [88N1] the vibrational modeling approach of [79K1] was used to calculate the entropy of MgSiO_3 perovskite. In [89H3] the expansion coefficients were calculated by using the observed shifts in the MIR spectra [87W1]. The calculated volume of MgSiO_3 perovskite under pressure and temperature was in close agreement with experimental data [98S2]. Models of ab initio potentials have been applied to MgSiO_3 perovskite [85W3, 87C2, 87H4, 87W3, 89H2, 89H3]. The latter study [89H3] was

in particular successful in reproducing experimental values of normal pressure structure parameters and elastic moduli.

In [82Y1] the following order for compressibilities of lattice parameters in MgSiO_3 perovskite was determined: $a > b \approx c$. In [87K2] was found $c \approx b \approx a$ and [87K3] reported the sequence $c > a > b$ for a single crystal. In [89M2, 90Y1] was found $c > a > b$ and in [90R3] $c \approx a > b$ – Table 4b. According to [90R3], between normal pressure and 5 GPa, the primary response of the structure to pressure is compression of the Mg-O and Si-O bonds. Above 5 GPa, the SiO_6 octahedra tilt particularly in the (bc) -plane. The distortion of the MgO_{12} polyhedra increases under compression.

The elastic moduli were reported [87K3, 89H3, 90R3, 90Y1]. Some elastic properties are listed in Table 4a.

The results of lattice static simulations on the surface structure of Fe^{2+} and Ca^{2+} -doped orthorhombic MgSiO_3 perovskite were studied [05A2]. The energies of the doped surfaces are lowered with respect to the pure surfaces. The calculations suggest that Fe^{2+} and Ca^{2+} ions tend to segregate onto the crystal surface.

For crystal structure of MgSiO_3 perovskite see also [77M1, 79O5, 87H5, 89H2, 93F1, 93S5]. For MgSiO_3 garnet see [66M1, 69P1, 77A1, 85K1, 85K2, 89H1] and for $(\text{Mg, Fe})\text{SiO}_3$ garnet see [67R2] as well as chapter 8.1.1.5 (subvolume 27I 1).

MgSiO_3 ilmenite

MgSiO_3 ilmenite is a high-pressure polymorph of enstatite that is characterized by a relatively narrow stability field in the 21...25 GPa pressure range, at 1100°C, bounded at low pressure by the β - or γ - Mg_2SiO_4 + stishovite assemblage stability field and at high pressures and temperatures by the MgSiO_3 perovskite stability field, and marginally at high temperatures (> 2200 K) by the majorite stability field [76L1, 77I2, 81I1, 82I2, 85I1, 87S3, 89I2, 93Y1]. The MgSiO_3 ilmenite was first synthesized by [74K1]. The MgSiO_3 ilmenite crystallizes in a trigonal structure having space group $R\bar{3}$ [74I2, 76L1]. The structure was refined later [82H1]. The structure is obtained by substituting Mg for Fe and Si for Ti in ilmenite structure. The Mg and Si atoms are completely ordered – Fig. 11. The arrangement of oxygen atoms is based on a distorted hexagonal closest packing having a wide range O-O distances. In particular, the edge shared O-O distance between two SiO_6 octahedra is shortest, and it is shorter even than the O-O distance of the shared face between MgO_6 and SiO_6 octahedra.

The temperature dependence of the lattice parameters is nearly linear [88A3]: $a [\text{\AA}] = 4.720 + 3.346 \cdot 10^{-5} T [\text{K}]$; $c [\text{\AA}] = 13.52 + 1.346 \cdot 10^{-4} T [\text{K}]$. The compression of MgSiO_3 ilmenite is anisotropic with the c -axis being twice as compressible as the a -axis [96R2]. Compression along the c -axis is achieved through flattening of the M^{2+}O_6 octahedron, which is more compressible than the M^{4+}O_6 octahedron, causing a reduction in the $\text{M}^{2+}\text{-M}^{4+}$ distances across face-sharing octahedra and $\text{M}^{4+}\text{-M}^{4+}$ distances across a vacant site. On the other hand, compression of the a -axis causes a reduction of the $\text{M}^{2+}\text{-M}^{2+}$ and $\text{M}^{2+}\text{-M}^{4+}$ distances across shared edges within the monocationic layer. The latter distances are less compressible in ilmenite because of the large $\text{M}^{4+}\text{-M}^{4+}$ repulsion.

MgSiO_3 ilmenite has been theoretically studied by using a periodic ab initio Hartree-Fock method in order to characterize the chemical nature of the Si-O bond [92N1]. Density of states and electron charge density maps have been calculated. The Si-O bond appears to be more covalent in MgSiO_3 ilmenite than in SiO_2 stishovite, whereas the oxygen atoms are more ionic and more polarized in ilmenite structure because of the presence of Mg ions. The result of ab initio periodic Hartree-Fock calculations of ilmenite MgSiO_3 , obtained using all electron and core-pseudopotential basis sets were extended. In this framework the effects of two basis sets on the structural properties (unit-cell volume and compressibility) and on the electronic properties were analyzed [93N1]. The pseudo-potentials used to describe core electrons accurately reproduce the all-electron results.

Hydrous MgSiO_3 akimotoite (ilmenite-type structure), containing 350 ppm (wt) H_2O as hydroxyl, was synthesized at 19 GPa and 1300°C [02B1]. In [96R2] the compression of akimotoite was found to be anisotropic with the c -axis being twice as compressible as the a -axis. This is due to the alternating stacking of MgO_6 and SiO_6 octahedral layers normal to the c -axis, which causes the compression along the c -axis to be achieved through flattening of the more compressible MgO_6 octahedra, whereas compression along the a -axis is controlled by the compressible SiO_6 octahedra. In [02B1] was shown in hydrous MgSiO_3 akimotoite that the bulk modulus is not the only factor controlling the compressibility of hydrogen bonds. It was concluded that the relative compressibility of hydrogen bonds within the structure is governed by a combination of the directionality of hydrogen bonds and the anisotropy of compression, whereas the rate of compression is a function of the bulk modulus (see also section 8.1.4.1.12).

FeSiO₃

The phase diagram of FeSiO₃ (Fs) shows also the presence of polymorphs: **OFs orthoferrosilite** (s.g. Pbca) and **CFs clinoferrosilite** (s.g. P2₁/c and C2/c) [65A1, 65L1, 66B2, 94H2]. At pressures below 4 GPa, [65L1] reversed a phase boundary between orthoferrosilite OFs (Pbca) and low clinoferrosilite LCFs (P2₁/c) [65L1], whereas [65A1] reported the recovery of the same LCFs phase, from experiments that would lie in the stability field if the boundary of [65L1] was extrapolated at high pressure. The low clinoferrosilite LCFs (P2₁/c) transforms to **high-pressure clinoferrosilite**, HPCFs [81S2, 83S2, 84S4, 85S2, 90P1, 94H2]. The OFs – HPCFs boundary was determined [97W3]. There is also a transition from OFs to **high-temperature clinoferrosilite** HTCFs (C2/c) [76S1].

A partial view of projection along *a** of the orthoferrosilite (OFs) structure is given in Fig. 12. The M1 and M2 sites are occupied by Fe²⁺, and, at room temperature, both are six-coordinated with the M1 coordination polyhedron being the smaller and more regular of the two. There are two symmetrically independent tetrahedral sites, confined to A and B chains. The B chain is more kinked and more distorted than the A chain. The tetrahedra of both chains are completely occupied by silicon. There are six crystallographically nonequivalent oxygen atoms in the structure. O1A, O2A, O1B, and O2B are nonbridging oxygen (each bonded only to one Si) and O3A and O3B are bridging oxygen (each bonded to two Si atoms) – Table 2. The nonbridging oxygens connect tetrahedral chains and M1 octahedral strips vertically along *a** and laterally along *b*, whereas the bridging oxygens connect individual tetrahedra in the silicate chains.

The high-temperature studies show a rapid transition from OFs to HTCFs that was reversible and topotactic [76S1, 81S2]. The crystal structure of HTCFs, after the transition at 1025°C, is of space group C2/c [84S4, 85S2]. The Fe1 cation is always coordinated by six oxygens through the studied temperature range 24...1050°C. However, the number of Fe2-O distances less than 3.00 Å (a value arbitrary chosen [72S1, 73S1, 76S1]) changes from six, at 24°C, to seven, between 600°C and 800°C, and back to six at high temperatures. In the HTCFs structure, the coordination number of Fe2 is six. The polyhedral volume calculation reveals that the six-coordinated M1 polyhedron (13.40 Å³) is larger than the six-coordinated M2 polyhedron (11.93 Å³) in the HTCFs, at 1050°C. This is related to the large distortion of the Fe2-polyhedron in the high-temperature clinoferrosilite structure.

The LCFs with space group P2₁/c transform to a HPCFs with space group C2/c at high pressure [94H1]. The transformation has been reversed at RT and pressures between 1.48 and 1.75 GPa. The transformation is of first order in character and is accompanied by 3 % decrease in the volume of the unit cell. The structure of this C2/c polymorph has been refined at 1.87 GPa [94H1] and contains a single, symmetrically distinct silicate tetrahedral chain with a mean Si-O bond length of 1.63 Å and a chain extension angle (O3-O3-O3) of 138.4(9)°. The M1 and M2 cation sites are octahedrally coordinated with mean bond lengths of 2.14 and 2.18 Å, respectively. This phase is the Fe analogue of the C2/c structure found in MgSiO₃ at *p* > 7 GPa [92A1]. The high-pressure C2/c structure of ferrosilite differs from the C2/c phase found at elevated temperatures with a *β* angle about 7° smaller and a silicate chain more kinked than in the high-temperature form. There is no significant difference in shape or size of the M1 sites in the Pbca and C2/c phases stable at high pressure, the M2 site being somewhat less distorted in HPCFs. In both phases, the M2 cation is octahedrally coordinated with identical average M2-O bond length and polyhedral volume. Within experimental uncertainties, the tetrahedral sites in both pyroxene polymorphs are identical in their average Si-O bond lengths and polyhedral volumes. The transformation P2₁/c – C2/c is nonquenchable, so that the C2/c polymorph reverts to the P2₁/c form on pressure release.

The transformation between orthopyroxene and the HPCPx occurs at pressures and temperatures characteristic of the earth in upper mantle [65A1, 90P1], with the metastable extension of this boundary in the FeSiO₃ system failing at ≅ 1 GPa at ambient temperature. Orthoferrosilite, thus exist metastably with respect to the HPCFs (C2/c) phase above this pressure. In [96H4] single crystals of synthetic OFs were compressed in a diamond anvil cell to ~5.8 GPa in order to determine the range of their metastability and to establish whether transformation to high-pressure C2/c phase is indeed possible at ambient temperature. At *p* ≅ 4.2 GPa, the OFs transforms to a new phase. The final product is predominantly LCFs (P2₁/c) with a few small islands of metastable HPCFs. The presence of high-pressure clinoferrosilite and the fact that this phase transforms readily to LCFs upon decompression below ≅ 1.5 GPa in hydrostatic conditions, seems to confirm that the HPCFs was formed by the breakdown of OFs at ≅ 4.2 GPa [96H4]. According to [96H4] the sequence of transformations is: OFs(Pbca) $\xrightarrow{p > 4.2 \text{ GPa}}$ HPCFs(C2/c) $\xrightarrow{p < 1.5 \text{ GPa}}$ LCFs(P2₁/c). The transformation of OFs to HPCFs (C2/c) is

highly time-dependent and first-order in character, accompanied by a 2.6 % volume discontinuity. The morphology and microstructure of the recovered transformation products is indicative of a reconstructive transformation similar to that proposed for other OPx to CPx transformations. The thermal expansion of MSiO_3 (M = Fe, Mg) ortho- and clinopyroxene were analyzed [97H2] – Table 5.

CoSiO₃

The crystal structure of CoSiO₃ orthopyroxene is stable under high pressure and is of space group Pbca [65A1]. Single crystals were synthesized from equimolar mixtures of Co₂SiO₄ olivine and quartz at 1300°C and $p = 5$ GPa for 20 min.

MSiO₃ (M = Mg, Fe, Co); electron density distribution

The net atomic charges and electron density distributions of synthetic orthopyroxenes, MSiO_3 (M = Mg, Fe, Co) are shown in Table 6 [80S1, 82S1]. An average charge of cobalt in CoSiO₃ has been found to be + 0.95 and that of iron in OFs is + 1.12. These values are smaller than + 1.82 for Mg in OEn. In the same species of orthopyroxenes, the cation at M1 tends to be more ionic than that at M2. In the case of CoSiO₃, the former has a charge + 1.3(1) and the latter + 0.6(1). The net charges determined for Si in the above orthopyroxenes yield an average value + 2.25. Thus, the transition metals contained in orthopyroxene solid solutions, will be preferentially located at the M2 site because the electrostatic site energies appear to be one of the governing factors for atomic site preference. In addition, the polyhedra about M2 of orthopyroxenes are larger compared to those of M1. It follows that the M2 site is strongly favorable for transition metals whose ionic radii are larger than that of Mg, as experimentally evidenced [77H2].

Residual Fourier peaks occurring between Si and bridge oxygen atoms are significantly different in peak height and distances from Si, as compared to those between Si and non-bridge oxygen atoms – Fig. 13 [82S1]. Those occurring around Fe atoms at the M1 and M2 sites in OFs, each having point symmetry 1, have features which are similar respectively to those around M2 and M1 of fayalite, Fe₂SiO₄ – see Chap. 8.1.1.3 (subvolume 27I 1). A pair of positive peaks appears around Fe at the M1 site at the distances of 0.61 Å and 0.64 Å from the center of the atoms. The two peaks and the center of Fe are nearly in the same line which is roughly parallel to the *c*-axis and passing through the centers of a pair of triangular faces of the octahedron. In case of Co OPx, there are positive and negative peaks around Co at the M1 site. The positions of the positive peaks at the M1 site and the center of Co are almost coplanar with the plane parallel to (100) – Fig. 13c. Major negative peaks are approximately in a plane parallel to (010) and passing through the center of Co. The residual peaks around Co at M2 are similar to those of Co at the M1 site. In the difference Fourier map of OEn, no peaks with heights greater than $|\pm 0.3| e/\text{\AA}^3$ were observed around the Mg atoms.

For a review of electron density distribution in MSiO_3 (M = Fe, Co, Mg) see [90T1].

Fe_xMg_{1-x}SiO₃

Under ambient conditions, Fe_xMg_{1-x}SiO₃ orthopyroxenes (OPx) crystallize in orthorhombic structure having space group Pbca [30W1, 35I1, 65G1]. The A and B chains running parallel to *c* are kinked and kinking angles (O3-O3-O3) deviate considerably from 180°, the characteristic value for a fully extended chain. The B chain is kinked by $\approx 20^\circ$ more than the A chain. At high temperatures, Fe_xMg_{1-x}SiO₃ OPx transforms reconstructively to different phases depending on the chemical compositions [66P1, 69S4, 69S5, 84S4, 91S2]. The enstatite (Mg-rich) transforms to the protoenstatite with space group Pbcn at ≈ 1300 K [74S2, 82M5], whereas ferrosilite (Fe-rich) transforms reversibly and topotactically to clinoferrosilite with space group C2/c, at 1300 K [66P1, 69S4, 81S2, 83S2, 84S4, 85S2, 91S2]. Intermediate composition with $x = 0.13$ transforms to C2/c CPx [69S5, 85S2] but the transition is irreversible and nontopotactic. The transition temperatures decrease from ≈ 1500 K to 1250 K with increasing Fe content [71P1]. In Mg_{0.31}Fe_{0.67}Ca_{0.015}SiO₃ clinohypersthene the presence of a first-order transition from space group P2₁/c to C2/c at 998(10) K was shown [74S1]. Upon cooling, the C2/c phase (HTCPx), undergoes a reversible and displacive transition to LCPx [69S5, 72S1, 81S2, 83S2, 85S2] whereas protoenstatite transforms to either P2₁/c clinopyroxene or a mixture of P2₁/c CPx and OPx, depending on cooling rates [74S2, 87L1, 90S1, 91B1]. Both Fe_xMg_{1-x}SiO₃ orthopyroxenes and low-pressure clinopyroxenes transform at high pressures to unquenchable high-pressure clinopyroxene [90P1, 92A1, 94H2, 96H4, 97W1]. The temperature induced orthorhombic (Pbca) – monoclinic (C2/c) pyroxene transition was also analyzed [81S2].

The intercrystalline Fe^{2+} - Mg^{2+} exchange between two crystallographically nonequivalent octahedral M1 and M2 sites was studied, in many cases, for modeling the thermal history of the host rocks. The thermodynamics and kinetics of the Fe^{2+} - Mg^{2+} exchange reaction have been extensively investigated in Pbca orthopyroxenes [70V2, 71S2, 73S1, 76S1, 89S2, 91M2, 93S6, 96G1, 97K2, 99S2] as well as in C2/c clinopyroxenes [76M2, 82D2, 82G1, 91M3]. Various approaches were used to calculate the ordering-disordering kinetic constant in minerals [01B1]. Several authors have investigated theoretical kinetic models of the two site order-disorder process [35B1, 55D2, 67M2, 69M3, 82G1]. In [67M2, 69M3] the theories of [35B1, 55D2] based on a two cation exchange reaction in a binary alloy were modified and an explicit solution for binary solid solution-type minerals with two non-equivalent sites was found. The model by [67M2, 69M3] has been widely applied to describe experimental ordering-disordering data in orthopyroxenes [70V2, 71S2, 81B1, 88A2, 89S2, 92S5, 93S6]. A more general approach to calculate kinetic constants of a sub-solidus reaction is the Ginzburg-Landau theory, which describes a quite complex transition behavior over a wide range of temperatures and compositions [88S1, 89C2, 90C1, 90C2, 91S1, 96R1]. In [89C2] was demonstrated that application of the Landau and associated Ginzburg-Landau kinetic theory has practical implications in the treatment of cation ordering transitions. Another kinetic model was proposed [96S1] and it was stressed that caution must be used when applying the model [67M2, 69M3] to a multicomponent solid system, which cannot be simplified as binary solid solutions in general sense. An explicit form of the ordering-disordering in minerals was presented [96S1] with two nonequivalent sites and for two cation ordering-disordering in multicomponent solid solutions.

As already mentioned, in OPx, the octahedral M1 site is smaller and nearly regular, whereas the M2 site is larger and more distorted. Long-range order-disorder occurs between divalent Mg^{2+} and Fe^{2+} ions in the two M sites with Fe^{2+} preferring the larger M2 site [61G1]. The distributions of Mg^{2+} and Fe^{2+} vary as function of temperature (becoming more ordered at low temperatures) and chemical composition. Fe^{2+} - Mg^{2+} order-disorder in natural and equilibrated orthopyroxenes have been investigated experimentally [65G1, 66W1, 67B1, 67B2, 67E2, 67G1, 69S2, 69V1, 70V2, 71B3, 71S2, 73R1, 73S1, 77G1, 81B1, 85D2, 86S3, 86W1, 88A2, 89S2, 91M2, 92D1, 93H1, 93S6, 94Y2, 95Y1, 97W2, 01V1]. The kinetics of intercrystalline distribution in orthopyroxenes were performed by ^{57}Fe NGR [69V1, 81B1, 88A2] or by single crystal diffraction studies [89S2, 91M2]. A comparison of site occupancy results from both ^{57}Fe NGR and single crystal X-ray diffraction was made [92S5]. The occupancy of Fe^{2+} at M1 and M2 sites in OPx with different concentrations of ferrous ions is given in Fig. 14 [01V1]. The Fe^{2+} enrichment takes place at the M2 site.

Studies were made on the (Fe^{2+} , Mg^{2+}) distributions as function of cooling rates. For example, in [93S6], the equilibrium site occupancies were studied in $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ with $x = 0.61$ and 0.85 samples, heated and unheated. Heating was continued until cation distributions reached steady state, which was considered equilibrium. A distinct step was found in the activation energies with higher activation energies ($\cong 60$ kcal/mol) for Mg-rich samples and lower activation energies ($\cong 50$ kcal/mol) for Fe-rich samples. The rapid quenched crystal with $x = 0.44$ displays a high degree of disorder at M1 and M2 octahedral sites [93H1]. In situ high-temperature study of Fe^{2+} - Mg^{2+} distribution over the M1 and M2 sites was taken at $1100 \text{ K} \leq T \leq 1300 \text{ K}$ by X-ray diffraction [94Y2]. The data were obtained up to 1300 K only for composition $x \leq 0.51$. For $x \geq 0.75$ there is a phase transition, orthopyroxene – clinopyroxene at $\cong 1255 \text{ K}$. The asymmetry in the distribution of Fe and Mg over M1 and M2 sites – Fig. 15 [94Y2] – was confirmed in the range $1000 \dots 1200 \text{ K}$, although it is much less pronounced than that determined from quenched natural samples at lower temperatures ($873 \dots 1073 \text{ K}$) [71S2]. The (Fe^{2+} - Mg^{2+}) distribution in orthopyroxenes was studied also in order to derive meaningful cooling rates from the orthopyroxene geospeedometer ([97K2] and references therein). For calculating cooling rates, the rate equation given by [67M2], which requires that the (Fe^{2+} , Mg^{2+}) equilibrium distribution coefficient $K_D = x^{M1}(1 - x^{M2})[x^{M2}(1 - x^{M1})]^{-1}$ and k_{dis} , which is the rate constant of microscopic ordering reactions proportional to the joint probability of finding Fe^{2+} and Mg^{2+} in the wrong sites, for the disordering reaction, are determined as function of temperature and composition x . The $\ln K_D$ was calculated from published K_D values as well as from their data [97K2]. The analysis revealed internal inconsistencies related to the origin of the crystal (natural or synthetic) and the data collection and site refinement strategies. Rate constants, k_{dis} , were calculated from the (Fe^{2+} , Mg^{2+}) site occupancies determined in isothermal kinetic experiments. Coefficients for the dependence of k_{dis} on T and x , assuming a continuous and a stepwise behaviour, respectively, of $\ln k_{\text{dis}}(x)_T$ were obtained. The results were in agreement for $0 < x < 0.55$ but disagree for $0.55 < x < 1$. It was concluded that due to inconsistencies detected in the available set of $\ln K_D$ values, this should be determined as a function of temperature for every crystal.

The pressure effects experienced by pyroxenes in partition of Fe^{2+} - Mg^{2+} between the M1 and M2 sites were generally neglected. In [69V1] the pressure effect on the distribution of Fe^{2+} between M1 and M2 sites in orthopyroxenes was studied in the pressure range of 0.72 to 1.82 GPa. Fe^{2+} was found to be ordered in M1 site, at elevated pressures.

The iron partitioning between basaltic melts and clinopyroxene as a function of oxygen fugacity was analysed [04M1].

The thermal behaviour of structure and lattice parameters of orthopyroxenes was studied [73S1, 76S1, 82D2, 82M5, 94Y1, 95Y1]. The thermal behaviour of Mg-rich orthopyroxenes ($x \leq 0.2$) is quite different from Fe-rich ones ($x \geq 0.4$) – Fig. 16 [94Y1]. The a and c parameters and the unit-cell volume increase nonlinearly with positive curvature with rising temperature, whereas the b parameter behaves differently, depending on the total iron content. For Mg-rich orthopyroxene ($x < 0.3$) the b parameter expands similarly to the a and c parameters, but it exhibits a nonlinear increase with a negative curvature for $x > 0.30$. The thermal expansion coefficients, α_a and α_c , increase as the temperature is elevated, with α_c increasing faster, while α_b changes gradually from increasing Mg-rich OPx to decreasing for Fe-rich OPx [76S1, 94Y1]. The relative magnitudes of the linear thermal expansion coefficients are always in the order $\alpha_b > \alpha_c > \alpha_a$ between 300 and 500 K, but at higher temperatures, the order changes to $\alpha_c > \alpha_b > \alpha_a$ for Mg-rich OPx and $\alpha_c > \alpha_a > \alpha_b$ for Fe-rich ones. The linear thermal expansion behaviour was interpreted on the basis of the structural mechanical model [82W1]. The anomalous behaviour of α_b was mainly attributed to the change in the Fe^{2+} population at the M2 site and relative stiffness of the $\text{M2}(\text{Fe}^{2+})\text{-O}$ bonds compared to $\text{M2}(\text{Mg}^{2+})\text{-O}$ bonds.

In [93S6] was suggested that there is a gap in the activation energy for the Fe-Mg ordering between Mg-rich and Fe-rich OPx, respectively. In [73O2, 79P1] the existence of a high-temperature orthorhombic phase and a possible new structure type was predicted, which has the same space group as orthopyroxene. An intermediate phase between enstatite and protoenstatite at 1273 K was also reported by [82M5], which is characterized by an a parameter similar to that of OPx, but the intensity distribution of the strong reflections are similar to that of PEn. Presumably, the silicate chains in this phase are stretched and are similar to those in PEn, but the basic stacking sequence of the OPx structure is still maintained. Later on, [95Y1] studied the $(\text{Mg}_{0.75}\text{Fe}_{0.25})_2\text{Si}_2\text{O}_6$ single crystal OPx as function of temperature. When increasing T , the silicate B chain straightens much faster, especially above 1200 K, and becomes straighter than the A chain at 1300 K, with the O3-O3-O3 angles of the A and B chains being 170.8° and 173.1° , respectively. The $\ln K_D$ varies linearly with T^{-1} between 1000 and 1200 K, but nonlinearly between 1200 K and 1300 K. The drastic straightening of the silicate chains at 1300 K is accompanied by the attainment of very similar configurations of the SiO_4 tetrahedra (SiA and SiB) in shapes, sizes and out-of-plane tilting. The M1 octahedron remains nearly regular from 296 K...1300 K, whereas the M2 coordination changes from sixfold (296 K) to sevenfold (1200 K) and sixfold (1300 K) – Fig. 17 [95Y1]. At 1300 K, the highly distorted M2 octahedron shares two edges with SiA and SiB rather than one with SiA at 296 K, and the structure has the features of the high-temperature OPx phase predicted by [79P1], which, in fact, is a transitional structure state between OPx and PEn. On the basis of the configurations of the silicate chains in Mg-rich and Fe-rich OPx, at high temperatures, may be explained why Mg-rich OPx tends to transform to the PEn structure with increasing T , whereas Fe-rich ones tend to transform to CPx(C2/c). The anomalous behaviour of the Fe-Mg order-disorder, above 1200 K, was attributed to the existence of the transitional state, particularly the changing charge distribution around the M2 site [95Y1].

According to [93H1], a single crystal of $(\text{Mg}_{0.56}\text{Fe}_{0.44})_2\text{Si}_2\text{O}_6$ orthopyroxene has been recovered from a synthesis experiment at approximately 11 GPa and 1600°C. This rapid-quenched crystal displays a high degree of disorder for orthopyroxene M1 and M2 octahedral sites ($K_D = 3.9$). The high-pressure measurements were made on synthetic and natural $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ orthopyroxenes containing significant Ca^{2+} and Al^{3+} [97H3]. These studies have shown that while the mechanisms of compression operating below ≈ 8 GPa for all synthetic OPx are very similar, the compression of Ca^{2+} -containing natural orthopyroxene occurs via a somewhat different mechanism. The compression mechanism of synthetic $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ OPx was analyzed [97H3]. Significant compression of the previously incompressible Si-O bond (and changes in the conformations of the silicate chains) was observed in $\text{Fe}_{0.4}\text{Mg}_{0.6}\text{SiO}_3$ OPx at $p \geq 3.5$ GPa.

The elastic (bulk and shear) moduli of some orthopyroxenes are plotted in Fig. 18 [99J1]. The effects of chemical composition on the elasticity are well represented by the decrease of K and G when increasing the Fe content. In synthetic $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ and natural pyroxenes containing Ca^{2+} and Al^{3+} , the variation of Fe^{2+} content

has an effect on K_o and K_o' [97H2]. Even a small amount of Ca^{2+} or Al^{3+} to the orthopyroxene structure causes an increase in K_o by $\approx 14\%$.

The lattice parameters for $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ LCPx with $0 \leq x \leq 0.899$ were studied [98A3]. The diffraction data show that there is no significant ($< 0.25\%$ for $x = 0.5$) excess volume of mixing in the studied composition range. The linear behaviour of volume with composition arises from the compensating effects of non-linear changes in the unit-cell parameters with composition. The lattice parameters – Fig. 19 – may be described by the following relationship: $a [\text{\AA}] = 9.6100(15) + 0.105(2)x$; $b [\text{\AA}] = 8.8156(28) + 0.218(12)x + 0.0481(117)x^2$; $c [\text{\AA}] = 5.1702(4) + 0.0879(21)x - 0.0214(21)x^2$; $\beta [^\circ] = 108.345(8) + 0.947(30)x - 0.805(26)x^2$. The strong positive deviation of β from linearity was correlated to the difference in site occupancies between M1 and M2 as determined by ^{57}Fe NGR and arises directly from the expansion of M2-O1 and M2-O3 bonds upon initial substitutions of Fe for Mg in enstatite. The data are consistent with no significant clustering of Fe or Mg within the samples.

The intracrystalline distribution of Mg^{2+} and Fe^{2+} on the M1 and M2 octahedral sites, in high-pressure $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ clinopyroxenes, has been determined in quenched samples by using the ^{57}Fe NGR method [97W2]. The data obtained at 81 K indicate that Fe^{2+} is strongly ordered into the M2 sites. Because the samples were quenched from high temperatures (1200...1275°C), at 9.5 GPa, the temperature to which the measured ordered state corresponds is problematic. In general, the state of ordering in OPx and HPCPx is similar, with iron strongly portioned onto the M2 site [97W2]. This is consistent with the observed structural similarities between the two polymorphs.

Protopyroxene is the high-temperature stable form of Mg-rich orthopyroxene. Its crystal structure was first determined by [59S1, 69S3] and refined using in situ high-temperature data by [69S1, 71S3, 84M3, 85M2].

Although orthopyroxene is nominally anhydrous, it is able to dissolve traces of OH as point defects [92B1] and may be a major host for the water in the mantle. Diffusion of hydrogen in orthopyroxene was studied [99C1, 03S1]. In natural orthopyroxene $\text{En}_{90}\text{Fs}_{10}$, small but significant differences in diffusivities along the three crystallographic axes were observed, [001] being the fastest direction followed by [100] and [010] [03S1]. Hydrogen diffusion in pure synthetic enstatite proved to be about two orders of magnitude slower and isotropic.

The $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ **perovskite** structure has the Si^{4+} distributed on small and undistorted octahedral sites, while the large distorted sites are filled by Mg^{2+} and Fe^{2+} ions [87H3, 92M2]. A phase transition of $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ to **perovskite**-type structure, in the deep mantle, was suggested [62R1]. The perovskite-type $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ was subsequently predicted to be an important mineral phase in the earth's lower mantle [66R1] and was thought to contribute to seismic velocity discontinuities in the mantle at the depth of 650 km, as mentioned for MgSiO_3 [79L2]. Phase equilibria in the $\text{MgO} - \text{FeO} - \text{SiO}_2$ system, particularly near composition $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$, in connection with perovskite structure formation were studied [79Y1, 82I1, 84I1, 87H3, 88I1, 88K3]. Experiments on $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ samples show that perovskite maintains its orthorhombic symmetry at 38 GPa and 1850 K [95M1]. Measurements at 65 and 70 GPa provide evidence for a temperature induced orthorhombic to cubic phase transition and then dissociation to an assemblage of perovskite and mixed oxides. These results are consistent with diamond cell studies showing orthorhombic silicate perovskite as the primary phase in quenched experiments after moderate laser heating at $p \geq 25$ GPa for samples with comparable iron content [87K2].

The volumes of $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ perovskites with $x = 0.1$ and 0.2 , under high pressure and temperature, were calculated [98S2]. The results were in close agreement with experimental data.

The thermal expansion of $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ perovskite was analyzed up to 800 K and 1 bar [86K4]. See also Table 5.

For crystal structures of $(\text{Mg}, \text{Fe})\text{SiO}_3$ perovskites see also [77S1, 87L2, 89C2, 92H1].

Akimotoite, ilmenite

The stability field of ilmenite structure polymorph has been investigated in $\text{MgSiO}_3 - \text{FeSiO}_3$ [82I1, 89C1] and $\text{MgSiO}_3 - \text{Al}_2\text{O}_3$ [87I1, 87K1, 90G1] systems. The ilmenite crystallizes in a trigonal-type structure (space group $R\bar{3}$).

In [99T2] a new silicate mineral $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ of the ilmenite group was reported. The approximate composition is $\text{Mg}_{0.79}\text{Fe}_{0.21}\text{SiO}_3$ and it crystallizes in space group $R\bar{3}$. **Akimotoite**, in this occurrence is thought to have been transformed from original orthoenstatite in a solid-state reaction produced by a shock event at 22 GPa $< p < 26$ GPa and $T > 2000^\circ\text{C}$.

$\text{Mg}_{1-x}\text{Cr}_x\text{SiO}_3$

The $\text{Mg}_{1.425}\text{Cr}_{0.611}\text{Si}_{1.964}\text{O}_6$ pyroxene is monoclinic, similar to low clinoenstatite, having space group $\text{P}2_1/\text{c}$ [89A2]. Refined site occupancy is: M1 (0.946(6)Mg + 0.054(6)Cr); M2 (0.479(6)Mg + 0.521(6)Cr); TA (0.983(7)Si + 0.017(7)Cr); TB (0.981(7)Si + 0.019(7)Cr). Most of Cr is accommodated on the M2 site of the structure, which is consequently much more distorted than found in the end-member structure, MgSiO_3 . The chromium seems to be in the divalent state.

II. Mn- and other transition metal based silicates

MnSiO_3

The presence of MnSiO_3 polymorphs was reported [67R4, 72A2, 85A2]. Four polymorphs have been identified and designated I to IV in order of increasing pressure. At 1273 K, MnSiO_3 **rhodonite** (I), stable at atmospheric pressure, first transforms to **pyroxmangite** (II) at 3.6 GPa, to **clinopyroxene** (III) at 7.6 GPa and further to distorted **garnet** (IV) (tetragonal symmetry) at 12.5 GPa. The garnet phase decomposes into a mixture of MnO (rocksalt) and SiO_2 (stishovite) at about 22 GPa and 1273 K [74I3, 77I2]. High-temperature solution calorimetry was used to measure the enthalpies of these transitions [85A2]. Values 520(490) and 8270(590) cal/mol were reported for the rhodonite-clinopyroxene and clinopyroxene – garnet transitions, respectively. The equilibrium phase boundary between rhodonite and pyroxmangite was determined as p [GPa] = $1.0 + 0.0026 T$ [°C] [72A2]. Pyroxmangite transformed to MnSiO_3 (III) with a monoclinic pyroxene structure on the boundary curve represented approximately as p [GPa] = $1.9 + 0.0057 T$ [°C]. The density increase in the course of the high-pressure transformations was calculated, at zero pressure, as 0.5 % for I – II, as 1.3 % for the II – III and as 13.1 % for III – IV transformation [72A2]. Over the pressure range 0.35...3 GPa, pyroxmangite is the stable low-temperature polymorph and rhodonite is stable at higher temperatures [76M1]. When extrapolated to lower pressure, the trend of these data suggests that at 0.1...0.2 GPa pressure, the pyroxmangite – rhodonite inversion lies at 400°C.

Rhodonite, MnSiO_3 , has the structure of triclinic pyroxenoid with space group $\text{P}\bar{1}$ [63P1, 72A2, 72I2, 75D1, 75O2, 85T2, 86H3, 89R1]. The structure contains chains of $[\text{SiO}_4]$ tetrahedra with a repeat unit of five tetrahedra. Layers of chains alternate between planes of close packed oxygen ions with layers of coordinated cations. There are five equally populated cation positions: four designated M1, M2, M3 and M4 give sixfold coordination and the fifth, M5, gives an irregular sevenfold coordination. Site M4 has one elongated M-O bond, making this site nearly five-coordinated. Three types of oxygen ions occur in the rhodonite structure – Fig. 20. Type A is coordinated to 2Si and one M ion, type B is coordinated to one Si and 3M ions and type C to one Si and 2M ions. The three types of oxygen ions will have different effective charges in the order $A < B < C$. Single crystals of rhodonite were grown from a mixture of MnO + SiO_2 using MnCl_2 as a flux in sealed graphite crucible [89R1].

Pyroxmangite, MnSiO_3 , crystallizes in a triclinic-type structure [72A2, 72I2, 75O2, 88P1] – Table 3. MnSiO_3 **clinopyroxene** has a monoclinic-type structure. The MnSiO_3 **garnet** was synthesized by [67R3] and subsequently indexed in a tetragonal lattice [72A1]. Single crystals of MnSiO_3 garnet were first grown by [86F2], who determined the space group to be tetragonal of $\text{I}4_1/\text{a}$ type. MnSiO_3 garnet was grown at 1500°C and about 12 GPa [86F2]. The Mn and Si atoms are fully ordered into different octahedral sites. The Si octahedron is very regular in shape.

The natural rhodonites have been examined, in normal state and after thermal treatment, by high-resolution electron microscopy [80A1, 80J1]. Planar faults parallel to (001) and (110) have been observed. The (001) faults strips of pyroxmangite structure are inserted into the parent rhodonite matrix. The second type of faults has been found to be equivalent to the stacking faults observed in wollastonite.

Pyroxferroite

Pyroxferroite, $(\text{Fe,Mn,Ca})\text{SiO}_3$, has a triclinic-type structure [70C2].

Mn_xMg_{1-x}SiO₃

The phase diagrams of the Mn_xMg_{1-x}SiO₃ system were studied [72I2, 86H3]. According to [72I2] a pyroxmangite – rhodonite peritectic exists on the liquidus, at a composition of approximately $x = 0.67$, at 1350(5)°C in air. Unit-cell dimensions for the continuous solid solutions of pyroxmangite- and rhodonite-types are given in Fig. 21. These values vary linearly with composition. At 1200°C, in air, the joint MnSiO₃ – MgSiO₃ consists of four phases, i.e., triclinic rhodonite at $0.55 \leq x \leq 1.0$; triclinic pyroxmangite at $0.25 \leq x \leq 0.50$; clinopyroxene at $0.15 \leq x \leq 0.20$ and orthorhombic protoenstatite for $0 \leq x \leq 0.10$. The phase transition at fixed p and T appears to be controlled by the mean cationic radii for the variable Mn and Mg contents. A narrow but distinct rhodonite-coexistence region was found below the solidus around $0.50 \leq x \leq 0.55$ [72I2]. According to [86H3], at 1 kbar and temperatures up to 850°C, the orthopyroxene-type structure was shown at $0 \leq x \leq 0.3$, clinopyroxene at $0.4 \leq x \leq 0.5$ and pyroxmangite for $0.65 \leq x \leq 1.0$. In [80B1] the available compositional data were assembled and the phase equilibria at metamorphic temperatures corresponding to the Mg-Fe-Mn-Ca system were inferred. There are some discrepancies between the data reported by various authors. The Mn-rich pyroxenes and pyroxenoids have been studied [77H2, 77P1, 78P1, 80A2, 80A3, 80B1, 81G2].

Kanoite, MnMg[Si₂O₆]

MnMg[Si₂O₆] was first reported as a P2₁/c clinopyroxene [77K1]. The structure refinement of a synthetic kanoite, with composition Mn_{0.9}Mg_{1.1}[Si₂O₆], was performed by [75G2]. In [81G2] a structure refinement of P2₁/c kanoite coherently intergrown with a C2/c pyroxene (Mn-rich diopside Ca_{0.43}Mn_{0.69}Mg_{0.82}Si₂O₆) was reported. Ordering of Mg on M1 and Mn on M2 site was confirmed by a single crystal X-ray study of natural kanoite [96G2]. A P2₁/c → C2/c-type transition was reported in kanoite at 330(20)°C [81G1] and in MnMg[Si₂O₆] at $\approx 240^\circ\text{C}$ [97A2, 98A4] and is of first order. The temperature dependences of the cell dimensions show considerable deviations from linearity at the phase transition – Fig. 22 [97A2]. The two symmetry independent [Si₂O₆]⁴⁻ chains of the P2₁/c phase become equivalent in the C2/c phase. The M2 site (enriched in Mn) of the low-temperature phase is irregularly sevenfold-coordinated (5+2), whereas it is sixfold-coordinated (4+2) in the high-temperature phase.

Donpeacorite, (Mn,Mg)MgSi₂O₆

The name donpeacorite applies to the ordered orthopyroxene of end member composition MnMgSi₂O₆. Refinements show that the crystal structure is of space group Pbca. Mn is completely ordered into the M2 site and comprises over 50 % of that site [84P2].

The fractionation of cations over different crystallographic sites, also known as order/disorder or intracrystalline exchange reaction, has been extensively studied in Fe-Mg orthopyroxenes as already mentioned [81B1, 88A2, 91M2, 94G1, 99S2, 03Z1], but only few data exist on the partitioning behavior of Mn. In fact, Mn was often treated as equivalent to Fe²⁺ and the two elements were combined as the fictive species Fe* = Fe²⁺+Mn [96G1, 97Z2, 03Z1 and references]. Partitioning of Fe* was rationalized by [78H1], who refined the structure of synthetic Mn-rich orthopyroxene (Mg_{0.925}Mn_{0.075}SiO₃) and reported that Mn is fractionated over both octahedral sites (M1 and M2), preferentially ordering at M2. In [84P2] was noted that in naturally occurring Mn-rich/Fe-free orthopyroxene (donpeacorite) Mn was totally ordered at M2. The above studies showed that the ordering trend of Mn is the same as that of Fe²⁺ in Fe-Mg orthopyroxenes. The equilibrium intracrystalline distribution of Mn and Mg between the M1 and M2 sites in single crystal donpeacorite Mn_{0.54}Mg_{1.43}Ca_{0.03}Si₂O₆ was later investigated by XRD in samples annealed at temperatures between 980 and 800°C [05S1]. The data show that Mn, as does Fe²⁺ in Fe-Mg orthopyroxenes, preferentially orders at the M2 site. Mn has a much stronger preference for the M2 site relative to Fe²⁺.

Mn_{1-x}Fe_xSiO₃ rhodonites

In (Mn, Fe, Ca, Mg)SiO₃ rhodonites, where all the Ca is located in the M5 site and the iron magnesium ions in the M4 site the manganese ions are distributed so as to give all five sites equal population [63P1]. Later on, it has been shown that in Mn_{1-x}Fe_xSiO₃ rhodonites, all the iron is in the ferrous state and is distributed among the five cation sites [75D1]; most of the iron is in the octahedrally-coordinated M1, M2 and M3 sites. The Fe²⁺ ions show a small preference for the near five-coordinate M4 site and little iron enters the seven-coordinate M5 site.

Mg(Cu,Mg)Si₂O₆

The crystal structure of Mg(Cu_{0.56}Mg_{0.44})Si₂O₆ orthopyroxene was reported [97T1]. The substitution of Cu²⁺ for Mg²⁺ produces distortion of the M2 site possibly due to Jahn-Teller nature of Cu²⁺ and extreme preference of Cu²⁺ for the M2 site. This implies that Cu²⁺ tends to be excluded from undistorted octahedral sites even in silicates others than orthopyroxene. In the M2 site, one of the M-O bonds, M-O3B, is extremely expanded and thus the coordination polyhedron around the M2 site is regarded as square pyramidal rather than square planar or octahedral. The M1 site is occupied almost exclusively by Mg, while the M2 site is almost evenly occupied by Mg and Cu.

ZnMgSi₂O₆

The single crystal of ZnMgSi₂O₆ has been synthesized at 1400°C and 7 GPa from a mixture of ZnO, SiO₂ and MgSiO₃ glass [75M3]. The structure of the orthorhombic ZnMgSi₂O₆ is intermediate between that of enstatite (MgSiO₃) and the orthorhombic ZnSiO₃. Zn1 atoms are near the centers of rather regular octahedra of oxygen atoms as in enstatite [69M1]. However, Zn2 atoms are located in deformed octahedra with four oxygen atoms at mean distances of 2.019 Å and two at 2.548 Å. The shapes of the A and B chains are also intermediate between those of ZnSiO₃(0) and enstatite. The Zn atoms are partially ordered in the M1 and M2 sites with site occupancies of 36 and 64 %, respectively [75M3]. The structural study of orthorhombic Zn_{0.45}Mg_{1.55}Si₂O₆ silicate [74G2] indicates the site occupancy of M1 (Zn 0.067, Mg 0.933) and M2 (Zn 0.383, Mg 0.617).

CrMgSi₂O₆

A first-order high-pressure transition from P2₁/c to C2/c was observed in CrMgSi₂O₆ [98A4].

Mg₂Si₂O₆ – doped with Al

The intracrystalline distribution of Al in orthopyroxene was analyzed [73W1, 75W1, 76O1, 77F1, 78D1, 79G1]. In [79G1] structure refinements were performed on aluminous orthopyroxene in the Mg₂Si₂O₆ system doped with Al. It was suggested that the tetrahedral Al is ordered nearly completely in the B site, but the octahedral Al disorders between M1 and M2 sites with a preference for M1. A model was developed for the disordering of Al between the octahedral sites as function of temperature and composition.

Magnesium – transition metal silicates

In Mg_{1.562}Mn_{0.175}Co_{0.263}Si₂O₆ orthopyroxene, consideration of the mean octahedral bond lengths together with the site refinement results, indicate the following site populations: M1 = 0.904(4)Mg + 0.065Co²⁺ + 0.031Mn²⁺; M2 = 0.658Mg + 0.198Co²⁺ + 0.144Mn²⁺ [77H2]. Structural distortion in the orthopyroxene structure is dominated by the bond strength requirements of the anions; superposed upon this is relaxation across shared polyhedral elements in order to reduce cation-cation repulsion. These distortions are operative under the general constraint that the *c*-axis repeats of the octahedra and both chains in the structure must be identical.

The site populations in other orthopyroxenes have been determined as (Mg,Mn)SiO₃, (Mg,Co)SiO₃ [78H1]; (Mg,Mn)SiO₃, (Mg,Co)SiO₃, (Mg,Ni)SiO₃, (Mg,Zn)SiO₃ [75G2]; (Mg,Zn)SiO₃ [75M3]; (Mg,Cu)SiO₃ [76G1]; (Mg,Co)SiO₃ [74G2]; (Mg,Co,Mn)SiO₃ [77H2]. The preference for the M2 site in orthopyroxenes is according to Mn > Co > Mg [74G2, 77H2, 78H1]. The M2 preference Mn > Mg is also exhibited by the P2₁/c phase in (Mg,Mn)SiO₃ [74G2]. In [75G2] was suggested that the M2 site preference is Mn²⁺ > Zn²⁺ > Fe²⁺ > Co²⁺ > Mg²⁺ > Ni²⁺ for the (Mg,M²⁺) orthopyroxenes. In (Co,Ni,Zn)SiO₃ orthopyroxenes the atomic ratios at M1 and M2 sites are 0.53:0.20:0.27 and 0.14:0.46:0.39, respectively, in the order of Ni, Zn and Co atoms [85T1, 90T2]. Thus, Ni atoms prefer the smaller M1 sites, while Co atoms show a strong preference for the smaller sites than do the Zn atoms, even though the ionic radii for the two atoms are almost identical. It was shown that there is a strong correlation between the partition coefficients and ionic radii. The distribution of the ions in various sites for some pyroxenes are listed in Table 7. We note that the site preference, particularly in (Mg,Fe)SiO₃ orthopyroxene as already described above, is a function of thermal history. Thus, the differences in the data listed in Table 7 would be due from differences in equilibration temperatures resulting from various synthesis conditions. The site population observed in natural and synthetic orthopyroxene can be used as a thermal indicator on the basis of thermodynamic and kinetic arguments [73B1]. In addition to the thermal history, the

distribution equilibrium may be modified by high pressures arising for example, from shock (meteoric impact). When a shock is applied to an orthopyroxene crystal, a permanent alteration of the cation distribution takes place, meaning that the initial crystal structure has been destroyed and a new phase has been reached [71D2, 73H1]. The valence state partitioning of Cr, Fe, Ti and V in pyroxenes from planetary basalts were studied [05P1]. The sites that accommodate these cations are M2 and M1.

The electron irradiation effects in natural orthopyroxenes $\text{Fe}_{0.55}\text{Mg}_{0.45}\text{SiO}_3$ and $\text{Fe}_{0.88}\text{Si}_{0.12}\text{SiO}_3$ orthopyroxenes were studied [80S2]. After irradiation, species were formed at the expense of iron from M2 site.

III. Ca-, Cr-, Ba- and Zn-based silicates

CaSiO₃

CaSiO₃ shows a number of polymorphs. At atmospheric pressure, CaSiO₃ crystallizes in α -wollastonite (pseudowollastonite) or β -wollastonite (parawollastonite) forms. Several structure types were proposed for the monoclinic β -CaSiO₃ [36B1, 55D1, 56D1, 58T1, 61B2, 68T1, 69W1, 79V1]. The structure was finally refined in space group $P2_1/a$ [68T1]. We note that the two structures proposed from X-ray data for monoclinic parawollastonite in [58T1] and [68T1] were identical within the limit of experimental errors, as shown by [79V1].

Pseudowollastonite (PWo) is the stable form of CaSiO₃ at temperatures above ≈ 1400 K. Several studies were devoted to analyze the crystal structure of this phase [53J1, 54D1, 56M1, 61B1, 64K1, 77I1, 78O2, 81M1]. The matter has been clarified only later [81Y1, 93I1, 99Y2, 99Y3]. Owing to the different stacking sequence of the octahedral layer and ternary rings, various polytypes could exist in pseudowollastonite. In [81Y1] three polytypes of pseudowollastonite were observed: a dominant four-layer phase, a six-layer and a disordered structure. The layers referred to here are composed of one layer of ternary rings plus one layer of CaO_{6+2} octahedra [81Y1]. The six-layer polytype was thought to be isostructural with SrGeO_3 [62H1] having a pseudosymmetry $C2/c$. For the four-layer polytype, in [81Y1] a triclinic unit cell was obtained with systematic reflection absences corresponding to a C-centered lattice and a pseudo c -glide plane perpendicular to the b -axis, leading to the conclusion that PWo has pseudo-monoclinic $C2/c$ symmetry. The structure was solved based on space group $C\bar{1}$. A re-determination of the four-layer PWo synthetic crystal [99Y2] shows that it has monoclinic $C2/c$ symmetry. Each of the four layers is composed of a layer of ternary (Si_3O_9) tetrahedral rings and a layer of distorted-bicapped Ca octahedra. A distorted bicapped octahedron is formed by eight O atoms, with six of them in an octahedral arrangement plus two from bridging O atoms of the Si_3O_9 ternary rings, one above and one below the octahedron. The ternary rings are elongated along the stacking [001] direction, whereas the CaO_{6+2} polyhedral layers are compressed in the same direction. The basic features of the $C2/c$ structure are similar to those with a $C\bar{1}$ symmetry [81Y1], but fewer sites exist for the monoclinic space group. Compared to the $C\bar{1}$ structure, which has seven crystallographically distinct Ca sites, six Si sites and eighteen O sites, the $C2/c$ structure has only five symmetrically distinct Ca sites, three Si sites and nine O atoms. All polyhedra in the $C2/c$ structure are slightly less distorted than those in the $C\bar{1}$ structure.

Pseudowollastonites, crystallized from glass and annealed as 1350°C for 50 h, showed two-, four- and six-layer coexisting polytypes in the form of lamellae parallel to (001) [93I1]. It is likely that a higher annealing temperature (1440°C), prolonged annealing time (160 h) and a fast quenching [99Y2] were responsible for the preservation of a single “equilibrium” polytype of PWo (four layer). In [99Y3] the crystal structure of a synthetic two-layer polytype of PWo was reported. It is monoclinic with space group $C2/c$. The silicate is isostructural with two-layer SrSiO_3 [82M1, 97N1]. We note that in [82M1], the crystal structure of SrSiO_3 was described in space group $C2$, but later was shown [83M2, 97N1] to have the space group $C2/c$. The basic structural features are similar to those found in four-layer CaSiO₃ PWo, except the stacking sequence of layers of CaO_6 octahedra and Si_3O_9 ternary rings. No phase transition was observed up to 9.94 GPa. The axial compression ratios are $\beta_a:\beta_b:\beta_c = 2.25:2.36:1.00$. The greater compressibility in the a and b directions is a consequence of the structural topology and distortion of CaO_6 octahedra. In the two-layer structure, not only all CaO_6 octahedra forming layers parallel to the (ab)-plane are compressed along [001], but there also exists considerable space among Si_3O_9 ternary rings that are sandwiched by CaO_6 octahedral layers. Hence, the structure is much less packed along the a and b -axes than along the c -axis, giving rise to the apparent anisotropy of the structure as it is compressed. The high-temperature properties of PWo were studied in [98R3].

The thermal variations of lattice parameters for pseudowollastonite are plotted in Fig. 23 [98R3]. The changes in the β unit-cell angle are very small. In pseudowollastonite, Si_3O_9 rings alternate with layers of CaO_6 octahedra along c -axis. Most of the expansion is likely due to a dilatation of the CaO_6 octahedra, the Si_3O_9 rings remaining largely unaffected. This structural feature would cause expansion to be nearly the same along the a - and b -axis, which correspond to the equatorial plane of the octahedra, and slightly higher along the c -axis where the main contribution is dilatation of CaO_6 octahedra along their polar axis. Such a scheme is consistent with the relative increase in lattice parameters observed when Sr is substituted for Ca to make SrSiO_3 pseudowollastonite [75M4]. In [96S5] thermal expansion of pseudowollastonite was calculated. The thermal expansion of wollastonite was also studied in [96S3]. Both polymorphs have similar expansivities.

At high pressure and temperature, CaSiO_3 transforms to a **walstromite** II phase [69T1, 94G2, 04A1] and further transforms to perovskite above 10 GPa [67R4, 75L3]. The high-pressure phase (three-layer CaSiO_3) crystallizes in space group $\text{P}\bar{1}$ [69T1]. The basic features of this structure are CaO layers and Si_3O_9 rings. The layers contain two types of Ca atoms, one coordinated by six oxygen atoms, the other by eight oxygen atoms. The Si_3O_9 rings are located between these layers. The third type of Ca atom, also coordinated by six oxygen atoms, connects neighbouring layers, thus sharing the space with the Si_3O_9 rings.

The phase relations in the CaSiO_3 system under high pressure were studied in [91K3, 94G2]. According to [94G2], below solidus, a field of $\text{Ca}_2\text{SiO}_4 + \text{CaSi}_2\text{O}_5$ is stable between that of CaSiO_3 walstromite II at lower pressure and CaSiO_3 perovskite at higher pressure within the following limits: p [GPa] = $7.9 + 0.0014 T$ [°C] and p [GPa] = $9.0 + 0.0021 T$ [°C]. These invariant boundaries intersect the solidus and two triple points: one at 10.4 GPa and 1800°C, the other at 13.5 GPa and 2150°C [94G2].

In addition to common triclinic wollastonite (1T) and monoclinic parawollastonite 2M [84H2], the types 3T, 4T, 5T [83H1] and 7T [78H2] were determined. The polytypes are distinguished by symbols nT and nM, where T and M stands for triclinic and monoclinic symmetry of the polytype and n indicates the number of subcells with $d_{\text{subcell}}(100) \cong 7.7 \text{ \AA}$ in the unit cell of the polytype. In [83H1] the polytypism was analyzed in terms of stacking (100) slabs, each being one unit cell thick of the 1T wollastonite structure. If T is denoted a slab in a continuous position with respect to the preceding one and G a slab that is displaced by $b/2$, then the 1T polytype (triclinic wollastonite) is represented by TTT... or (T), and the 2M polytype (monoclinic parawollastonite) by TGTG... or (TG). Similarly, the stacking sequence for 3T (3-layered structure) is given by TTG TTG TTG... or (TTG) which may be rewritten as (2T1G). There are two kinds of modes in the stacking sequences having four slabs in the repeating units: the triclinic 4T polytype and the monoclinic 4M polytype. The stacking sequence of the former is represented by (TTTG) and the latter by (TTGG). The polytypes with five slabs in the repeating units have the following three kinds of modes in the stacking sequences: TTTTG, TTTGG and TTGTG. They are all triclinic and are called the 5T polytypes. The 7T polytype [78H2] has the stacking sequence of TTGTGTG (4T3G) which is one of the eight possible stacking sequences. We note that stacking faults were observed in wollastonites [76J1].

β - CaSiO_3 was prepared by unidirectional crystallization of calcium metasilicate from glasses and melts [79R1]. The high-temperature polymorph, α - CaSiO_3 , could be crystallized dendritically such that the primary arms were aligned, and the growth of secondary arms inhibited, by mutual impingement. β - CaSiO_3 has a chain silicate structure and crystallized as fibres by the spherulitic crystallization mechanism. The pressure induced transformations in chain silicates, based on their molecular structure were analysed in CaSiO_3 ($\text{P}\bar{1}$), $\text{Ca}_{0.5}\text{Mg}_{1.5}\text{Si}_2\text{O}_6$ (C2/c) and MnSiO_3 ($\text{P}\bar{1}$) [00S1].

The **CaSiO_3 perovskite** was synthesized in solid solution with CuGeO_3 [67R4, 71R2]. Later on, at high pressure (16 GPa), a cubic-type perovskite was obtained [75L3]. The structure is stable above 11...15 GPa [75L3, 94G2]. The CaSiO_3 perovskite undergoes a crystalline-amorphous transition when decompressed from their high-pressure stability field [75L3, 93S1, 95H1]. According to [93S1] the amorphisation occurs because the phase transition wollastonite – perovskite is kinetically impeded. The amorphous phase is considered as a defective long period modulated wollastonite phase. Theoretically it has been shown that the amorphization is initiated by a thermally activated step involving a soft polar optic mode in the perovskite phase at the Brillouin zone center [95H1]. The structural distortions, lattice dynamics and the equation of state were studied at high pressures [87H4]. Molecular dynamics simulations have been used to calculate the structures and bulk moduli of CaSiO_3 (wollastonite and perovskite) [96M3].

The CaSiO_3 perovskite cannot be recovered at ambient conditions, as it readily transforms to glass on release of pressure after quenching from high temperature [71R2, 75L3]. In situ XRD studies [89M1, 94W2] indicate that the metastable limit of CaSiO_3 perovskite is between 0.8 and 2.5 GPa at 25°C, below which it transforms into an amorphous phase. In [89L2] was suggested that dissolution of other cations (Mg, Na, Al etc.) in CaSiO_3 , at high pressure and temperature, might stabilize this structure and allow recovery at ambient conditions. In [71R2] a recovery of quenchable perovskite in $\text{CaSiO}_3 - \text{CaTiO}_3$ up to 83 mol % CaSiO_3 was reported. In [98S3] perovskite in the above system up to 50 mol % CaSiO_3 was prepared.

The elastic properties of CaSiO_3 perovskites were studied [89M2, 96W1] and the volumes under high pressure [98S2] were determined. Models based on ab initio potentials have been applied to silicate perovskite CaSiO_3 [87H4, 87W3]. In [00W1] studied the melting temperature. This study shows that CaSiO_3 has a cubic structure near melting boundary and that the melting temperature is in good agreement with experimental data. The p - V equation of state for CaSiO_3 perovskite has been studied [89M1, 89T3, 94W2, 96W1]. In [84B1] was predicted that the zero-pressure bulk modulus of CaSiO_3 perovskite would be $K_0 = 227$ GPa. Measurements and calculation of the isothermal bulk modulus (K_0) and its pressure derivative (K_0') were performed [89M1, 89T3, 89T4, 94W2, 96W1] as well as theoretical studies [87H4, 93S2]. The most complete set of data from static compression was $K_0 = 232(8)$ GPa, $K_0' = 4.8(3)$ [96W1].

For CaSiO_3 perovskite see also [75L1, 86H1, 89H2, 93S7, 04A1] and for $\text{Ca}(\text{Ti,Si})\text{O}_3$ and $\text{Ca}(\text{Ge,Si})\text{O}_3$ perovskites see [66R1].

SrSiO_3

Three polymorphs have been obtained for SrSiO_3 [70S2]. The structure of $\alpha\text{-SrSiO}_3$ is monoclinic and consists of Sr^{2+} ions and $(\text{Si}_3\text{O}_9)^{6-}$ rings, which are alternately pseudo-hexagonally packed along the direction perpendicular to (001) [62H1, 82M1]. Because of this arrangement, the symmetry of $\alpha\text{-SrSiO}_3$ has been reported to be pseudo-hexagonal. There are two kinds of $(\text{Si}_3\text{O}_9)^{6-}$ rings: one comprising one SiO_4 and two Si_2O_4 tetrahedra, the other one Si_3O_4 and two Si_4O_4 tetrahedra. The $(\text{Si}_3\text{O}_9)^{6-}$ rings show twofold rotation symmetry. Atoms of Sr occupy the sites Sr1, Sr2 and Sr3. Each Sr is surrounded by eight O atoms to form a dodecahedron. The polyhedra Sr_1O_8 , and Sr_2O_8 and Sr_3O_8 are alternately connected with one another to form layers of SrO_8 on planes (004) and $(00\bar{4})$. The crystal lattice is a tridimensional arrangement of these layers, linked together with $(\text{Si}_3\text{O}_9)^{6-}$ rings by the O atoms.

SrSiO_3 has two high-pressure phases ($\delta\text{-SrSiO}_3$ and $\delta'\text{-SrSiO}_3$) in addition to $\alpha\text{-SrSiO}_3$ [82M1]. The above polymorphs were obtained by treatments of $\alpha\text{-SrSiO}_3$ at 4 and 6 GPa and $\cong 1275$ K. $\delta\text{-SrSiO}_3$ crystallizes in a triclinic lattice having space group $P\bar{1}$, and $\delta'\text{-SrSiO}_3$ in a monoclinic structure with space group $P2_1/c$ [82M1]. The lattice parameters are given in Table 3. In addition, the parameters for some doped SrSiO_3 [93L2] are also listed.

The $\text{CaSiO}_3 - \text{SrSiO}_3$ system has also been studied [75M4].

The symmetry of silicate perovskites is closely related with the ionic radii of eightfold-coordinated cations. As already mentioned, the CaSiO_3 perovskite is an unquenchable phase and the lattice has cubic ($\text{Pm}\bar{3}\text{m}$) symmetry [89M1, 02S2]. In the case of Mg^{2+} , whose radius is smaller than that of Ca^{2+} , the MgSiO_3 perovskite takes an orthorhombic lattice (Pnma) which is distorted from cubic symmetry [87H6]. The presence of **SrSiO_3 hexagonal silicate** having $6\text{H} - \text{BaTiO}_3$ was reported [05Y1]. The perovskite was crystallized from pressure induced amorphous SrSiO_3 in a diamond anvil cell, at $p = 35$ GPa, by laser heating. On releasing the pressure, the perovskite also changed into an amorphous state as does CaSiO_3 perovskite. The SrSiO_3 perovskite, with a tolerance factor greater than unity, forms a face-sharing SiO_6 octahedron, which leads to a structure with hexagonal symmetry [05Y1].

ZnSiO_3

The phase boundaries for the composition ZnSiO_3 are shown in Fig. 24 [89L1]. The reaction boundary willemite (Zn_2SiO_4) + quartz has a shallow negative slope of $-0.28(25)$ MPa/K [71S4, 89L1]. The transition boundary clinopyroxene – ilmenite has a p - T slope of $2(1)$ MPa/K [77A2]. The boundary determined by [79O4] is parallel to, and about 0.6 GPa lower than that of [77A2]. Other data on phase transitions in ZnSiO_3 were reported in literature [67R3, 74I1, 77I2, 77L2, 79O1]. At atmospheric pressure the composition ZnSiO_3 is not stable. At about 3 GPa, willemite and quartz react to form ZnSiO_3 clinopyroxene, which transform to ilmenite at

10...12 GPa. The ZnSiO_3 ilmenite decomposes into SiO_2 (stishovite) and ZnO with rocksalt structure at 20...30 GPa and 1000...2000 K [90A1]. The phase relations in ZnSiO_3 have some similarities to those of MgSiO_3 : clinopyroxene (C2/c) and ilmenite phases are stable in both systems. In [65H1, 71S4, 75M3] the presence of orthorhombic ZnSiO_3 (space group Pbca) was also reported which is metastable at all conditions. In the crystal structures of monoclinic ZnSiO_3 , Zn atoms are coordinated octahedrally at M1 sites and tetrahedrally at M2 sites. The Zn atoms at the M2 sites are not coordinated by the bridging oxygen, O3, of the SiO_3 chains. In the orthorhombic ZnSiO_3 , however, Zn atoms at the M2 sites have an irregular octahedral coordination including O3 atoms. Because of the difference in coordination of O3 to Zn atoms the shape of the SiO_3 chains in the two polymorphs is different. ZnSiO_3 (C2/c) has only one type of SiO_3 chain, while ZnSiO_3 (Pbca) has two types. As discussed already, in order to obtain the A and B chains of ZnSiO_3 (Pbca) starting from the chain of ZnSiO_3 (C2/c), it is necessary to consider the rotation of SiO_4 tetrahedra. However, the axes of rotation in ZnSiO_3 (Pbca) are not the lines connecting Si and O1 of the tetrahedra, but those through the shared corners, O2 of the tetrahedra and Zn1 octahedra [75M3]. The pressure studies of a single crystal ZnSiO_3 show a transition from the C2/c structure, at ambient conditions, to the $\text{P2}_1/\text{c}$ one at ≈ 1.9 GPa. The intermediate $\text{P2}_1/\text{c}$ phase further transforms to a second C2/c phase (HP - C2/c) at ≈ 5 GPa [89K2, 00A1]. The volume change of this transition is about 2.6 %, three times larger than in the first phase transition. The transitions are mostly displacive in character and are nonquenchable. The calculated phase boundary of ZnSiO_3 clinopyroxene – ilmenite transition is p [GPa] = $8.9(6) + 1.7(5) \cdot 10^{-3} T$ [K] [90A1].

Diopside, $\text{CaMgSi}_2\text{O}_6$

The crystal structure of $\text{CaMgSi}_2\text{O}_6$ is of space group C2/c [28W1]. The M1 site is occupied by Mg and M2 by Ca [68C1, 86R2]. A projection of the structure onto the (100)-plane is plotted in Fig. 1. Pressure studies were performed on diopside up to 5.3 GPa [81L1], 10 GPa [97Z1] and 40.8 GPa [00T3]. The unit-cell parameters decrease continuously with pressure – Fig. 25 [97Z1]. The larger polyhedra show more compression than the smaller ones. Diopside is more compressible than hedenbergite, as shown by their axial and volume compressibilities, because the FeO_6 octahedron is significantly more rigid than MgO_6 at high pressure. This implies that octahedrally-coordinated Fe^{2+} behaves differently from Mg^{2+} at high pressure, in contrast to their behaviour at ambient conditions. According to [00T2] the cell volumes decrease at almost the same rate for $\text{CaMgSi}_2\text{O}_6$ and $\text{Ca}_{0.8}\text{Mg}_{1.2}\text{Si}_2\text{O}_6$. A change in the mechanism of deformation at pressures higher than about 5...10 GPa was suggested. In diopside, at lower pressures, the deformation mainly occurs, at a similar rate, along the *b*-axis and a direction 145° from the *c*-axis on the (010)-plane. At higher pressures, instead, the deformation occurs mostly along the *b*-axis. In $\text{Ca}_{0.8}\text{Mg}_{1.2}\text{Si}_2\text{O}_6$, the orientation of the strain axes is the same as in diopside. The substitution of Ca with Mg in the M2 site induces, at a given pressure, a higher deformation on (010) with respect to diopside, but a similar change in the compressional behaviour was found. Changes in the M2 polyhedron with pressure can explain the above compressional behaviour. As seen in Table 4, the elasticity of diopside is not significantly affected by Mg substitution into the M2 site, in contrast to the significant stiffening occurring for Ca substitution into Mg-rich orthopyroxenes. The polyhedral volumes of M1 and M2 in diopside compressed under $p \approx 5.3$ GPa result in congruent behaviour of M1 and M2, which subsequently influence the distribution of Fe^{2+} between M1 and M2 sites [81L1, 96H2]. Phase transitions in $\text{CaMgSi}_2\text{O}_6$ diopside were analyzed [89I1, 89T1]. Above 17 GPa diopside dissociates into CaSiO_3 perovskite and Mg-Si-O components, the latter depending on temperature: β - or γ - Mg_2SiO_4 +stishovite, ilmenite and perovskite. For high-pressure transition see also [04A1].

The thermal expansion of diopside was studied [73C1, 73D1, 76F1, 98R3] – Fig. 26. The thermal expansion along the *a*- and *c*-axis is much smaller than along the *b*-axis (see also Table 5). The changes in the β unit-cell angle are very small especially above 1000 K, where they are within the error of determination. According to [73C1, 76F1], thermal expansion in diopside results from markedly expanding CaO_{6+2} and MgO_6 polyhedra where resulting mismatch with the rigid SiO_4 tetrahedra is resolved by rotation of the tetrahedra around the nonbridging oxygens and out-of-plane tilting of the tetrahedra. The molecular dynamics simulations were quite satisfactory in reproducing structure and bulk modulus of $\text{CaMgSi}_2\text{O}_6$ [96M3].

The X-ray diffraction intensity data [80S1] show that the final charges of atoms are less than the corresponding formal ones in $\text{CaMgSi}_2\text{O}_6$ (C2/c) silicate – Table 6. Residual electron densities between Si and O have been observed in difference Fourier maps [80S1].

Theoretical studies were performed on diopside. In [84M1] the structure and elastic constants were calculated in reasonable agreement with experimental data with a potential energy model in which Coulomb, Gilbert-type near neighbour repulsion, bond-angle bonding and bond stretching terms were included. In [86P1] an ionic model was applied to calculate the crystal structure of diopside and it was observed that a purely ionic model does not do well in reproducing the structure. The lack of consideration of covalency effects in the ionic model is the main reason for the failure of this description. In [89D1] a lattice energy minimalization calculation of diopside was performed by using a model potential in which covalent shell model, short-range repulsion and Coulomb-type interaction terms were included. By combining values for the interatomic potential parameters from various sources, an acceptable reproduction of the experimentally known crystal structure and elastic constants was obtained. The simulated properties from lattice dynamic calculations are similar to those obtained by molecular dynamic calculations with the same potential model. Some elastic properties are listed in Table 4.

The diffusion of atoms in diopsides has been studied. In [83B1] the average interdiffusion of Ca/(Mg,Fe) was determined. The maximum values for Ca, Mg, Al and Fe self-diffusivities were estimated [82F1]. The Al/(Mg,Si) interdiffusion was also measured [88S2]. In [94R2] the oxygen self-diffusion was analysed and in [96B1] the Si self-diffusion. The Ca self-diffusion in Fe-free and Fe-bearing diopsides were determined [95D1, 96D2, 98D2]. For example, in diopside single crystal the ^{44}Ca diffusion is almost isotropic at least in *b* and *c*-directions, perpendicular and parallel to the $(\text{SiO}_3)_n$ chains, respectively [98D2]. At least two different regimes were observed. At low temperatures ($T < 1230^\circ\text{C}$), diffusion is extrinsic, proportional to $(p_{\text{O}_2})^{-0.19(3)}$ and the activation enthalpy is 284(10) kJ/mol. These data are compatible with an interstitial mechanism and it was suggested that M3 and M4 interstitial sites in the octahedral and tetrahedral layers, respectively, are the best candidates for the interstitial Ca (for their location see [98D2]). At $T > 1230^\circ\text{C}$, diffusion is p_{O_2} -insensitive and has a very high activation enthalpy ($\cong 1006$ kJ/mol). It was proposed that this enhanced diffusion coefficient should be intrinsic, related to Ca-Frenkel defects (exclusively thermally activated pairs of Ca-vacancy and Ca-interstitial). This would correspond to an excess of disorder for the calcium, like a premelting phenomenon of its sublattice, and could be responsible for the excess of configurational entropy observed for diopside above 1250°C . It was suggested to be an additional evidence that in diopside the conduction by electronic transport is more likely [98D2]. The Sm and Sr diffusion was also studied [84S3]. In [95I2, 99H2, 00C5] hydrogen diffusion was measured.

For crystal structure of diopside see also [62C2, 68C3, 79L1].

CaMgSi₂O₆: Cr

Synthetic blue diopside has been suggested to contain Cr^{2+} because of blue color [71D1, 72I1]. Most terrestrial Cr-rich diopsides have a green color, indicative of Cr^{3+} . The occurrence of Cr^{3+} in tetrahedral lattice sites or the presence of lattice defects has also been postulated as cause of the color of synthetic blue diopside [71D1, 72I1]. Cr^{3+} readily substitutes into the favorable octahedral M1 lattice site. In [77S3] was shown that chromium diopside crystals, when synthesized in air at high temperatures from silicate melts, are often colored in a characteristic blue. The blue color of synthetic diopside was associated with the stabilization of a small portion of the total Cr as Cr^{4+} within the diopside structure. Cr^{4+} is not present initially in the silicate melts, but is produced by the reduction of Cr^{6+} during the crystallization.

The elastic constants of chrome-diopside $\text{Di}_{93}\text{Hd}_3\text{Ko}_2\text{X}_2$ were studied, where X is unknown [03I1].

Pyroxene crystals of diopside composition, doped with different cations were synthesized in order to study the OH incorporation [94S3]. Concentrations up to 1100 ppm H_2O , compatible with most hydrous pyroxene samples known, could be obtained.

Ca_{1-x}Sr_xMgSi₂O₆

In [82B3, 87B2] was shown that at least 30 % of Ca^{2+} can be substituted by Sr^{2+} in diopsides synthesized at 0.1 MPa and 1200...1300°C. In [98G1] $\text{Ca}_{1-x}\text{Sr}_x\text{MgSi}_2\text{O}_6$ solid solutions were hydrothermally synthesized, in equilibrium with 1mol (Ca,Sr)Cl₂ aqueous solution at 750°C and 240 MPa. Total substitution of Sr^{2+} for Ca^{2+} on M2 sites can be assumed. The lattice parameters vary linearly with the Sr content, a [Å] = 9.7454 + 0.0681x + 0.0545x_{Mg}; b [Å] = 8.9272 + 0.2823x - 0.0881x_{Mg}; c [Å] = 5.2555 + 0.0214x - 0.0204x_{Mg}; β [°] = 105.817 - 1.119x + 1.501x_{Mg} [98G1]. In the above relations, variations from normal composition corresponding to one Mg atom were also considered.

Ferridiopside, $\text{CaMg}_{1-x}\text{Fe}^{3+}_x\text{Si}_{2-x}\text{Fe}^{3+}_x\text{O}_6$

The pyroxene with composition $\text{CaFe}^{3+}\text{Fe}^{3+}\text{SiO}_6$ is unstable even under high pressure, relative to the formation of andradite (see Chap. 8.1.1.5, subvolume 27I1) and hematite [67H2] phases. About 33 wt % of $\text{CaFe}^{3+}_2\text{SiO}_6$ can be substituted in diopside [53S1, 67H2]. The substitution is of the type $\text{Fe}^{3+}\text{-Fe}^{3+}$ for $\text{Mg}^{2+}\text{-Si}^{4+}$. According to [88M4], diopside is called ferridiopside, if the Fe^{3+} content is greater than that of Fe^{2+} and ferrian diopside, when the number of Fe^{3+} cations is > 0.1 per six oxygens. Diopside is called subsilicic if $\text{Si} < 1.75$. As mentioned above, the structure of diopside was refined by [68C3, 73C1, 81L1]. In [90R1] the structure of fine grained clinopyroxenes was characterized along the join hedenbergite – diopside. In diopside, Ca^{2+} occupies strongly distorted eightfold-coordinated M2 polyhedra, Mg and Fe are found in a regular octahedral M1 site. M1 and M2 polyhedra form planes with the (bc) -plane, which are separated from each other parallel to the a -axis by corner-sharing single chains TO_4 -tetrahedra. The phase relations of clinopyroxenes $\text{CaMgSi}_2\text{O}_6$ – $\text{CaFe}^{3+}\text{Fe}^{3+}\text{SiO}_6$ was analyzed [69H3, 98R1]. The $\text{Fe}^{3+}\text{Fe}^{3+}$ substitution for $\text{Mg}^{2+}\text{Si}^{4+}$ increases lattice parameters a and c as a consequence of increasing size of the tetrahedra (significant increase of T-O bond length), whereas moderate shrinking of the size of the M1 octahedra, as seen by a decrease of M1-O distances, causes the shrinking of b [98R1]. The monoclinic angle β remains unaffected by ferric substitution.

Hedenbergite, $\text{CaFe}^{2+}\text{Si}_2\text{O}_6$; esseneite, $\text{CaFe}^{3+}\text{AlSiO}_6$

Hedenbergite is a ferrous chain silicate belonging to the pyroxene group with nominal composition $\text{CaFeSi}_2\text{O}_6$. The space group is C2/c [73C1]. Ferrous ions occupy octahedral M1 sites which form continuous chains parallel to c – Fig. 27. Chains of M2 sites are occupied by Ca, while SiO_4 tetrahedra share corners to form zig-zag $(\text{SiO}_3)_\infty$ chains. The structural conditions make us expect a pseudo-one-dimensional arrangement of magnetic cations – Fig. 27b. As in ferrosilite, the polyhedral bonds are sandwiched between single silicate chains, forming tetrahedral-octahedral-tetrahedral (T-O-T) strips or I-beams, which are packed in a pseudo-body-center fashion in the (ab) -plane – Fig. 2. The structure of end member hedenbergite was refined [69C1]. Hydrothermal synthesis of hedenbergite was performed [69N1, 69R1, 73T1, 74G3, 75K1, 82B5, 87H2, 88K1, 90M3, 90R2, 92P2, 94K1, 97Z1, 00R1]. The stability of hedenbergite at 0.2 GPa was determined as function of temperature and oxygen fugacity [74G3, 82B5].

Phase transformations in a synthetic hedenbergite were studied at $\cong 1200^\circ\text{C}$ [91K2]. $\text{CaFeSi}_2\text{O}_6$ first decomposes into spinel, stishovite and cubic perovskite phases at $\cong 16$ GPa, and spinel further decomposes into wüstite and stishovite at $\cong 19$ GPa. Between 19 GPa and 26 GPa the phase assemblage is wüstite + stishovite + perovskite. On the decompression to 0.1 MPa, all the high-pressure phases are retained except the cubic perovskite which reverts to a retrogressive phase of CaSiO_3 . A comparison of the results of [89R1] and [91K2] suggests that the garnet phase formed from natural hedenbergite is stabilized by Mn^{3+} , Na^+ , Zn^{2+} , Fe^{2+} , Mn^{2+} , Fe^{3+} , Al^{3+} .

The pressure studies performed between 0.1 MPa and 10 GPa show that the polyhedral volumes of CaO_8 , FeO_6 and SiO_4 decrease by 8.4, 6.6 and 2.9 %, respectively. The longest bonds of CaO_8 and FeO_6 show most compression. Significant compression in the two shortest Si-O1 and Si-O2 bond lengths of SiO_4 tetrahedra was observed at relatively low pressures, resulting in a tetrahedral volume compression of 1.6 % between 0.1 GPa and 4 GPa and 1.3 % between 4 and 10 GPa. The compression of the unit cell can be described by the volume compression of the individual CaO_8 and FeO_6 polyhedra, with the SiO_4 tetrahedra playing a minor role [97Z1] – see Fig. 25.

Esseneite is a clinopyroxene with the ideal formula $\text{CaFe}^{3+}\text{AlSiO}_6$ [68H1]. This pyroxene is stable at 1 atm [69H2] and has a wide range of stability field up to about 4 GPa [75O3, 78O1]. Esseneite crystallizes also in space group C2/c [75G2, 86G1, 86G2, 89C4]. The ferric ions occupy both octahedral and tetrahedral sites in synthetic CaFeAlSiO_6 [73O1, 75G2, 81K2]. For example, in the sample prepared at 2 GPa and 1375°C , the octahedral M1 site is occupied by 0.82 Fe^{3+} and 0.18 Al^{3+} . Within the tetrahedral T site, the distribution of cations is $\text{Si}^{4+}(0.50)$, $\text{Al}^{3+}(0.41)$ and $\text{Fe}^{3+}(0.09)$. The ions in T site are completely disordered although submicroscopic domains with short range order are very likely. The octahedral site preference energy of the Fe^{3+} ions with respect to Al^{3+} ions in $\text{CaFe}^{3+}\text{AlSiO}_6$ is about 10 kcal/mol [86G1]. Topologically, the structure of $\text{CaFe}^{3+}\text{AlSiO}_6$ is intermediate between that of diopside and calcium Tschermak's pyroxene. The refinement of natural esseneite $(\text{Ca}_{1.01}\text{Na}_{0.01})(\text{Fe}^{3+}_{0.72}\text{Mg}_{0.16}\text{Al}_{0.04}\text{Ti}_{0.03}\text{Fe}^{3+}_{0.02})(\text{Si}_{1.19}\text{Al}_{0.81})\text{O}_6$ shows that the M2 site is occupied by Ca and Na, M1 by Fe^{3+} and Mg^{2+} and the tetrahedral site by Al and Si [87C3]. There is no detectable Fe^{3+} in

the tetrahedral site in contrast to synthetic $\text{CaFe}^{3+}\text{AlSiO}_6$ which contains tetrahedral Fe^{3+} , implying a cooling rate dependence of Fe^{3+} and Al^{3+} ordering on the M1 and T sites, respectively.

Johannsenite, bustamite, $\text{CaMnSi}_2\text{O}_6$

The structure of $\text{CaMnSi}_2\text{O}_6$ (johannsenite) is of C2/c type [67F1]. The complete substitution of Mg by Mn in the M1 site of diopside structure does not distort the M1 octahedron [69G1]. For crystal structure of bustamite see [62P1].

$\text{CaCoSi}_2\text{O}_6$, $\text{CaNiSi}_2\text{O}_6$

The crystal structure of synthetic $\text{CaCoSi}_2\text{O}_6$ and $\text{CaNiSi}_2\text{O}_6$ clinopyroxenes are of C2/c type [75G3, 77R1, 77S2, 87G1]. Analyzing the crystal structures of $\text{CaM}^{2+}\text{Si}_2\text{O}_6$ ($\text{M}^{2+} = \text{Mg}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$) clinopyroxenes shows [87G1] that all polyhedra (including SiO_4 tetrahedra) are inherently flexible, and their absolute shapes and sizes are dependent on the interaction with the adjacent polyhedra.

$\text{CaAl}_2\text{SiO}_6$ (Calcium Tschermak's pyroxene, CaTs)

The crystal structures of $\text{CaAl}_2\text{SiO}_6$ were studied. A hexagonal polymorph was grown by reheating the glass between 950°C and 1050°C [73K1]. A monoclinic polymorph was also reported [62C1, 66H1, 67H1, 74O1]. The sample prepared at 1300°C and 18 kbar crystallizes in space group C2 [74O1]. According to [74O1] the Al-Si were completely disordered at tetrahedral sites. Later on, in addendum, extra reflections were shown which indicate Si-Al ordering in the tetrahedral chain [74O1] (see also section 8.1.4.5). Ca occupies the M2 site. A feature of the structure is the CaO_8 coordination polyhedron, which is smaller and more regular than that in diopside. This feature probably explains the stability of CaTs under high pressure.

$\text{CaMgSi}_2\text{O}_6$ – $\text{Mg}_2\text{Si}_2\text{O}_6$ and iron doped systems

In the above system the space groups at RT are P_2_1/c for Ca-poor (pigeonite) compositions and C2/c for Ca-rich samples. As mentioned already, the M2 site is eightfold-coordinated in C2/c end members and six-coordinated in the P_2_1/c structure. An immiscibility region separating the fields of Ca-rich and Ca-poor pyroxenes was proposed [52A1, 64B2, 66D1, 72K1, 72Y1]. For intermediate compositions, the M2 site was reported to be very irregular as a result of multiple occupancy of the large Ca and small Mg atoms in the site. For example in [70M2] was concluded that the irregular M2 coordination polyhedron was an average of eight and six coordinations. The M2 polyhedron becomes very irregular, thus highly unstable, in the middle of the solid solution [72T1]. This provided a structural explanation for the presence of the miscibility gap. The increased solid solution between Ca-poor and Ca-rich clinopyroxenes, at high temperature, was explained by the change in M2 coordination associated with the P_2_1/c – C2/c phase transition [73C1]. According to [75O1], the decrease in the average size of the M2 due to substitutions causes kinking of the tetrahedral chain and concomitant increases in out-of-plane tilting of the basal face of the tetrahedron. As the M2 polyhedron decreases further in size, the space group changes from C2/c to P_2_1/c . The orthorhombic phase has been shown to have stable regions, at high and low temperature, in the phase diagram of the Di – En system [80L3, 83J1, 85B1, 85C1, 86C1]. The clinopyroxenes from Di – En join were also studied [73S2, 74W2, 76O2, 82B4, 89T2]. The C2/c clinopyroxene, synthesized along the $\text{CaMgSi}_2\text{O}_6$ – $\text{Mg}_2\text{Si}_2\text{O}_6$ join, was later refined according to a M2-split model, in which the Mg cations order between the usual M2 position and a M2' split position at ≈ 0.7 Å from M2, along the diad axis [82B4]. Also, the similarity of the four-coordinated M2' site to the M2 polyhedron in the C2/c synthetic ZnSiO_3 crystal was stressed [75M3]. The average structures of $\text{Ca}_{0.8}\text{Mg}_{1.2}\text{Si}_2\text{O}_6$ and $\text{Ca}_{0.66}\text{Mg}_{1.34}\text{Si}_2\text{O}_6$ clinopyroxenes were refined according to a split model also for oxygen atoms (O-split model), in which Mg in M2' is six-coordinated [89T2]. They also observed that in the large M2 cavity, in C2/c pyroxenes, Ca atoms assumed diopside-like configuration (eight-coordinated) and Mg atoms, as suggested by [87R2], assume a pigeonite-like configuration (six-coordinated) [72B1]. Both configurations coexist in C2/c pyroxene solid solutions and explain the features observed in the average structures. Analyzing the structure of $\text{Ca}_{0.8}\text{Mg}_{1.2}\text{Si}_2\text{O}_6$ single crystal clinopyroxene in the temperature range $143 \text{ K} \leq T \leq 973 \text{ K}$, a residual electron density along the diad axis, indicating a M2 split position, has been observed up to 973K [89T2]. The most important feature observed in the average structure was the deformation of the M2 polyhedron with increasing temperature, leading to a decrease in Ca coordination from 8- to 6-fold. The temperature increase causes a M2 polyhedral deformation opposite to

that observed at room temperature, when there is an increase in the mean ionic radius of cation in M2 (chemical substitution). A possible interpretation is that at high temperature the M2 cavity retains the expansion along the diad axis imposed by octahedral expansion and by changes of the tetrahedral chain. Expansion of the M2 polyhedron becomes too great for the cations that occupy the cavity; tetrahedral chain shifting and consequent M2 polyhedral distortion allow reasonable bond lengths to be maintained through release of two of the four O3 [89T2].

In Ca-poor clinopyroxenes, a $P2_1/c - C2/c$ phase transition occurs at high temperatures [72B1, 72S1, 84S4] and with increasing pressure [92A1, 94H2]. Structurally, this transition is driven by changes in the tetrahedral chain arrangement. In the primitive structure there are two different chains. In the $C2/c$ structure the chains become symmetrically equivalent. In the high-temperature $C2/c$ structure, the two chains are elongated, whereas in the high-pressure form they are both kinked [92A1, 94A1, 94H2, 98A4, 99R2, 00A1]. It has been shown that the HT and HP $C2/c$ structures have different stabilities fields [00A1, 00A2] and the $P2_1/c$ structure, characteristic of pigeonite clinopyroxene, is intermediate between the two varieties. The structural changes that occur, with increasing T and at the transition, were determined by in situ high-temperature XRD and electron microscopy studies and the thermodynamic character of the transition was found to be of first order [72B1, 74S1, 84S4, 91S2, 97A2]. The TEM investigations of synthetic $Di_{40}En_{60}-Di_{60}En_{40}$ [00T3] have shown deviation from first order behaviour and also [02C1] a marked continuous behaviour in Fe-rich samples with Ca-content up to 0.2 Ca apfu. In [02T1] the high-temperature $P2_1/c - C2/c$ phase transition in $Ca_{0.15}Mg_{1.85}Si_2O_6$ pyroxene was studied. A first-order phase transition was found at $T_c = 926(39)^\circ\text{C}$. Prolonged heating at high temperatures induced a non-reversible increase in the transition temperature up to more than 1150°C without apparent changes in the order of phase transition. Coupling with strain due to incipient exsolution, in formerly almost defect free samples, was suggested to be responsible for the increase in T_c . The exsolution features observed by TEM in Ca-bearing sample, due to heating close to the temperature of transition, were likely to have given rise to local order parameter fluctuations. These fluctuations, being associated with compositional fluctuations were coupled with a strain, related to incipient exsolution. Similar fluctuations were also observed in Ca-rich samples [00T3]. There are minor changes in chain configurations, which are highly differentiated up to 1000°C , confirming the strong first order character of transition.

Experimental work of the high-temperature $P2_1/c$ to $C2/c$ phase transition has shown that the transition temperature decreases from about 1000°C to 200°C as the Ca and Fe content increases from a hypothetical clinoenstatite end member [65P1, 71P1, 72B1, 72S1, 74S1, 84S4, 00A1]. This high-temperature transition was analysed by using Landau theory [02C1, 02T1] and determining the effects of increasing Ca and Fe content of exsolution related microstructures and Fe-Mg cation order-disorder. For synthetic clinopyroxenes, along the diopside – enstatite join, the effect of Ca for Mg substitution and related microtextures on the phase transition can be well constrained. The TEM and XRD studies indicative of a P lattice are still present at RT in samples having 0.0 to 0.6 Ca apfu [00T2]. In clinoenstatite [01S1] and Ca-poor clinopyroxene, a first-order phase transition was observed with increasing temperature [91S2, 02T1], as mentioned above, or pressure [92A1, 02N1]. A decrease in transition temperature and pressure was noted with decreasing Ca content. In [01T1] the high-pressure transition $P2_1/c - C2/c$ in $Ca_{0.5}Mg_{1.5}Si_2O_6$ up to 14.2 GPa was investigated. The transition was observed at $p = 3 \dots 5$ GPa and is marked by a continuous decrease in a , c and β parameters in the transition range – Fig. 28 – and by the disappearance of reflections with $h+k$ odd. No hysteresis could be found. The spontaneous strain due to the transition occurs almost completely on the (010)-plane and is described by a strong compression at a direction of 150° from c -axis and a milder expansion at 60° from the c -axis. The transition occurs with a smeared strain tail between 3 and 5 GPa, and deviates from first order behaviour. In situ high-temperature single crystal TEM studies for samples having compositions $Di_{50}En_{50} - Di_{60}En_{40}$ show that reflections characteristic for P lattice are relatively strong up to relatively high temperature and become very diffuse, when the transition was obtained, up to $T \cong 900^\circ\text{C}$ (highest achievable) even in grains with compositions close to transition [00T2]. In situ high-temperature powder diffractions performed on $Ca_{0.52}Mg_{1.46}Al_{0.05}Si_{1.98}O_6$ ($Di_{52}En_{46}CaTs_2$) and $Ca_{0.59}Mg_{1.41}Si_2O_6$ ($Di_{60}En_{40}$) samples showed a $P2_1/c - C2/c$ displacive phase transition at $T_c = 550^\circ\text{C}$ and 300°C , respectively [03T3]. Landau modeling the phase transition showed a tricritical behaviour for sample $Di_{52}En_{46}CaTs_2$. Along the join Di – En, a decrease of T_c with increasing Ca content was observed in agreement with other data [71P1, 00A2], as well as a switch from first-order to tricritical behaviour as the Ca content increases. On the basis of the M2 average cation radius [00A2], one would predict for the samples $Di_{52}En_{46}CaTs_2$ and $Di_{60}En_{40}$, T_c values at 300°C and 100°C , respectively, lower than those experimentally determined. The presence of compositional modulations may account for the increase in T_c above expected

values. In $\text{Di}_{15}\text{En}_{85}$ it was observed that compositional modulations stabilize the $\text{P2}_1/\text{c}$ phase, increasing its T_c . The modulations for compositions higher than $\text{Di}_{60}\text{En}_{40}$ vanish with increasing Ca content and at $\text{Di}_{65}\text{En}_{35}$ no evidence of modulations can be observed [00T2]. Thus, the change in thermodynamic behaviour of transition can be related to increasing Ca content [02C1, 03T3] and to Ca-related microstructures. Microstructures induce a strain that may interact with the spontaneous strain of the transition. Ca substitution induces mottled textures, preliminary to exsolution, and is related to a decrease in the size of the antiphase domains [03T3]. Thus, the transition behaviour in samples with low and high Ca content along the Di – En join indicates that a decrease in T_c and a switch from first-order to tricritical behaviour, with increasing Ca content, are related to an interaction with the antiphase domains at the nanoscale [03T3]. For analysis of the structural transition see also section $(\text{Ca,Mg,Fe})_2\text{Si}_2\text{O}_6$.

$\text{CaMgSi}_2\text{O}_6$ – $\text{CaFeSi}_2\text{O}_6$

The relation between the chemical composition and the unit-cell parameters for the diopside – hedenbergite series has been studied for natural [66W2] and synthetic [69R1] samples. The composition dependences of lattice parameters are plotted in Fig. 29. The cell volume and cell edges a and b appear to change linearly over the entire compositional range, although β does not. The c dimension is not sensitive to the Mg/Fe ratio. No significant difference was observed for samples synthesized on different oxygen buffers [69R1].

$(\text{Ca,Mg,Fe})_2\text{Si}_2\text{O}_6$

According to [88M3, 88M5] the name of **pigeonite** was given for the minerals having space group $\text{P2}_1/\text{c}$ and **augite** for compositions crystallizing in space group $\text{C2}/\text{c}$. Later on, the **high** and **low pigeonite** were used for $(\text{Ca,Mg,Fe})_2\text{Si}_2\text{O}_6$ having $\text{C2}/\text{c}$ and $\text{P2}_1/\text{c}$ crystal structure, respectively. Earlier studies [56M2, 57B1] found that pigeonite has space group $\text{P2}_1/\text{c}$. Analyzing the $\text{Mg}_{0.34}\text{Fe}_{0.56}\text{Ca}_{0.10}\text{SiO}_3$ sample, an ordered distribution of Mg, Fe and Ca atoms in M1 and M2 sites was shown and also that M2 is coordinated by seven oxygen atoms as compared to diopside, where eight atoms were shown [60M1]. For $\text{Mg}_{0.39}\text{Fe}_{0.52}\text{Ca}_{0.09}\text{SiO}_3$ (space group $\text{P2}_1/\text{c}$) was reported that one position has almost regular octahedral coordination of oxygen atoms around and it is occupied by $0.73\text{Mg} + 0.27\text{Fe}$. The other position is in a rather irregular polyhedron coordinated by seven oxygen atoms and is occupied by $0.05\text{Mg} + 0.77\text{Fe} + 0.18\text{Ca}$ [70M2]. The kinetics of $\text{Fe}^{2+}\text{-Mg}^{2+}$ exchange between M1 and M2 sites ($\text{Fe}^{2+}_{\text{M2}} + \text{Mg}^{2+}_{\text{M1}} = \text{Fe}^{2+}_{\text{M1}} + \text{Mg}^{2+}_{\text{M2}}$) in augite $(\text{Ca}_{0.841}\text{Na}_{0.019}\text{Mg}_{0.888}\text{Fe}^{2+}_{0.151}\text{Ti}_{0.011}\text{Al}_{0.028}\text{Cr}_{0.003}\text{Fe}^{3+}_{0.054}\text{Mn}_{0.006})(\text{Si}_{1.914}\text{Al}_{0.086})\text{O}_6$ were followed by ordered experiments [01B1]. Kinetic constants (K) for each isotherm were calculated from the distribution coefficient $K_D = (\text{Fe}^{2+}/\text{Mg}^{2+})_{\text{M1}}/(\text{Fe}^{2+}/\text{Mg}^{2+})_{\text{M2}}$ measured during a series of experiments. The calculations of K_D were performed by using the Landau method (see for example [88S1]), Müller's kinetic law [67M2, 69M3] and the Sha-Chappell method [96S1] to check the responses of various kinetic models for a Ca-rich pyroxene on the same data set. The activation energy of $\text{Fe}^{2+}\text{-Mg}^{2+}$ exchange spans a narrow range, yielding values of 200(28) kJ/mol independent of the method used to calculate K_D .

The existence of a $\text{C2}/\text{c}$ -type structure was predicted by [69S4] and confirmed later [69S5, 70P1] as a non quenchable, high-temperature form. The studies performed evidenced the presence of space group $\text{C2}/\text{c}$ for Ca-rich and $\text{P2}_1/\text{c}$ for Ca-poor compositions [00T2]. The $\text{P2}_1/\text{c}$ structure contains two symmetrically distinct chains of SiO_4 tetrahedra. At high temperature it has space group $\text{C2}/\text{c}$. A $\text{C2}/\text{c}$ - $\text{P2}_1/\text{c}$ transition occurs by rotations of the tetrahedra until the two chains become symmetrically equivalent [72B1, 72S1, 74S1, 75S1, 84P1, 85S1, 00A2]. The thermodynamic character of the transition varies with composition. In case of crystals having compositions $\text{En}_{32}\text{Fs}_{66}\text{Wo}_2$ and $\text{En}_{92}\text{Wo}_8$, the transition was found of first order [74S1, 02T1]. A second-order-type transition was found for composition $\text{En}_{47}\text{Fs}_{43}\text{Wo}_{10}$ [02C1]. The Fe and Mg in pigeonite are distributed between M1 and M2 sites in a strongly temperature dependent manner [97W2, 98A3, 00P1, 02C1]. Calcium due to its larger ionic radius is considered to be fully ordered at the larger M2 site. The $\text{C2}/\text{c}$ – $\text{P2}_1/\text{c}$ transition was shown to be influenced by this nonconvergent ordering as well as by composition [02C1]. The simplest explanation for such a behavior is that increasing Fe/Mg disorder causes the average size of cations at the M2 site to decrease, which, in turn, destabilizes the $\text{C2}/\text{c}$ structure with respect to the $\text{P2}_1/\text{c}$ structure and the transition temperature increases. According to [03C2] it follows that, under equilibrium conditions, there is a complex relationship between the displacive order parameter, Q_D and the non-convergent order parameter Q_{OD} as function of Q_{OD} . Q_{OD} will change as consequence of the displacive transition and the displacive transition

temperature will change also as function of Q_{OD} . The Q_{OD} is defined by $Q_{OD} = (X_{Fe}^{M2} - X_{Fe}^{M1})(X_{Fe}^{M2} + X_{Fe}^{M1})^{-1}$ where X_{Fe}^{M2} and X_{Fe}^{M1} are the average occupancies by Fe atoms of the M2 and M1 sites, respectively. If the Fe/Mg ratio is not 1/1, in order to obtain $Q_{OD} = 1$ for complete order in the Fe rich end solid solutions, the Q_{OD} was expressed by $Q_{OD} = (X_{Mg}^{M1} - X_{Mg}^{M2})(X_{Mg}^{M1} + X_{Mg}^{M2})^{-1}$. When Ca is present, it is necessary to take account the fact that the M2 site is partially occupied by atoms which do not participate in the O/D process. Q_{OD} is non-symmetry breaking in the sense that it describes Fe/Mg ordering which does not lead to a phase transition. Q_D is a symmetry breaking order parameter, which transforms as the active representation for the C2/c to P2₁/c transition. A Landau potential with linear-quadratic coupling has been developed to describe interactions between a non-convergent order parameter Q_{OD} for Fe/Mg ordering and the order parameter Q_D for the C2/c – P2₁/c phase transition in pigeonite [03C2]. Lattice parameters determined, for En₄₇Fs₄₄Wo₉ in situ, up to 1050°C, revealed that increasing Q_{OD} could act to suppress Q_D by a mechanism which includes overlapping and opposing strain fields. The temperature dependence of Q_D^2 for different fixed values of Q_{OD} is consistent with the initial Landau model. A linear dependence of transition temperature on Q_{OD} was shown.

Microtextural observations of the antiphase domains originating from the C to P symmetry reduction and of their relation to exsolution lamellae were performed on P2₁/c pigeonites, in view of the potential geothermometric interferences that can be obtained from the size, shape and orientation of the domains [78C1, 79C1, 88F1]. It was found that domain size increases with decreasing Ca content [86F1]. At high temperatures, in situ TEM investigations on the P2₁/c – C2/c transition were reported [81G2, 86F1, 91S2, 92S4]. In [81G2] was shown that the antiphase domains form at the same position before and after the heating runs, which is the “memory effect” [00T2]. The observed memory effect was related to Ca clustering at the boundaries already present before heating. In [91S2] the transition was described as first order martensitic in view of the large hysteresis, which however decreases with repeat heat treatments. In [91S2] was also shown that the transition occurs by growth of the C2/c high-temperature phase from the antiphase boundaries.

The P2₁/c → C2/c transition was also observed at high pressures [92A1, 94H2, 95C1, 99R1]. The high-pressure phase transition is of first order with a C2/c-high-pressure phase displaying extreme kinking of the tetrahedral chains with respect to the high-temperature C2/c phase. In [99B1] the high-pressure transition in natural pyroxene was documented. The critical pressures for phase transition are sensitive to composition change being at $p_c = 6.5$ GPa in clinoenstatite and 1.7 GPa in clinoferrosilite. A significant hysteresis was observed in Mg-rich compositions, whereas in [94H2, 99R2] it was not able to demonstrate hysteresis for the more Fe-rich ones. Investigations of the high-pressure and high-temperature C2/c structures indicate significant difference between these. In particular, the tetrahedral chains are almost extended at high temperatures and are extremely kinked at high pressure [94H2]. This was confirmed by further in-situ investigations with changing p and T on enstatite [99S1] and kanoite [00A1] that indicated the presence of separated stability fields for high-temperature and high-pressure C2/c structures.

The transition can also be followed at room temperature, as Ca-rich clinopyroxenes are of C2/c type. Increasing Mg or Fe substitution at the M2 site gives rise to P2₁/c Ca-poor clinopyroxenes. There are data on both C2/c and P2₁/c-type lattices along the CaMgSi₂O₆ – Mg₂Si₂O₆ and CaMgSi₂O₆ – Fe₂Si₂O₆ series [75O1, 76O2, 82B4, 89T2, 00A1, 00T2]. In [00A1] was suggested that at RT a critical radius for the cation in the M2 site is 0.88 Å. Clinopyroxenes with higher average M2 cation radius are of C2/c type, while those with smaller cation size are of P2₁/c type [75O1, 00A1]. In CaMgSi₂O₆ (Di) – Mg₂Si₂O₆ (En), the transition occurs at a critical composition Di₆₀En₄₀ and M2 cation radius of 0.89 Å [00T1]. Thus, for samples with Ca content lower than 0.6 atoms pfu, selected area diffraction showed the presence of reflections violating the space group C2/c indicating a transition to the P2₁/c symmetry, at RT. At this composition, the transition is not marked by a prominent change in the cell parameters along the join – Fig. 30. For composition between Di₆₀En₄₀ to about Di₄₀En₆₀, the cell parameters deviate little with respect to the trend shown for Ca-rich C2/c structure, whereas for compositions richer in Mg than about Di₄₀En₆₀ a significant deviation is present, which is marked by discontinuities in the c and β parameters.

The temperature dependence of the intracrystalline exchange reaction $Fe_{M1} + Mg_{M2} \rightarrow Fe_{M2} + Mg_{M1}$ under equilibrium conditions in P2₁/c pigeonite with differing Mg/Fe ratios was analyzed in pigeonite [00P1] and augite [01B1]. The result implies negligible compositional effects on Mg-Fe partitioning in the CaSiO₃ – MgSiO₃ – FeSiO₃ system. A similar degree of order was evidenced as in P2₁ and Pbca orthopyroxene at a given temperature. There is a small effect of Ca on Fe-Mg ordering in pyroxene for CaSiO₃ content between 0 and 10 mol % [00P1].

For crystal structure of some binary clinopyroxenes see also Sect. 8.1.4.1.5 and Sect. 8.1.4.1.10.

For crystal structure of pigeonites see [89F1].

Ca(Mg,Fe,Al)Si₂O₆ perovskites

The Ca_{0.5}Mg_{0.5}SiO₃ perovskite (CM-perovskite) was reported as a high-pressure polymorph of diopside with cubic perovskite structure [87L3]. In other studies diopside breaks down into a cubic CaSiO₃ perovskite phase (Ca-perovskite) and an orthorhombic MgSiO₃ perovskite phase (Mg-perovskite) at $p > 21$ GPa [78M1, 89I1, 89T1]. In [94K3] was verified that (Ca,Mg)Si₂O₆ glass transforms to Ca_{0.5}Mg_{0.5}SiO₃ cubic perovskites at 13 GPa, whereas a diopside crystal decomposes to CaSiO₃ cubic perovskites, Mg₂SiO₄ spinel and stishovite at 17 GPa and 1000°C using a laser heated diamond anvil cell. They observed also that Mg₂SiO₄ spinel and stishovite recombine to form MgSiO₃ ilmenite at 22 GPa which, in turn, transforms to an orthorhombic MgSiO₃ perovskite above 24 GPa. They inferred that CM perovskite should be metastable, based on the volume difference between the CM-perovskite and a mixture of Ca-perovskite and Mg-perovskite. In [97O1] the phase relation of diopside was analysed at 18...24 GPa and 700...2100°C, using a multianvil apparatus and CM-perovskite was not observed. By in situ XRD experiments, at around 23 GPa, using a multianvil apparatus combined with synchrotron radiation, it was observed that crystalline CaMgSi₂O₆ decomposes to Ca-perovskite and ilmenite, whereas glassy CaMgSi₂O₆ transforms to a cubic perovskite at 1000°C [00I1]. Both of them transformed to cubic Ca-perovskite and orthorhombic Mg-perovskite above 1200°C. These studies showed that CM-perovskite is a metastable phase in diopside end-member composition under their experimental conditions [05A1]. In [00F1] was reported that CM-perovskite having orthorhombic structure was formed at 40...60 GPa and 2000...2500°C from a glass, using a laser heated diamond anvil cell. An amorphous phase with composition close to CM-perovskites was found [03T2], which might be vitrified from a perovskites structure in a shocked H chondrite. They suggested that CM-perovskite might be a stable phase which was formed at 18...24 GPa and less than 1900°C, rather than a metastable phase. The possibility of existence of CM-perovskites as a stable phase, which was formed under non-equilibrium shock condition was suggested [00L1]. The XRD experiments on high-pressure transformation of Ca_{1.03}Mg_{0.61}Fe_{0.23}Al_{0.14}Si₂O₆ pyroxene up to 32 GPa and 1900°C were performed [05A1]. Cubic Ca_{0.5}(Mg,Fe,Al)_{0.5}SiO₃ perovskite (CM) was found at about 1300°C and decomposed into cubic Ca-perovskite and orthorhombic Mg-perovskite and stishovite at 1800°C, when using a glass starting material. By using a crystalline pyroxene starting material, two cubic perovskites (Ca-perovskite, CM-perovskite) and orthorhombic Mg-perovskite formed simultaneously during the initial stage of the transformation. The cubic CM-perovskite subsequently decomposed into Mg- and Ca-perovskites and stishovite at 1200°C. These results indicate that the assembly of cubic Ca-perovskite, orthorhombic Mg-perovskite and stishovite is stable and cubic CM-perovskite is a metastable phase at around 32 GPa and temperature over 1000°C in the studied system. The Mg, Fe and Al were preferentially partitioned into Mg-perovskite and the compositions of Ca-perovskite were close to pure CaSiO₃. The CM-perovskite nucleates during the initial stage of Ca(Mg,Fe,Al)Si₂O₆ pyroxene transformation.

CaSiO₃ – CaTiO₃ perovskites

The perovskites solid solution in the system CaTiO₃ – CaSiO₃ were quenchable to 1 atm for compositions up to 83 mol % CaSiO₃ [71R2]. Phase relations in the system CaTiO₃ – CaSiO₃ were experimentally studied at 5.3...14.7 GPa and 1200...1600°C in multianvil apparatus [97K3]. As pressure increases, the stability field of perovskites solid solutions extends from CaTiO₃ to CaSiO₃ and the perovskites become stable for the entire composition range above $\cong 12.3$ GPa. Perovskite solid solutions containing 0 to 66 mol % CaSiO₃ could be quenched to 1 atm. The molar volume of perovskites linearly reduces from the value of CaTiO₃ to that of CaSiO₃. In [98S3] perovskites up to 49 % CaSiO₃ were prepared.

CaMgSi₂O₆ – Mg₂Si₂O₆ – Fe₂Si₂O₆ – CaFeSi₂O₆

In the quadrilateral (Di – En – Fs – Hd) clinopyroxenes, the structures, at RT, are of space groups P₂₁/c for Ca-poor (pigeonite) compositions and C2/c for Ca-rich (augite) compositions. The major differences between the P₂₁/c and C2/c structures as already mentioned are: (1) there is only one crystallographically distinct silicate chain in the C2/c structure, whereas two types of chains exist in the P₂₁/c structure and (2) the M2 site is eight-coordinated in the C2/c end members diopside [69C1], hedenbergite [73C1]) and six-coordinated in the P₂₁/c end members (clinoferrosilite [67B4], clinoenstatite [60M1]). In clinopyroxenes of intermediate composition, the M2 site is very irregular as result of multiple occupancy of the large Ca and small Fe or Mg atoms in the site. In [69G2] the relationship between the average size of M2 and kinking of the tetrahedral chain was studied. In [72T1] the variation of M2-O bonds in clinopyroxenes was discussed as function of Ca content and it was shown that M2 polyhedron becomes very irregular, thus highly unstable in the middle of the solid solutions. It was proposed that irregularity of the M2 polyhedral shape provided a structural explanation for the presence of a miscibility gap. In their crystal structural study of six end-member clinopyroxenes, [73C1] explained the increased solution between the Ca-poor and Ca-rich clinopyroxenes, at high *T*, by the change in M2 coordination associated with the P₂₁/c – C2/c phase transition. According to [75O1] the major structural change resulting from Ca-Fe substitution in four clinopyroxenes of intermediate compositions between Hd and Fs, at room temperature, is in the size and shape of the M2 polyhedron, whereas the M1 polyhedron remains essentially unchanged. The decrease in the average size of the M2, associated with a compositional change from Hd to Fs causes kinking of the tetrahedral chain and a concomitant increase in the out-of-plane tilting of the basal face of tetrahedron. As the M2 polyhedron decreases further in size, the space group changes from C2/c to P₂₁/c at the composition about Fs₈₀Wo₂₀. When the composition changes from Fs₈₅Wo₁₅ to Fs₁₀₀Wo₀ the A chain extends and finally reverses its kink direction.

CaScAlSiO₆

The crystal structure of CaScAlSiO₆ is isomorphous with that of CaFeAlSiO₆ and crystallizes in space group C2/c [78O1, 78O4]. The octahedral M1 site is occupied by Sc. Within the tetrahedral T site, Si and Al ions are completely disordered. In Ca_{1.00}Sc_{0.84}Ti_{0.27}Al_{1.16}Si_{0.73}O₆ single crystal pyroxene (space group C2/c), grown by the floating zone method, the octahedral M1 site is occupied by Sc (84 at %) and Ti (16 at %). Within the tetrahedral T site, Si (36.5 at %), Al (58 at %) and Ti (5.5 at %) ions are completely disordered [79O3].

Petedunnite, CaZnSi₂O₆

Petedunnite, CaZnSi₂O₆, crystallizes in the monoclinic space group C2/c. Ca occupies the distorted eightfold coordinated M2 polyhedra, whereas Zn²⁺ ions occupy the regular sixfold-coordinated M1 octahedra. Naturally occurring petedunnite was firstly described by [87E1]. Pure CaZnSi₂O₆ was not reported in nature, but was synthesized at 900 °C and 2 GPa [87E1]. The stability field of end member petedunnite is restricted to *p* > 1 GPa [98R4, 01F1]. The structure was refined by [96O2]. Plots of available chemical analyses suggest extensive solid solutions between petedunnite and diopside – hedenbergite – johannsenite.

Ferrobustamite

The X-ray analysis of Ca_{0.816}Fe_{0.152}Mn_{0.032}SiO₃ (ferrobustamite) crystal indicates that Ca and Fe atoms are located at four cation sites: M1 and M2 (twofold general positions) and M3 and M4 (onfold special position) [77Y1, 77Y2]. Fe atoms in a nontreated sample, which has a perfectly ordered structure, are concentrated in the M3 site, the smallest of the four sites [79Y2].

CaAl₂SiO₆ – CaMgSi₂O₆; CaAl₂SiO₆ – CaScAlSiO₆

The maximum solubility of CaAl₂SiO₆ in CaMgSi₂O₆ at 1 atm is 40 mol % [53S1, 62N1] and in CaScAlSiO₆ is 32 mol % at about 1400 °C [78O2, 79O3, 88S3]. According to [62C1, 74O1], under high pressures and temperatures, there is a continuous solid solution between diopside and CaTs. For CaAl₂SiO₆ – CaScAlSiO₆ the cell parameters (*a*, *b*, *c* and β) are linearly dependent on composition increasing with the CaScAlSiO₆ content [78O2].

CaAl₂SiO₆ – CaFeAlSiO₆ – CaMgSi₂O₆

The maximum solubility of CaAl₂SiO₆ in CaMgSi₂O₆ at 1 atm is about 12 wt % at $\approx 1250^\circ\text{C}$ [70S1]. The solubility of CaAl₂SiO₆ in CaFeAlSiO₆ – CaMgSi₂O₆ pyroxene solid solution increases with increasing CaFeAlSiO₆ contents, and the maximum solubility of CaAl₂SiO₆ in CaFeAlSiO₆ pyroxene can be about 35 wt % at about 1250°C [75O4].

CaFe³⁺AlSiO₆ – CaMgSi₂O₆

There is a complete solid solution between diopside and CaFe³⁺AlSiO₆ below 1250°C at 1 atm [69H2]. Ordering of ferric iron and aluminium between octahedral and tetrahedral sites of sample with 5 mol % CaFeAlSiO₆ proceeds with increasing pressure [73O3].

CaFe³⁺AlSiO₆ – CaTi⁴⁺Al₂O₆

The stability of the pyroxenes in the above joint system was investigated by [80O1, 83A2]. See also [74M1].

CaFe³⁺AlSiO₆ – CaMgSi₂O₆ – CaTiAl₂O₆

The above system was analyzed by [80A4] as well as its bearing on the Ti-rich fassaite-type pyroxenes.

CaFeAlSiO₆ – CaAl₂SiO₆

The maximum solubility of CaAl₂SiO₆ in CaFeAlSiO₆ can be about 35 wt % at $\approx 1250^\circ\text{C}$ [75O3].

CaFeSi₂O₆ – CaZnSi₂O₆

The synthesis of the hedenbergite (CaFeSi₂O₆) – petedunnite (CaZnSi₂O₆) solid solutions has been reported [97F1, 04H1]. In [04H1], the samples were obtained under hydrothermal conditions and different oxygen fugacities at temperatures of 700 to 1200°C and $p = 0.2 \dots 2.5$ GPa. The composition dependences of the lattice parameters are plotted in Fig. 31. Parameters *a* and *b* exhibit a linear decrease with increasing Zn content while the monoclinic angle increases linearly. Parameter *c* is not affected by composition and remains constant [04H1].

CaMgSi₂O₆ – CaNiSi₂O₆

The above pyroxenes crystallize in a monoclinic C2/c-type structure [90R1]. Cell parameters and mean bond lengths vary linearly as function of composition along the join. The refined site occupancy of Ni in M1 site is somewhat less than the nominal Ni content.

Ca(Mg²⁺, Fe³⁺, Ti⁴⁺, Al³⁺)(Si, Al)₂O₆

The analysis of the structure of the above pyroxenes shows that approximately 25 % of tetrahedrally-coordinated sites were occupied by Al. Ordering of cations was complete within the accuracy of the data with Ca in M2 site and only Al substituting for Si [67P1].

CaMgSi₂O₆ – Mg₂Si₂O₆ – CaAl₂SiO₆

The refinement of the C2/c pyroxenes in Di – En – CaTs silicates, synthesized in the temperature range $1275 \dots 1525^\circ\text{C}$ and $p = 1.4 \dots 1.8$ GPa, shows the following features [94T2]: (1) The M2 site coordination changes continuously along the Di – En join from eightfold to sixfold, with a shift in tetrahedral chains along *z*. The displacement parameters suggest the coexistence of two structural configurations, clinoenstatite-like and diopside-like. (2) The M2-O bond lengths become more regular along the Di – CaTs join, as imposed by charge balance requirements. The change in bond lengths is associated with a chain shift along *z* which is opposite to that observed along the Di – En join. The small values of the displacement parameters suggest an actual change in atomic positions along the join, but with no positional disordering. (3) In Di – En – CaTs ternary clinopyroxenes the opposite chain shifts, observed along the two joins, compensate. However, displacement parameters are greater than those observed along the join Di – En, suggesting the coexistence of two structural

configurations in the average structure. These results suggest that the M2 polyhedron in Al-rich clinopyroxenes is less able to accept extreme Mg at the site than Al-free clinopyroxenes. This can explain the lower enstatite solubility observed in Al-rich clinopyroxenes [93T1].

CaScAlSiO₆ – CaTiAl₂O₆

Solid solutions were prepared in the composition range 0...30 mol % CaTiAl₂O₆, [83O2]. In the sample with 30 mol % CaTiAl₂O₆, Al and Si were not randomly distributed throughout tetrahedral sites.

CaFe³⁺Ga³⁺SiO₆ – CaGa³⁺₂SiO₆

In a 90 CaFe³⁺Ga³⁺SiO₆ – 10CaGa³⁺₂SiO₆ clinopyroxene, the Fe³⁺(M1):Fe³⁺(T) ratio is 65:35 [97A1].

CaAl₂SiO₆ – SiO₂; CaAl₂SiO₆ – CaMgSi₂O₆ – SiO₂

Synthesis of nonstoichiometric aluminous pyroxenes were carried out on the systems CaAl₂SiO₆ – SiO₂ and CaAl₂SiO₆ – CaMgSi₂O₆ – SiO₂ [78W2]. It was found that the degree of nonstoichiometry increases with increasing pressure. The study suggested that nonstoichiometric pyroxenes are characteristic of a high-pressure product and that vacancies predominate at M2. In [86M1] was also reported, for a natural nonstoichiometric omphacite, that vacancies are mainly concentrated at the M2. Later on, [91O1] allocated all vacancies in several natural pyroxenes to the M2 site. In [98O1] the structure of the nonstoichiometric clinopyroxene crystal (Ca_{0.742}Mg_{0.087})(Mg_{0.016}Al_{0.888}Fe_{0.075})(Al_{0.500}Si_{1.500})O₆ was refined, and it was shown that vacancies are also located mainly at M2 sites. Despite replacement of Si by Al, the crystal has a smaller cell volume than diopside primarily owing to a significant amount of Mg at M1 being replaced by Al.

BaCuSi₂O₆

BaCuSi₂O₆ crystallizes in a tetragonal structure having space group $I\bar{4}m2$ [89F2]. The structure consists of isolated 4-rings of silicate tetrahedra. Cu atoms are almost ideally planar coordinated to four oxygens. The four oxygens deviate significantly from a square. Two Cu atoms link each set of four adjacent 4-rings to form (001) layers. These CuSi₂O₆ layer units, a unique feature of the structure, are interconnected parallel to the *c*-axis by eight-coordinated Ba1 atoms and twelve-coordinated Ba2 atoms half-way between the Cu-Si-O layers. Each Ba is coordinated to four 4-rings, two in the layer above and two below.

IV. Na silicates

Na₂SiO₃

The crystal structure of sodium metasilicate was determined by [52G1, 67M1]. The structure (space group Cmc2₁) consists of infinite chains of silicate tetrahedra. The metasilicate chains are parallel to the *c*-axis and have mc2₁ symmetry with two tetrahedra in the repeat unit. The silicon and the bridging oxygen lie in the mirror plane. The oxygen atoms are further coordinated to sodium atoms, which link the chains together in the *a* and *b*-directions. Na₂SiO₃ undergoes a transition at about 850 K from orthorhombic Cmc2₁ symmetry, to lower symmetry (possibly Pmc2₁) and shows changes in Raman spectra near 1200 K which correlate with premelting effects [96R3].

Jadeite, NaAlSi₂O₆

The jadeite is monoclinic having space group C2/c [66P2, 72P2]. The structure is similar to that of pyroxene diopside and contains parallel sheets of octahedrally-coordinated Al and eight-coordinated Na polyhedron connected by silicate chains running parallel to the *c*-axis. For elastic constants see [76O1, 81O1, 88K2].

Aegirine, NaFeSi₂O₆

Aegirine (acmite) is a sodium ferric clinopyroxene with ideal formula <Na>{Fe³⁺}[Si₂]O₆. The silicate crystallizes in the monoclinic structure having space group C2/c [69C1]. The structure has iron in single zig-zag chains of edge-sharing octahedral M1 sites and sodium in the eightfold-coordinated M2 sites. The comparison of the crystal structure of aegirine [69C1] and hedenbergite [73C1] shows that in hedenbergite the chains are more

kinked than in aegirine with the interchain Fe-Fe distance being larger in hedenbergite (i.e. 5.711 Å) than in aegirine (i.e. 5.434 Å). Thus, the *c*-axis is shortened, while the *a* and *b*-axes are lengthened. The interchain Fe-Fe distances are larger in aegirine (i.e. 3.189 Å) than in hedenbergite (i.e. 3.109 Å).

NaM³⁺Si₂O₆ (M = Sc, Ti, V, Cr, Mn, Ga, In)

The crystal structure of the above pyroxenes is monoclinic, having space group C2/c as evidenced for compositions: NaAlSi₂O₆ [66P1]; NaAlSi₂O₆, NaCrSi₂O₆ [65F1, 69C1]; NaScSi₂O₆ [68I1, 73H2, 94O1]; NaInSi₂O₆ [67C1, 69C1, 74H1]; NaTiSi₂O₆ [82O2]; NaGaSi₂O₆ [83O3]; NaMnSi₂O₆ [87O3]; NaVSi₂O₆ [94O2, 97S1]. We note, the name used in mineralogy for NaScSi₂O₆ is **jervisite** while for NaCrSi₂O₆ is **kosmochlor**. The structure of NaScSi₂O₆ pyroxene, formed at 6 GPa pressure [94O1], is isomorphous with that formed at atmospheric pressure [68I1], although the cell parameters and atomic coordinations are different. In NaMnSi₂O₆ pyroxene, Mn occupies a strongly distorted octahedral M1 site. The distortion shows that there is Jahn-Teller stabilization of Mn³⁺ [87O3]. The short Mn-Mn distance of 3.131(1) Å was correlated with the small Mn-O1-Mn angle of 97.1(1)°, reflecting the repulsion between the O1 atoms and the non-bonding electrons of Mn ion. In NaGaSi₂O₆ there are two different electronic states, Ga(α) and Ga(β) for the octahedral Ga³⁺ ions. Ga(α) occurs in the Mn-Fe-Ga(α) series of silicates and Ga(β) in the Al-Ga(β)-In series [95O2, 96O1]. In NaM³⁺Si₂O₆ pyroxenes, the Si-O distances correlate with the electronegativity of the M³⁺ ions and has two different trends [94O1]. One is Sc-Cr-V-Ti-Al and another In-Fe-Ga series. The electronegativity of Ga³⁺ ion has been found to be 1.9 in the Pauling scale.

Natalyite, Na(V,Cr)Si₂O₆

Natalyite crystallizes in a monoclinic structure having space group C2/c [85R1, 87H1, 94O2].

Na₂ZnSi₂O₆

The Na₂ZnSi₂O₆ crystallizes in space group Fdd2 [80S3].

Na₂BaSi₂O₆

Na₂BaSi₂O₆ crystallizes in the monoclinic structure of space group P2₁ [73G2]. The structure comprises infinite single chains of silicate tetrahedra parallel to the *b*-axis, with two tetrahedra per chain repeat. Each chain is linked to its neighbours through the Ba²⁺ and Na⁺ ions. Individual chains have no symmetry, but each is related to neighbouring chains by the screw axis. This results in a pairing of chains in the direction of the *a*-axis. The Ba²⁺ ions occupy the larger cavities between adjacent pairs of chains, while the Na⁺ ions are held in the smaller cavities within.

Na(Mg_{0.5}Si_{0.5})Si₂O₆

In [88A1, 88G1], at 15 GPa and 1600°C, Na(Mg_{0.5}Si_{0.5})Si₂O₆ (NaPx) clinopyroxene was synthesized that contained both four- and six-coordinated silicon. An ordered space group P2₁/n was shown. The octahedrally-coordinated Mg²⁺ and Si⁴⁺ ions occupy two crystallographically distinct sites. The existence of clinopyroxene with six-coordinated silicon in natural mantle rocks having NaPx₁₆En₈₄ was shown [96W2]. A (Na_{0.56}Ca_{0.36}Mg_{0.08})Si_{0.27}Mg_{0.73}Si₂O₆ clinopyroxene containing both four and six-coordinated silicon was synthesized at 15 GPa and 1600°C [05Y2]. The sample was shown to have C2/c symmetry and no detectable ordering between Mg²⁺ and Si⁴⁺ in the M1 site was shown.

NaScSi₂O₆ – NaCrSi₂O₆

The pyroxenes in the system NaScSi₂O₆ – NaCrSi₂O₆ have been synthesized at 1500°C and 5 GPa. The solubility of the NaScSi₂O₆ component in NaCrSi₂O₆ pyroxene is more than 30 mol %. This decreases to about 5 mol % for samples obtained at 1200°C and 2 GPa [79O1, 81O1].

NaScSi₂O₆ – NaInSi₂O₆

The NaScSi₂O₆ – NaInSi₂O₆ silicates, crystallized at 1770 K and 6 GPa, are isomorphous with other sodium pyroxenes having space group C2/c [90O1]. The M1-M1 distances and the M1-O1-M1 angles correlate with the mean M1-O1 distances in such a way as to follow two different trends, suggesting that there are two different electronic states for the octahedral In³⁺ ions. The Si-O distances constitute two populations which can be related to the mean electronegativity of the octahedral M1 ions. From the Si-O distances, the electronegativities of the two In³⁺ ions are 1.2 and 1.7 on Pauling's scale [90O1].

NaAlSi₂O₆ – NaCrSi₂O₆

The NaAlSi₂O₆ – NaCrSi₂O₆ system was studied at 800°C [76A1]. The authors reported that at this temperature solid solutions are formed in all the composition range for samples obtained at $p > 1.8$ GPa. Later on, a miscibility gap between 25 and 50 mol % kosmochlor was suggested [86M2]. In [87O1] was also concluded that there are no complete solid solutions at any pressure condition.

V. Calcium - natrium pyroxenes**Omphacites**

Since there is different nomenclature concerning the Ca-Na pyroxenes, in the following we present the classification made by [88M3]. The Na pyroxenes **jadeite** and **aegirine** commonly contain more than 90 % of the NaAlSi₂O₆ or NaFe³⁺Si₂O₆ component, respectively. Both jadeite and aegirine show extensive solid solutions with the Ca-Mg-Fe pyroxenes, especially with the diopside – hedenbergite series and augite leading to the Ca-Na pyroxenes. The Na and Ca-Na pyroxenes are classified on the Q – Jd – Ae diagram with normalized Q (Wo + En + Fs), Jd and Ae components – Fig. 32. The arbitrary division between the Ca-Mg-Fe, Na-Ca and Na-pyroxenes are defined at 20 and 80 % of Q = (Wo + En + Fs). Omphacites display a C2/c \rightleftharpoons P2/n polymorphic transition, and both high-temperature C2/c (C-type) and low-temperature P2/n (P-type) polymorphs appear in nature. The omphacites P2/n, which show a unique crystal structure, different from that of jadeite and augite, was accepted as an independent pyroxene species. Aegirine – augite was also accepted as an independent species to keep balance with omphacite, though it is not known to occur with the P2/n structure.

Ca-Na pyroxenes solid solutions have a peculiar behavior [88M6]. End members crystallize in the space group C2/c, whereas intermediate members have either the same space group C2/c, or the lower symmetry P2/n. Ordering of cations located in the sixfold (M1) and/or eightfold (M2)-coordinated sites of the structure has been suggested to be the driving force for such behavior [68C1, 69C1, 75C2, 75M2, 78A1, 78F1, 83R1, 90C1, 90C2, 97M1]. The accepted model of Ca-Na pyroxenes [83R1, 98B1, 98C2, 99M1] can be described by: (1) Mg and Al are randomly distributed (disordered) over only one type of site (M1, a very slightly distorted octahedron with point symmetry 2) in C2/c pyroxenes – Fig. 33a. These are diopside (Di), jadeite (Jd) and the intermediate pyroxenes compositionally closest to the end members (C-omphacites). The Mg and Al tend to be partitioned (i.e. ordered) over two nonequivalent, differently distorted octahedral sites (M1 and M11 with point symmetry 2) in pyroxenes near the ratio Di:Jd = 1:1. The symmetry lowers to P2/n (P-omphacites). In ideal case – Fig. 33b – Mg would occupy only M1 and Al only M11 (full octahedral order), although not completely, because of the possible presence in M1 of minor Fe²⁺ and Mn²⁺ and in M11 of Fe³⁺, Mn³⁺ and Cr³⁺. In the real case, there is a certain amount of Mg-Al disorder that increases as the pyroxene composition deviates from Di₅₀Jd₅₀ [99M1]. (2) Na and Ca are totally disordered over only one type of eightfold-coordinated site of C-pyroxenes (M2, an irregular polyhedron with point symmetry 2 – Fig. 33a). By contrast, in P-omphacites these tend to be locally ordered over two eightfold-coordinated sites (M2 and M21) that differ in shape and size (partial eightfold site local disorder – Fig. 33b).

There are many studies on crystal structures of omphacites. A short review of their evolution is given below. The structure of Di_{0.42}Jd_{0.38}Hd_{0.10}Ae_{0.10} was solved in space group P2 [66C1] as containing 4M1, 4M2 and 4T independent sites per unit cell [68C1, 69C1]. They also showed that the ordered structure is compositionally limited in the region of the roughly symmetrical astride composition Di_{0.50}Jd_{0.50}. Thus, as mentioned above, there are two types of Ca-Na pyroxenes which fall in the omphacite compositional field, the C- and P-type omphacites. Later on, [70M1, 75C3, 75M2, 78F1] showed that the choice of space group P2 was incorrect and that the space group of ordered omphacites is P2/n. The structure can be solved with 2M2, 2M1 and 2T individual cation sites. Electron diffraction studies [78C3, 79C2] showed that during topotactic replacement of

augite for omphacite, other space groups, such as P2/c or P2, occur. They were interpreted as metastable products of sliding replacement reaction, the outcome of which, at equilibrium, is the space group P2/n. Alternatively, however, they may reflect local ordering conditions at a very small scale, i.e., short-range order (SRO), while the space group P2/n reflects long-range order (LRO) [97M1]. In [73C2] a possible order-disorder relationship was suggested which could occur in omphacites, crystallized as the C-type, at high temperature, and transformed to P-type on cooling. In [78F1] the critical temperature of such a continuous order-disorder transition was assessed, at constant pressure. Then, kinetics of disordering as function of pressure, temperature and time was analyzed and an equilibrium order-disorder at $T_0 = 865(10)^\circ\text{C}$ for a natural omphacite was obtained [81C2]. This transition of omphacite, at fixed temperatures, has been shown to be close to being tricritical [90C1, 90C2]. The degree of cation ordering was a function of composition [83R1]. The omphacites degree of ordering reflects the complex interplay of p - T - t conditions [83M1].

The ^{57}Fe NGR studies [82D3] established that: (a) there is no evidence of Fe^{3+} in any site other than M1 in C-pyroxenes, and M11 in P-pyroxenes; (b) the near-neighbour environment of Fe^{2+} is independent on Mg-Al long-range order (LRO), while size considerations suggest that this cation mostly concentrates in M1 regardless of symmetry; (c) the occurrence of Fe^{2+} in M2 was not proven. However, Fe^{3+} in M2 was independently determined by single crystal X-ray refinement (SC-X Ref) [83R1, 98B1]. The effect of Fe^{2+} and Fe^{3+} replacing Mg and Al in the M1 and M11 sites has been investigated by using a combination of TEM and SC-X Ref methods [98C2]. Ordering was found to decrease significantly with increasing total Fe, up to complete disordering for $x_{\text{Ae}} > 20\%$ and $x_{\text{Ae+Hd}} > 47\%$ even for composition close to the Ca : Na = 1:1 ideal ratio. For recent XANES studies see section 8.1.4.1.10.

As above mentioned, the NN interaction effects of Ca, Na on Fe^{2+} did not change appreciably on going from C- to the P- space group in spite of the rearrangement of Mg^{2+} , Fe^{2+} and Al, Fe^{3+} [78A1]. The interpretation of [78A1] was that Na readjusts easily to occupy the M2 positions surrounding a M1 site occupied by Al, Fe^{3+} , while Ca does the same for those occupied by Mg, Fe^{2+} . However, these configurations modify the random population of the M2 sites, typical of a C2/c pyroxene, and because of charge-balance and space-fitting requirements they induce SRO into both sixfold and eightfold-coordinated cation sites. The amount of such local disorder is a matter of debate [97M1]. In [83R1, 90C1, 90C2] it was claimed that M2 and M21 tend to a “maximum” possible state of order such as $(3/4)\text{Na} + (1/4)\text{Ca}$ for M2 and $(1/4)\text{Na} + (3/4)\text{Ca}$ for M21. They confute the “ideal” omphacite model [78F1, 83M1] on the basis of considerations of local charge balance requirements. However, [78F1] warned against conclusions drawn from XRD evidence only, since the X-ray scattering factors of Mg^{2+} and Al^{3+} are very similar and the ordered Mg-rich omphacite is largely associated with the partial order of the M2-type cations. In [78F1] was argued that the ionic radius difference contributes as driving force for LRO; therefore Mg and Al may indeed be completely ordered over M1 and M11 but the tendency of Ca and Na to LRO over M2 and M21 is diminished and SRO around each of them is kept on going from the ordered to disordered phase. Thus, in the P-omphacite structure Ca and Na are partially ordered in M2 and in [97M1] was only assumed that there is a full ordering of Mg and Al. Electron channeling study showed that some Fe and Mg ($\text{Fe} > \text{Mg}$) reside in the M2 site [86M1]. A schematic view of omphacite structure (space group P2/n) is shown in Fig. 34.

The coupled substitution $\text{Ca}^{2+} + \text{Mg}^{2+}(\text{Fe}^{2+}) \leftrightarrow \text{Na}^{1+} + \text{Al}^{3+}(\text{Fe}^{3+})$ along the binary join augite – jadeite is known for positive deviations from ideal mixing [80W1, 83H2, 85G1, 88B2, 90H1]. According to [80C2] it appears that the stability field for the ordered omphacites (P2/n symmetry) is superimposed on a miscibility gap.

Annealing experiments were carried out on aegirine – jadeite crystals with different degrees of order (P2/n) and complete disorder (C2/c) at compositions between 35 and 60 % Jd, for natural omphacites, as well as on synthetic C2/c pyroxene with composition $50\% \leq \text{Jd} \leq 80\%$ [98B1]. For both C2/c and P2/n pyroxenes, the a , b , c lattice parameters and unit-cell volume, as well as tetrahedral and octahedral mean bond distances, depend linearly on composition – Fig. 35 [98B1]. Only the angle β of ordered omphacites slightly deviates from the linear trend of C2/c samples. This shows that the out-of-plane tilting of the basal face is sensitive to the different degrees of order.

The study of C2/c clinopyroxenes by X-ray structure analysis evidenced a feature, which has been initially overlooked [82B4, 82D1, 83R1, 84C1, 84D1]. A maximum of residual electron density was observed at $0.6\ldots 0.7 \text{ \AA}$ from the location of M2 site and along the diade axis – Fig. 36 [87R2]. This peak, denoted M2' when present is 5 to 10 times higher than the residual density that is found midway between the silicon and the nonbridging oxygen atoms O1 and O2 in (Na,Ca) C2/c clinopyroxenes. The M2' is interpreted in terms of the

simultaneous coexistence of two different structural models in the crystal, approximately diopside and clinoenstatite [87R2].

TEM studies on natural P2/n omphacites [73C2, 73P2] indicate the presence of antiphase domains, which were considered [73C2] to be the evidence of a temperature dependent $P2/n \leftrightarrow C2/c$ inversion reaction. In [76Y1] was established that the critical temperature for the $P2/n \leftrightarrow C2/c$ inversion is within the stability field of natural omphacite. In [78F1] heating experiments on natural omphacites at 1.5 to 1.8 GPa have established the critical temperature for the order-disorder $P2/n \leftrightarrow C2/c$ transition of 725(20)°C. The disordering reaction $P2/n \leftrightarrow C2/c$ is quite abrupt, and the observed transformation temperature is independent of the run duration. Reaction rate data give an activation energy for disordering, of $\cong 12 \text{ kcal mol}^{-1}$, which suggest that the cation disorder in omphacite is a cooperative process involving both M1- and M2-types of cations.

The observation of lamellar intergrowths of augite – omphacite, jadeite – omphacite and two ordered omphacites [78C2], lead to interpret the phase relations [80C2]. In [87D1] a model was developed for binary solutions that have coupled mixings on nonequivalent sites which was applied to omphacites. For omphacite pyroxene solutions, ordering within the M1 sites is linked to ordering within M2 sites, so that disordering occurs at a single critical temperature. The prediction of the model agrees qualitatively with experimental observations.

We note that the lattice parameters of samples having Ca, Na or Li in the M2 site of the ordered $C2/c$ structure were expressed in terms of valences and effective ionic radii of non-tetrahedral atoms [77R1].

Some data on the omphacite systems are presented shortly in the following.

CaMgSi₂O₆ – NaMSi₂O₆ (M = Fe, Al)

The solid calcic pyroxenes systems CaMgSi₂O₆ – NaFeSi₂O₆ and CaMgSi₂O₆ – NaAlSi₂O₆ can form a complete series of solid solutions at various pressure conditions [66Y1, 67B2, 71C1]. In case of binary Ae – Di, the replacement of Mg²⁺ by Fe³⁺ in the M1 site is accompanied by a Ca²⁺ replacement by Na⁺ in the M2 site, to assure the charge balance. The M2 site is eightfold-coordinated, while the M1 site is occupied by Fe³⁺ or Mg²⁺ ions in an approximately octahedral site [67B3].

Pyroxenes in the Di – Jd join are of interest as geobarometers. Such a geobarometer, however, is strongly affected by the thermodynamic character of the solid solution [83H2]. Due to different ionic sizes of Mg and Al ($r_{\text{Mg}} = 0.720 \text{ \AA}$, $r_{\text{Al}} = 0.535 \text{ \AA}$), diopside and jadeite do not mix regularly throughout the join. Not only a miscibility gap (Di₄₀Jd₆₀ – Di₂₀Jd₈₀) under the most geological conditions, but a field of ordering is also present essentially from Di₆₀Jd₄₀ – Di₄₀Jd₆₀, where the silicates acquire the space group P2/n instead of the normal, disordered $C2/c$ symmetry typical of the end members [83M1]. Both types of irregularity in the solid solution system depend upon the difference in the ionic size of the exchanging Al and Mg cations in M1, but also affect the M2 site, occupied by Na and Ca, due to the requirement of electrostatic neutrality. The difference in the size between Ca and Na in eightfold coordination (1.12 and 1.18 Å, respectively) is not sufficient to imply irregular mixing. From XANES analysis [87D2] was found a distortion of the polyhedron around the M2 site varying as function of Ca content. This was attributed to compression of the site in a selected direction with an unchanged average distance, so that the coordination around the Ca atom changes. In diopside, the predominant configuration is 4-2-2 type, typical of the M2-centered polyhedron when the centering atom is Ca and involve: four M2-O2 and M2-O1 bonds (2.35...2.36 Å), i.e. the two couples of bonds involving oxygen bridging the M2 with M1 cations, and two longer and weaker bonds (2.56 and 2.70 Å) that bridge the M2 cation to the Si-centered tetrahedral chain. In jadeite, the M2 site is centered by Na and the configuration is 6 - 2 with only two longer bonds and six of 2.36...2.41 Å. Thus, the polyhedron becomes more symmetrical. Such a configuration is evidenced for low Ca content. The change of coordination is not gradual. For Na/Ca = 1/1 equal contributions from 4-2-2 and 6-2 configuration were seen. Thus, the Ca sites in these omphacites, are of two types M2 and M21 as evidenced by X-ray studies [68C1]. The presence of these two sites causes ordering in the structure and decreases the space group from $C2/c$ to P2/n.

NaCrSi₂O₆ – CaMgSi₂O₆

The phase equilibrium study on the NaCrSi₂O₆ – CaMgSi₂O₆ was investigated at 1 atm [72I1]. The maximum solubility of NaCrSi₂O₆ in CaMgSi₂O₆ is 24 wt % at 1140°C, while the CaMgSi₂O₆ is not soluble at all in NaCrSi₂O₆. The solubility of CaMgSi₂O₆ in NaCrSi₂O₆ is increased with pressure and there is only a narrow miscibility field [74I1, 79O2]. The limits of solubility at 1300°C and 1.5 GPa were found to be 24 mol % of

NaCrSi₂O₆ in CaMgSi₂O₆ and about 55 mol % of CaMgSi₂O₆ in NaCrSi₂O₆ [74I1]. The lattice parameters were determined [79O2]. It was expected that when the content of Cr³⁺ increases and the average M1 distances decrease, a part of Cr³⁺ could form Cr-O-Cr couplings and phase separation could occur. Although the crystal structure of NaCrSi₂O₆ is isomorphous with other sodic pyroxenes [69C1], the Cr-Cr distance of 3.089(4) Å is unusually short, resulting from the repulsion between the O1 oxygen and the non-bonding 3d electrons of the Cr ion [87O2, 87O3].

The analysis of the crystal structure of (Na_{0.45}Ca_{0.55})(Cr_{0.45}Mg_{0.55})Si₂O₆ pyroxene synthesized at 1200°C and 2.2 GPa shows that the repulsion effects exist in the NaCrSi₂O₆ side of the miscibility gap where Cr³⁺ ions occupy a smaller octahedral site [87O2]. The repulsion effects do not exist in the CaMgSi₂O₆ side, in which the Cr³⁺ ions occupy larger octahedral sites.

NaScSi₂O₆ – CaNiSi₂O₆

The system NaScSi₂O₆ – CaNiSi₂O₆, crystallized at 1100...1300°C and atmospheric pressure, form a complete series of solid solutions. The unit-cell dimensions show an almost smooth change with composition [88O1]. In case of samples crystallized at 1500°C and 6 GPa an immiscibility field has been found [89O3]. The 0.6NaScSi₂O₆ – 0.4CaNiSi₂O₆ sample decomposes.

NaFeSi₂O₆ – CaAl₂SiO₆

The maximum solubility of CaAl₂SiO₆ in NaFeSi₂O₆ is 6 mol % [75Y1, 78O3].

NaFeSi₂O₆ – CaZnSi₂O₆

The NaFeSi₂O₆ – CaZnSi₂O₆ silicates, crystallized at 1470...1570 K and 6 GPa pressure, form solid solutions [96O2]. Sc and Zn occupy a distorted octahedral M1 site.

NaScSi₂O₆ – CaZnSi₂O₆

According to [96O2] the NaScSi₂O₆ – CaZnSi₂O₆ solid solutions, crystallized at 1470...1570 K and 6 GPa, have the space group C2/c. Sc and Zn occupy a distorted octahedral M1 site.

NaScSi₂O₆ – CaMgSiO₆

The system was analyzed by [71Y1].

NaVSi₂O₆ – NaCrSi₂O₆ – CaMgSi₂O₆

Natalyite, NaVSi₂O₆, was found in nature [85R1] and the complete NaVSi₂O₆ – NaCrSi₂O₆ – CaMgSi₂O₆ ternary solid solutions were described later [98R2, 99R1]. Synthetic end members natalyite [94O2], kosmochlor [69C1] and solid solution diopside – kosmochlor [79O2] were studied. In [02S1] crystal structures of eleven natural clinopyroxenes from the ternary join NaVSi₂O₆ – NaCrSi₂O₆ – CaMgSi₂O₆ were studied. The T site is almost completely occupied by Si, so that the Na(V³⁺,Cr³⁺) → CaMg substitution mechanism ensures charge balance. Changes in M1 site geometry were explained by the aggregate ionic radius and are influenced by Mg occupancy and V³⁺/(V³⁺+Cr²⁺) ratio. The M2 site geometry depends both on the Na content and on the (V³⁺,Cr³⁺) → Mg substitution in the M1 site. The T site geometry is affected by chemical and geometrical variations at the M1 and M2 sites, mainly the M1 sites occupancy [02S1].

NaFeSi₂O₆ – CaMgSi₂O₆ – CaFeSi₂O₆

The aegirine – diopside – hedenbergite ternary system [69N1] can be represented by the general chemical formula XYSi₂O₆ where X = Na⁺, Ca²⁺ and Y = Fe²⁺, Fe³⁺, Mg²⁺. The crystal symmetry of these pyroxenes is monoclinic (space group C2/c). There are two crystallographically distinct positions M1 and M2. The M1 sites are occupied by Y cations, while X cations occupy the M2 sites. The characteristic structure consists of infinite chains of SiO₃ groups linked by cations of the M1 and M2 sites, the continuous chains extending along the *c*-axis.

For crystal structures of omphacites see also [67E1, 69B2, 72M1, 81C2]. For elastic properties see [92B2].

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The intercrystalline Fe^{2+} - Mg^{2+} ordering between M1 and M2 sites in natural Ca-rich clinopyroxenes was determined at various temperatures [76M2, 91M3]. This ordering was reported to be suitably employed as a geothermometer which records the “equilibrium” temperature, i.e. the closure temperature for the Fe^{2+} -Mg intercrystalline exchange between M1 and M2 sites [91M3].

VI. Lithium silicates

Li_2SiO_3

The Li_2SiO_3 metasilicate crystallizes, at RT, in an orthorhombic structure with space group $\text{Cmc}2_1$ [55S1, 77H3, 78H3]. In [55S1, 67M1, 96R3] it was pointed out that for the isostructural Na_2SiO_3 , the sodium occupies the approximate center of a trigonal bipyramid while in Li_2SiO_3 the lithium ion has moved to one corner of bipyramid, giving a $[4 + 1]$ coordination. Li_2SiO_3 may be regarded as a framework of corner-linked $[\text{LiO}_4]$ and $[\text{SiO}_4]$ tetrahedra. The topology of this is identical with that of wurtzite [77H3]. The lack of premelting effects was evidenced by calorimetric studies [96R3].

Spodumene, $\text{LiAlSi}_2\text{O}_6$

Three different polymorphs have been reported in literature for the spodumene composition, $\text{LiAlSi}_2\text{O}_6$. The only naturally occurring monoclinic polymorph is the stable low-temperature form called α -**spodumene**. The high-temperature tetragonal modification was called β -**spodumene**. A third high-temperature form, which is a stuffed derivative of β -quartz is known as γ -**spodumene**. All three polymorphs are related by reconstructive transformation. The prefixes α , β and γ to the mineral name spodumene imply that displacive transformations relate these phases. Therefore, it was proposed in [68L2] that the phases be referred to as $\text{LiAlSi}_2\text{O}_6$ -I (monoclinic), $\text{LiAlSi}_2\text{O}_6$ -II (tetragonal) and $\text{LiAlSi}_2\text{O}_6$ -III (hexagonal). The hexagonal form has previously also been called as β -eucryptite solid solution [49R1, 60S1], β -quartz solid solution [67K1] or silica O [59R1].

The $\text{LiAlSi}_2\text{O}_6$ -I is a chain silicate belonging to the family of pyroxenes. The crystal structure is monoclinic having space group $\text{C}2/c$ [73C1]. The structure consists of Si-centered tetrahedra linked at two corners, forming chains along the z -axis. These chains are laterally linked by Al-centered octahedra which, in turn, form chains of edge-sharing polyhedra, also running along z . The Li ions occupy cavities formed in the frame of the Si and Al-centered polyhedra. In the structure there are three non-equivalent oxygen ions: O1 which coordinates one Li, two Al and one Si; O2 which is bonded to one Li, one Al and one Si; O3, the bridge between two Si-centered tetrahedra, which coordinates two Si and one Li.

Charges of oxygen ions were calculated [03P1] by application of Pauling's valence bond rule [40P1], the Brown-Shannon method [73B2], the Hoppe method [89H4] and by integration of the charge density over the attraction basin of each oxygen [94B1] – Table 6b. The maps of Laplacian scalar field along O1, O2, O3 are shown in Fig. 37. In particular O1 shows a maximum of charge concentration along the Si-O bond path and two other maxima, which can be regarded as lone pairs, pointing in the opposite direction with respect to the silicon position. O2 shows a torus of local charge concentration, whose axis is parallel to the Al-Si direction, with a bulge on the external side of the Si-O2-Al angle. Even if no maximum exists in the Si direction, the valence shell of O2 appears to be strongly polarized toward the silicon. A slight polarization also exists along the Al-O bond path. A similar situation is displayed by O3, whose charge concentration has a torus-like shape, with the axis parallel to the Si-Si direction, and a bulge on the external side of the Si-O3-Si angle. As in case of the O2, a significant polarization of the valence shell of O3 was observed towards the two Si directions. By recasting the calculated electron distribution in terms of the valence bond theory, a correlation has been found between structural details (bond lengths) and the hybridization state of oxygen atoms [03P1].

According to [60S1, 68L2, 87R4], $\text{LiAlSi}_2\text{O}_6$ -II is tetragonal. It is a stuffed derivative of the quartz structure (keatite). The structure consists of a three-dimensional aluminosilicate framework. One third of the silicon atoms is replaced by aluminium atoms at random in the keatite structure. The charge of an AlO_4^- group is in each case compensated by a lithium ion. The structure is dominated by interlocking five-membered rings of (Si,Al) tetrahedra. All the five-membered rings run approximately parallel to either (010) or (100) and thus help to create zeolite-like channels. These channels have a free diameter of about 3 Å and are appreciably wider than

those parallel to the [001]-axis. Lithium atoms are stuffed in interstitial positions but occupy a general eightfold site. There are four sets of paired sites for Li atoms per unit cell. Each Li atom occupies one of the two sites in each pair. The distance between the two sites is only 1.3 Å which is too short for the Li atoms to occupy both simultaneously. The distances from a pair of sites to the next pair is about 4.5 Å. The thermal expansion coefficient is $9 \cdot 10^{-7}/\text{K}$ between 297 and 1273 K [51H1]. The X-ray diffraction intensity data show that the charges of atoms are less ionic than the corresponding formal ones [80S1] – see Table 6.

The structure of $\text{LiAlSi}_2\text{O}_6$ -III is hexagonal, space group $P6_222$ (or $P6_422$) [68L1]. The structure consists of a three-dimensional aluminosilicate framework. The distribution of Si and Al in the tetrahedra is completely random. There is only one symmetry independent (Si,Al) tetrahedron. The (Si,Al) tetrahedron is similar to those in $\text{LiAlSi}_2\text{O}_6$ -II [68L2]. The (Si,Al) tetrahedra form interconnecting 6- and 8-membered rings. The channels created by 6-membered rings are parallel to the three crystallographic axes. The neighbouring 6-membered rings share one or no common tetrahedron. Wherever the two neighbouring 6-membered rings do not share any common tetrahedron, eight out of the twelve (Si,Al) tetrahedra form an 8-membered ring. At the center of this 8-membered ring, there is a channel parallel to the c -axis which is occupied by the lithium atoms – Fig. 38. For every 6-membered ring, the 6(Si,Al) tetrahedra are arranged in double-helical fashion. A large cavity which has sixfold coordination with oxygen is formed within each ring. Lithium atoms are 4-coordinated and stuffed in interstitial positions and occupy equipoints of rank 3. There is one lithium atom per unit cell. As in case of $\text{LiAlSi}_2\text{O}_6$ -II, the hexagonal form has a low thermal expansion.

α - $\text{LiAlSi}_2\text{O}_6$ with space group $C2/c$ at RT undergoes a phase transition at 3.19 GPa to a $P2_1/c$ -type structure [00A1].

XRD studies were performed on lithium-aluminosilicate glass-composite with nanometer sized $\text{LiAlSi}_2\text{O}_6$ crystals embedded in a host matrix [05L2]. The starting composition for the glass precursor material was (in wt %): SiO_2 – 65, Al_2O_3 – 22, Li_2O – 5, Na_2O – 2, K_2O – 2 with $\text{TiO}_2(2)$ $\text{ZrO}_2(2)$ (wt %) added as nucleation agents. The components were sintered, melted at 1600°C and cast. A thermal treatment at 750°C resulted in the creation of ZrTiO_4 nuclei and at 850°C in the growth of $\text{LiAlSi}_2\text{O}_6$ crystals around the nuclei. On the compression cycle from ambient pressure up to 20 GPa, the unit-cell volume of the $\text{LiAlSi}_2\text{O}_6$ phase decreased by about 22 %. The XRD patterns revealed the presence, at high pressure, of the ZrTiO_4 phase that was nucleated in the matrix prior to the crystallization of the main $\text{LiAlSi}_2\text{O}_6$ phase. After quenching from 50 GPa to close to ambient conditions the XRD patterns show that the high-pressure phase was retained to some extent although the decompressed structure carried the signature of the initial ambient $\text{LiAlSi}_2\text{O}_6$ phase. Values of bulk modulus $K_0 = 71(2)$ GPa and $K'_0 = 4.4(6)$ were obtained.

$\text{Li}_2\text{Al}_2\text{Si}_3\text{O}_{10}$ ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$)

A stuffed high-quartz solid solution may be obtained in general by heat treating a glass to the general compositions $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$, when n ranges from 2 through 10 or higher. The high-quartz solid solution transforms into the keatite solid solution at elevated temperatures, when n is larger or equal to 3.5 [70L1]. The silicate with $n = 4$ has the composition $\text{LiAlSi}_2\text{O}_6$ -II (β -spodumene). $\text{Li}_2\text{Al}_2\text{Si}_3\text{O}_{10}$ ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) has space group $P6_222$ (or $P6_422$) [70L1]. The structure is a stuffed derivative of high-quartz. The (Si,Al) tetrahedra form interconnecting 6- and 8-membered rings. Half 8-membered rings are made up by portions of two 6-membered rings and the other half by portions of three 6-membered rings. The neighbouring 8-membered rings of the same kind share one, two or three tetrahedra, while those of different kind share one, two, three, or six tetrahedra with one another. The neighbouring 6-membered rings share one, two or three tetrahedra with one another. The structure is very similar to $\text{LiAlSi}_2\text{O}_6$ -III (γ -spodumene).

$\text{LiFeSi}_2\text{O}_6$, $\text{LiCrSi}_2\text{O}_6$

Li-aegirine, $\text{LiFe}^{3+}\text{Si}_2\text{O}_6$, is the homologue to the spodumene, $\text{LiAlSi}_2\text{O}_6$ and aegirine and crystallizes at RT in a monoclinic-type structure having space group $C2/c$ [69C1, 72B2, 84B3, 84B4]. In [84B4] a phase transition to $P2_1/c$ -type lattice at 228 K was proposed. This phase transition was further studied [01R1]. For $T > 300$ K, the a , b and c parameters and the unit-cell volume follow a positive and linear correlation with temperature; the monoclinic angle β decreases distinctly and more or less linearly with increasing T – Fig. 39a. Sharp discontinuities were observed upon cooling at $T \cong 245$ K. Below this kink, the decrease in a and c cell parameters with decreasing temperature is larger than above 245 K, while b increases between 245 and 210 K,

and decreases upon further cooling. The monoclinic angle β decreases with decreasing temperature below a marked kink at $T \approx 245$ K. At $T < 25$ K, there are additional discontinuities, especially for the b and c cell parameters and for the monoclinic angle – Fig. 39a inset. A transition temperature of 230 K was reported [01R1]. The most pronounced feature of the low-temperature structure is the presence of two nonequivalent Si^{4+} sites giving rise to two tetrahedral chains with different rotation sense and tetrahedral kinking angles. The coordination of Li^+ decreases from six to five upon the $\text{C2/c} \rightarrow \text{P2}_1/\text{c}$ phase transition and becomes slightly more regular. The low-temperature contraction of the lattice is consistent with the magnetic phase transition. The most pronounced magnetostriction of the lattice is observed within the (bc) -plane, and only weak magnetostriction is found parallel to a . This is in agreement with the fact that the magnetic moments are mainly aligned parallel to c with a small angle toward a (section 8.1.4.1.2). The decrease in b and in the monoclinic angle β reflects the antiferromagnetic coupling between neighbouring Fe^{3+} chains. $\text{LiCrSi}_2\text{O}_6$ undergoes the $\text{P2}_1/\text{c} - \text{C2/c}$ phase transition at 343 K [84B4].

$\text{Li}_x\text{Na}_{1-x}\text{FeSi}_2\text{O}_6$

The structure of the two end member compounds is rather similar, except for the coordination of the M2 position, which is occupied by Na and Li, respectively. In $\text{NaFeSi}_2\text{O}_6$, the M2 site is eightfold-coordinated [69C1, 00R1], whereas in $\text{LiFeSi}_2\text{O}_6$, the M2 is sixfold-coordinated at 298 K [69C1, 01R1]. At 298 K, $\text{Li}_x\text{Na}_{1-x}\text{FeSi}_2\text{O}_6$ solid solutions have space group C2/c – Fig. 39b [02R1]. Replacing Na^+ by Li^+ in aegirine causes a distinct decrease of the b lattice parameters by 1.54 % and an increase of the monoclinic angle β by 2.60 %. The oxygen coordination of the M2 cation decreases from 6+2-fold in aegirine to sixfold in pure $\text{LiFeSi}_2\text{O}_6$, the $\langle \text{M2-O} \rangle$ bond length decreases by 7.1 % with increasing replacement of Na^+ by Li^+ . The decrease of the M2 oxygen coordination number correlates with a straightening of the tetrahedral chains, which are slightly kinked in aegirine and fully extended in Li-aegirine (O3-O3-O3 bridging angle $174.2(1)^\circ$ and $180.8(1)^\circ$, respectively). Small variations of individual and mean Si-O bond lengths and distinct changes in O-Si-O bond angles were also found. Within the Fe^{3+}O_6 -M1 octahedra, structural rearrangements mainly affect the O-O interatomic distances (= edges of the octahedra). At 85 K, the compounds with $x > 0.75$ crystallize in the space group $\text{P2}_1/\text{c}$ – Fig. 39c. For the compounds with $x < 0.75$, no phase transition from $\text{C2/c} \rightarrow \text{P2}_1/\text{c}$ was observed down to low temperatures (30 K). The characteristics of the $\text{P2}_1/\text{c}$ low-temperature form of the $\text{Li}_x\text{Na}_{1-x}\text{FeSi}_2\text{O}_6$ compounds agree with that of $\text{LiFeSi}_2\text{O}_6$ [01R1]. For the appearance of the low-temperature modification it seems to be important that the M2 site has a sixfold coordination [02R1]. In kanoite, $\text{MgMnSi}_2\text{O}_6$, where the $\text{P2}_1/\text{c} \rightarrow \text{C2/c}$ phase transition takes place at 513 K, the M2 site is sixfold-coordinated [97A2] as well as in $\text{LiGaSi}_2\text{O}_6$ [95S1], $\text{LiCrSi}_2\text{O}_6$ and $\text{LiScSi}_2\text{O}_6$ [02R1], where the $\text{C2/c} \rightarrow \text{P2}_1/\text{c}$ phase transitions were found at 286.5(5) K, 328(2) K and 234 K, respectively.

LiVSi_2O_6

The LiVSi_2O_6 pyroxene is monoclinic having space group C2/c [94O2, 97S1]. The structure contains isolated chains of VO_6 edge-sharing octahedra running along the c -axis. These chains are separated by double chains of distorted SiO_4 tetrahedra.

ATiSi_2O_6 (A=Li,Na)

$\text{LiTiSi}_2\text{O}_6$ was synthesized by a solid-state reaction under high pressure. The silicates crystallize in a monoclinic unit cell with space group C2/c [82O2]. The structure includes isolated zig-zag chains made up of edge-sharing TiO_6 octahedra. Each chain is bridged by SiO_4 tetrahedra. The alkali metal ions A^+ occupy the tunnel sites in the framework formed by TiO_6 octahedra and SiO_4 tetrahedra. The lattice structure of ATiSi_2O_6 (A = Li,Na) silicates consists of characteristic one-dimensional (1D) chains of skew edge-sharing TiO_6 octahedra – Fig. 40a [04H2]. The TiO_6 chains are bridged and well separated by SiO_4 tetrahedra and therefore (section 8.1.4.1.2) the interchain couplings are considered to be much weaker than interchain interactions. In each TiO_6 chain – Fig. 40b – the edges of octahedra in the xy and yz planes are alternatively shared between neighbouring octahedra which leads to the zig-zag structure. $\text{NaTiSi}_2\text{O}_6$ shows a change to triclinic structure at 210 K [03N1], see also section 8.1.4.1.3.

LiGaSi₂O₆

The structure of the low-temperature form of gallium metasilicate is of P₂₁/c type. Li is coordinated by seven O atoms and Ga by six O atoms. As in the above systems, there are two crystallographically different kinds of silicate chains in the structure. The low-temperature form (P₂₁/c) transforms to the high-temperature form (C2/c) at 285 K [94S1, 95S1].

LiScSi₂O₆, LiSnSi₂O₆, ZnZnSi₂O₆

The LiScSi₂O₆ [77H1] and LiSnSi₂O₆ [83G1] crystallize at low temperature in space group P₂₁/c, and at high temperatures the structure changes to the C2/c-type. LiScSi₂O₆ with the space group C2/c at ambient conditions undergoes phase transitions at 0.6 GPa to the P₂₁/c type. A similar phase transition was observed for ZnZnSi₂O₆ at 1.92 GPa and then to a high pressure phase at 4.9 GPa [00A1]. The transitions are mostly displacive in character and are nonquenchable [00A1].

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There are phase transitions in spodumenes as already mentioned. A comparative analysis of the P₂₁/c – C2/c phase transition seems to be useful. Most of the synthetic Li-clinopyroxenes crystallize at RT in space group C2/c. At lower temperatures, the space group is P₂₁/c and a relation between the transition temperature, T_c , and the composition of the M1 site is apparent: 228 K in LiFeSi₂O₆ [98L1, 01R1], 286 K in LiGaSi₂O₆ [95S1] and 343 K in LiCrSi₂O₆ [84B4]. In [00A1] an inversion relation of T_c with the size of the M1 cation was inferred. Accordingly, no phase transition could be detected for synthetic LiScSi₂O₆ and LiInSi₂O₆ clinopyroxenes, which host larger M1 cations although this was shown experimentally. Since the ionic radius of Al³⁺ is smaller than that of Cr³⁺, LiAlSi₂O₆ should have the space group P₂₁/c at least up to 373 K. On the contrary the above spodumene has space group C2/c at RT and ambient pressure, and also shows a unique S-rotation of the chains of tetrahedra. Moreover, the stability field of spodumene is a function of pressure, the space group P₂₁/c being stable at RT for $p > 3.19$ GPa [00A1]. The data on pyroxenes (pigeonites) show a direct relation of the P₂₁/c – C2/c phase transition with composition and temperature [71P1, 72B1, 84S4, 97A2, 00A2, 00T2]. In particular, it was proposed that T_c depends on the aggregate ionic radius of the M2 cations [00A2]. In order to analyse this matter ^{M2}(Li_{0.85}Mg_{0.09}Fe²⁺_{0.06})^{M1}(Fe³⁺_{0.85}Mg_{0.15})Si₂O₆ ferrian-magnesian spodumene was studied [03C1]. The structure, at RT, is topological equivalent to that of ferrian spodumene LiFeSi₂O₆ and has two symmetrically independent tetrahedral chains (A and B) and two independent octahedral sites M1 and M2. Li⁺ is ordered at the M2 site and Fe³⁺ is ordered at the M1 site, whereas Mg (Fe³⁺) distribute over both octahedral sites. The temperature dependences of the lattice parameters are plotted in Fig. 41. A reversible displacive P₂₁/c – C2/c phase transition is evident at 379 K (106°C). The aggregate ionic radius at M1 is larger than that of ferrian spodumene having $T_c = 229$ K (–44°C). The higher transition temperature was explained [03C1] on the basis of the smaller aggregate radius at the M2 site (due to presence of Mg substituting after Li) in keeping with the results obtained for ferromagnesian P₂₁/c pyroxenes. The aggregate ionic radius in the sample studied by [03C1], at the M1 site, is 0.011 Å greater than in LiFeSi₂O₆ and the transition temperature according to [00A1] should be lower. Therefore, the presence of 0.15 apfu of divalent cations at the M2 site which changes its aggregate ionic radius by only 0.002 Å, is according to [03C1] likely to affect thermodynamic behavior more than that at the M1 site. However, the actual site population and changes in charge distribution due to heterovalent substitutions are important factors to be considered. A local development of highly strained areas was shown in the temperature range 343...368 K which disappears after the phase transition [03C1].

The P₂₁/c – C2/c phase transition in ferrian magnesian spodumene is coelastic (i.e. the spontaneous strain scales with the strain volume) and tricritical. This is the first case of tricritical behavior reported for the high- T displacive phase transition in clinopyroxenes. For other compositions either first-order [74S1, 97A2, 02T1] or a second-order behavior [02C1] was shown. In [02C1] evidence was provided that the character of the transitions mainly depends on the M2 site composition. The presence of microstructures has been proposed to be also a non-negligible factor [02T1].

LiAlSi₂O₆ – LiGaSi₂O₆

Unit-cell dimensions have been determined in synthetic LiAlSi₂O₆ – LiGaSi₂O₆ spodumenes, crystallized at 1500°C and 6 GPa [89O2]. The atmospheric pressure LiGaSi₂O₆ silicate is a tetragonal polymorph of the

β -spodumene type. The monoclinic polymorph is not stable at atmospheric pressure. The unit-cell dimensions show smooth changes with composition.

LiGaSi₂O₆ – NaGaSi₂O₆

The synthetic samples crystallized at 1770 K and 6 GPa have space group C2/c [96O1]. The structure of lithium-rich spodumenes is similar to that of spodumene and the structures of sodium-rich pyroxenes are similar to that of jadeite. It was suggested that there are two different electronic states for the octahedral Ga atoms.

Virgilite

Virgilite, Li_{0.61}(Si_{2.37}Al_{0.60}Fe_{0.02}P_{0.01})O₆ shows a β -quartz-type hexagonal structure having the space group P6₂22 or P6₄22 [78F2]. It is the only naturally occurring representative of the solid solution series between β -quartz (Qz) and LiAlSi₂O₆ (Sp) with a stuffed β -quartz structure. The composition corresponds to Sp₆₁Qz₃₉.

LiScSi₂O₆ – MgSiO₃; LiScSi₂O₆ – MgSiO₃ – CoSiO₃

In the MgSiO₃ – LiScSi₂O₆ series, the protoenstatite field, at 1523 K, occurs in the range of about 65 [76I1] or 60 [84T1] mol % up to 95 mol % MgSiO₃. The crystals are nonquenchable if the LiScSi₂O₆ component is less than \approx 10 mol %. In the composition range (Li,Sc)_{0.60}Mg_{0.40}SiO₃ to LiScSi₂O₆, clinopyroxene-type crystals were obtained. At temperatures above those of the protoenstatite field, the existence of a new phase was shown, the liquidus of the phase existing between 1823...1658 K. Below about 1673 K this phase is decomposed into the protoenstatite-type. This phase was called enstatite IV (En-IV) [77T1]. However, this does not necessarily imply that the compositional range of En-IV extend up to the very pure composition of MgSiO₃. The crystal structure of MgSiO₃ has been studied at around 1673 K [84M3]. The En-IV phase, in fact, consists of a series of subphases, each bearing a superstructure related to a clinopyroxene. Thus, in [Mg_{(x-12)/3}Sc₄][Li_{4/3}Si_{(x-4)/3}]O_x three basic subphases, denoted En-IV-8, En-IV-9, En-IV-10 having x = 100, 112 and 124, respectively, were reported [84T1] – Table 3. Their structures bear superstructure relations to a C-centered clinopyroxene (CPx) and consists of cuts (or slabs) parallel to (10 $\bar{1}$), of the CPx structure, the cuts being 10-tetrahedra wide for En-IV-10, and 9- and 8-tetrahedra wide for En-IV-9 and En-IV-8, respectively. Each cut in the structure of En-IV-10 and En-IV-8 is related to its adjoining cuts by an *a*/2 glide, while that in En-IV-9 is by a *b*/2 glide. The silicate chains in the cut retain their continuity through tetrahedra (T), which occur at the boundaries; T play a role which is similar to that of the offset tetrahedra in pyroxenoids. The contents of the Sc at the cation positions of the slab show the general trend that they increase as the positions approach to the slab boundaries. As the difference in structure type is related to the Sc/(Mg+Sc) ratio, the structure series provides an example of topochemical cell twinning of the CPx structure; with (10 $\bar{1}$) as the twin plane and glides of either *a*/2 or *b*/2 as the twin operation. The lower the Sc/(Mg+Sc) ratio, the less frequent the cell twinning.

A new chemical series, which is similar to “enstatite-IV”, but free from Li has been denoted **Sc series of enstatite IV'** [84T2]. Like the crystal of En-IV, these series were denoted En IV'-10, En-IV'-9 and En-IV'-8. Structure analyses revealed that, unlike En-IV, they characteristically contain Mg at the T site with an occupancy of at most 33.3 %, giving structural formulae which may be well approximated by the general form [Mg_{(x-7.5)/3}Sc_{~3}][Mg_{2/3}Si_{(x-4)/3}]O_x with x = 124 for En-IV'-10, x = 112 for En-IV'-9 and x = 100 for En-IV'-8. Their structural data, such as bond lengths and bond angles, are closely to those of the corresponding En-IV structures.

The structure of the Li_xSc_xMg_{2-2x}Si₂O₆ system was studied [75S3, 77S4]. In [70T1], as already discussed, possible space-group symmetries of pyroxenes based on ideal close-packing of O atoms were reviewed. Many investigators have attempted to explain why the observed space groups of orthopyroxenes (Pbca) and protopyroxenes (Pbcn) do not correspond to the non-centrosymmetric space group (P2₁ca and P2₁cn) characteristic of the ideal structure [73P1]. Some investigators observed reflections in both OPx and PPx diffraction patterns that appeared to violate the *b*-glide symmetry, but invariably in all cases these extra reflections could be ascribed to other causes such as multiple diffraction or the presence of an exsolved phase. In [84S1] was shown by high-pressure studies that the Pbcn protopyroxene structure undergoes a reversible, displacive first-order transformation to a new pyroxene structure type with P2₁cn symmetry at high pressure. In [99Y1] the crystal structure of Mg_{1.54}Li_{0.23}Sc_{0.23}Si₂O₆ was studied. The pressure dependences of the lattice

parameters are plotted in Fig. 42. A first-order displacive phase transformation from space group Pbcn to P2₁cn was observed between 2.03 and 2.50 GPa, which is characterized by a discontinuous decrease in a , c and V by 1.1, 2.4 and 2.6 %, respectively, and an increase in b by 0.9 %. The prominent structural changes associated with the Pbcn-P2₁cn transformation involve the abrupt splitting of one type **O**-rotated silica chain in low-pressure protopyroxene into **S**-rotated A and **O**-rotated B chains in high-pressure protopyroxene, coupled with a marked decrease in O3-O3-O3 angles and a reconfiguration of O-atoms around the M2 site. The kinking angle of the silicate chain in the low-pressure phase, at 2.03 GPa, is 165.9°, whereas the angles are 147.9° and 153.9° for the A and B chains, respectively, in the high-pressure phase at 2.50 GPa. Strikingly, the two types of silicate chains in the P2₁cn structure alternate along the b -axis in a tetrahedral layer parallel to (100). Compression anisotropy of the protopyroxene structure is affected by the phase transition. The relative linear compressibilities ($\beta_a:\beta_b:\beta_c$) are 1.00:1.72:0.99 for low-pressure protopyroxene, but are 1.00:1.28:1.65 for high-pressure protopyroxene. The bulk moduli of low and high-pressure phases are 130(3) and 111(1) GPa, respectively. It was concluded that the Pbcn – P2₁cn phase transition results from the differential compression between SiO₄ tetrahedra and MO₆ octahedra [99Y1].

Protopyroxene, Mg_{0.7}Co_{0.1}Li_{0.1}Sc_{0.1}SiO₃, isotypic with protoenstatite was sluggishly transformed at around 1250°C to a twinned enstatite IV, approximately retaining c -axis [85M2]. Diffraction intensity studies have been carried out at 298 K and 1413 K. The M2-O3 distances O3-O3-O3 angles of protoenstatite remain unchanged with increasing temperature while those of protopyroxene increase. Since in the above system both M2-O3 distance and O3-O3-O3 angle increase with T , such structural mode of variation of protopyroxene is similar to those of clinohypersthene and ferrohypersthene.

For crystal structure of (Li,Na)M³⁺Si₂O₆ see [82B2].

Binary and ternary systems of pyroxenes based on Li, Na, Ca, Mg and Zn were studied. A synthesis of the crystal structure and lattice parameters was published [03O1].

VII Other MSiO₃ silicates

Cs₂CoSiO₆

Cs₂CoSiO₆ crystallizes in a monoclinic structure having space group P2₁/n [01H1]. The characteristic structure feature is a dimer formed by edge connection of [CoO₄] and [SiO₄] tetrahedra. The [MO₄] units are drastically distorted with a bridging angle O-M-O of only $\cong 80^\circ$ for the Co site and 92° for the Si site.

Alamosite, PbSiO₃

Alamosite, PbSiO₃, has space group P2₁/n [68B1]. The crystal structure consists partially of chains of tetrahedra extending parallel to $[10\bar{1}]$ with a lattice translation repeat of twelve tetrahedra. The three independent Pb atoms are coordinated by 3 or 4 oxygen atoms, in each case the nearest oxygen neighbours being distributed on one side of Pb atom, indicating covalency in Pb-O bonding. The Pb atoms and their coordinating oxygen atoms are related by an approximation to a 3₁ screw axis parallel to $[010]$ so that they form a continuous spiral of bonded Pb, O atoms.

CdSiO₃

The crystal structure of CdSiO₃ is believed to be similar to that of the pseudo-wollastonite CaSiO₃ [99H1, 04L2]. Sm³⁺ doped CdSiO₃ was also prepared [04L2].

HAISi₂O₆

From the keatite-type aluminosilicate, LiAlSi₂O₆ II (β -spodumene), the silicate HAlSi₂O₆ has been prepared by ion exchange [90V1]. The framework of keatite is characterized by bands of interconnected 5-rings of SiO₄ tetrahedra running parallel to the a and b -directions. The keatite topology is not affected by the Li-H exchange, but the framework geometry changes considerably. The bands of 5-rings extending in the a and b -directions are stacked much more closely in the c -direction than in LiAlSi₂O₆. This is primarily due to hydrogen bonds parallel to c that pull neighbouring 5-ring bands close together. The space group is P4₃2₁2 or (P4₁2₁2) [90V1]

(KH)₂Si₂O₆

The metasilicate, (KH)₂Si₂O₆, crystallizes in an orthorhombic-type lattice having space group Cmca [64H1, 65H2, 84D2].

VIII Lintisite, Na₃LiTi₂[Si₂O₆]₂O₂·2H₂O; lorenzenite (ramsayite) Na₄Ti₄[Si₂O₆]₂O₆; vinogradovite (Na,Ca)₄(Ti,Nb)₄[Si₂O₆]₂O₁₀(Si,Al)₄O₄·3H₂O, aërinite, joesmithite

Lorenzenite (ramsayite) crystallizes in space group Pbn̄c [87S4] or Pn̄ca [90M1], **vinogradovite** in a monoclinic structure having space group A2/a or I2/c [84R1], and **lintisite** in the monoclinic structure of C2/c type [90M1]. The transformation matrices between the above two space groups of ramsayite are [001/100/010]. The crystal structure of lintisite as seen along [001] is presented in Fig. 43a. The structure is formed by pyroxene-like chains of [SiO₄] tetrahedra, chains of edge-sharing [TiO₆] and [Na(O,H₂O)₆] octahedra, columns of edge-sharing [LiO₄] tetrahedra and distorted [NaO₈] cubes. All these modules are interconnected. According to [84R1] vinogradovite crystallizes in a monoclinic-type structure of A2/a type. By using the transformation matrices from the original cell (A2/c-I2/c) to those of lintisite [101/010/100], the lattice parameters given in Table 3 were obtained. There are two different silicon-oxygen chain radicals (the dimetasilicate bands [Si₄O₁₀]_∞ and the single pyroxene [Si₂O₆]_∞ chain). Along [100] there are zig-zag channels of two types. The smaller channel lies in the layer of edge-linked Ti octahedra and is occupied by Na atoms. The Na polyhedra with eight vertices, linked via a base edge, form zig-zag columns along [100] lying between two Ti ones. Each Na polyhedron is in contact with its neighbours via edges. Paravinogradovite crystallizes in a triclinic-type structure having space group P1 [03K1].

The modular nature of the above silicates and its structural relationships may be analyzed by a description in terms of structural “slabs” periodic in two dimensions and finite thickness which are stacked along [100]. In lintisite four different slabs are present. Slab 1 is formed by columns of edge-sharing [LiO₄] tetrahedra and zig-zag chains of edge-sharing [Na(O,H₂O)] octahedra (Na₂ atoms). Such a module is presented in Fig. 43b. Slab 2 is formed by pyroxene-like chains of [SiO₄] tetrahedra (Si₂ atoms) and water molecules. The water molecules are shared with the preceding slab. Slab 3 is formed by chains of edge-sharing [TiO₆] octahedra and Na⁺ cations in eightfold coordination (Na₁ atoms). Slab 4 is formed by pyroxene like chains of [SiO₆] tetrahedra (Si₁ atoms). As difference from slab 2, the slab 4 is closely similar to the corresponding slabs in pyroxene, with two tetrahedral chains per unit *b* translation. Some of these modules are present also in **vinogradovite** [84R1] and **lorenzenite** (ramsayite) [87S4]. In vinogradovite the slabs 2, 3 and 4 occur, in lorenzenite the slabs 3 and 4 occur. It is possible to describe the structure of these silicates by giving the sequences of modules in the stacking direction [100].

lorenzenite	334334...
vinogradovite	2343223432...
lintisite	123432123432...

The structure of lintisite may be derived from vinogradovite by disjoining the double [Si₄O₁₀] chains and inserting between them the structural slabs formed by [LiO₄] tetrahedra and [Na(O,H₂O)₆] octahedra (slab 1). The lattice parameters are given in Table 3. In addition, the data for “mineral X” are tabulated [86K1]. According to [90M1] its chemical composition and unit-cell parameters, when conveniently transformed, strongly indicate that this mineral is vinogradovite.

Joesmithite

Joesmithite, (Pb_{0.6}Ca_{0.6}Ba_{0.1}Mn_{0.8})Ca_{4.0}Fe³⁺_{2.0}(Mg_{6.3}Fe³⁺_{1.4}Fe²⁺_{0.8}Al_{0.3})(Si_{13.8}Be_{0.1})(OH)_{14.9}O_{39.7}, crystallizes in a monoclinic structure of space group P2/a [68M2, 68M3].

Aërinite

The mineral having the composition Ca₄(Al,Fe,Mg)₁₀Si₁₂O₃₆(OH)₁₂CO₃·H₂O crystallizes in a monoclinic-type structure – Table 3 [88A4].

Nchwaningite

Nchwaningite, $\text{Mn}^{2+}_2\text{SiO}_3(\text{OH})_2 \cdot \text{H}_2\text{O}$, is an orthorhombic chain silicate (space group $\text{Pca}2_1$) [95N1]. The structure – Fig. 44 – consists of double layers of laterally linked so-called truncated pyroxene-building units formed by a double chain of octahedra, topped with a zweier single chain of Si tetrahedra. Symmetry equivalent units are linked laterally but turned upside down. This yields a double layer structure with H bridges linking the layers. A striking feature of the structure is that one MnO_6 corner is formed by a H_2O molecule. The tetrahedral chain and the octahedron distortion were compared with pyroxenes having Mn^{2+} in M1 (synthetic MnSiO_3 , $\text{P}2_1/\text{c}$ clinopyroxene) and johannsenite [$\text{CaMnSi}_2\text{O}_6$].

8.1.4.1.2 Neutron diffraction data

$\text{Fe}_2\text{Si}_2\text{O}_6$

The Fe^{2+} in the M1 and M2 sites of the Pbca structure occur in two sets of eightfold general positions. Each octahedral band is created by two sets of M1 and M2 octahedra, which are related by the c -glide normal to b (see Fig. 12). The Fe^{2+} moments are ordered ferromagnetically within one octahedral band, which are antiferromagnetically coupled to neighbouring bands, the spin direction being parallel and antiparallel to b [86W3, 88G2]. Below $T_F = 8$ K, the Fe^{2+} moments direction, at the M2 site deviates slightly from the b -axis. The temperature dependencies of the iron moments at the M1 and M2 sites are very similar from 1.5 to 10 K. At $T = 10$ K both show a break – Fig. 45a. Above 10 K, Fe^{2+} magnetic moments diminish rapidly; the moment at M2 much more rapidly than that at M1, both showing a Néel temperature $T_N = 38$ K. For the M1 site, the iron moment is slightly higher than the spin-only value due to a lack of complete quenching of orbital contribution. The M2 moment is considerable less than the spin-only value – Table 8 – due to a complete quenching of the orbital angular momentum as a result of considerable octahedral distortion and to a substantial covalency contribution at this site [88G2].

$\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$

According to [85W2, 86W3] the magnetic structure of natural orthopyroxene with $x = 0.87$ is similar to that of ferrosilite. The linear chains of M2 sites are almost saturated by Fe^{2+} (94 %) and the zig-zag chains are strongly diluted by diamagnetic Mg^{2+} ions. The refinement of individual moments was impossible, and only the mean value per site was obtained. This value corresponds to the average moment which was found in orthoferrosilite, $\langle p_{\text{Fe}} \rangle = 3.70(25) \mu_B$.

$\text{CaFeSi}_2\text{O}_6$

In hedenbergite (space group $\text{C}2/\text{c}$), the Fe^{2+} ions occupy the M1 site and Ca the highly distorted M2 site. The Fe^{2+} moments are ferromagnetically arranged within one chain, which is antiferromagnetically coupled to the adjacent chains [88G2]. The magnetic space group is C_p2/c . The magnetic moments are perpendicular to b – Fig. 27. The spin direction was found to lie about 132° from c in the (ac) -plane. The magnetic moment as function of temperature shows a smooth variation – Fig. 45b.

$\text{CaFe}_{0.8}\text{Mg}_{0.2}\text{Si}_2\text{O}_6$

In $\text{CaFe}_{0.8}\text{Mg}_{0.2}\text{Si}_2\text{O}_6$ (space group $\text{C}2/\text{c}$), the Fe^{2+} moments which are located only on zig-zag chains of M1 sites are aligned parallel to each other in the (ac) -plane and form an angle of 45° with the a -axis [86W3]. The moments on adjacent chains are aligned antiparallel. The dominating coupling between nearest neighbours inside the chain is ferromagnetic, resulting from superexchange paths via oxygen bridges.

$\text{CaCoSi}_2\text{O}_6$

The magnetic structure of $\text{CaCoSi}_2\text{O}_6$ ($\text{C}2/\text{c}$ type) is plotted in Fig. 46 [96D3]. The components of the cobalt magnetic moments are $p_x = 1.91(23) \mu_B$; $p_z = -2.23(12) \mu_B$ corresponding to $p_{\text{Co}} = 3.30(15) \mu_B$ and to an angle $\alpha = 41^\circ$ between p and the a -axis. There are ferromagnetic interactions inside the CoO_6 chains that order antiferromagnetically to each other at low temperature.

NaFeSi₂O₆

The principal magnetic mode has the periodicity of the crystallographic structure and is made of ferromagnetic chains, coupled antiferromagnetically [89G1]. Moments are oriented in a direction close to the chain axis *c*. The antiferromagnetic exchange between adjacent Fe³⁺ ions in the same chain is overcome by their coupling to a common Fe³⁺ neighbour in the next chain. This indicates that the whole SiO₄ group can act as a superexchange ligand in silicates. The ability for significant superexchange interactions to be transmitted across an SiO₄ group is attributed to the covalent bonding of the group. For aegirine this is the dominant magnetic exchange path.

LiFeSi₂O₆

Although it was not possible to clearly decide between C2/c (anisotropic refinement) and P2₁/c (isotropic), in [98L1] the space group P2₁/c was adopted for the low-temperature structure, in agreement with [84B4]. The first occurrence of magnetic reflections can be observed at 16.5 K. A significant increase of the background between 10°...20°(2 θ), observable already in the pattern at 25 K, indicates preordering phenomena. At *T* < 16 K, the magnetic moments are aligned in the (*ac*)-plane, with the main magnetic component along the crystallographic *c*-axis (4.88 μ_B at 1.4 K) and a small component (0.8 μ_B at 1.4 K) aligned along the *a*-axis [01R1]. The resulting magnetic moment amounts to *p* = 4.93 μ_B with an angle of 8.3° between the *p* and the *c*-axis at 1.4 K. The temperature dependence of the magnetic moments along the crystallographic axes *a* and *c* is shown in Fig. 47a. The angle between the moment *p* and the *c*-axis changes with temperature. The P2₁/c was considered as being the magnetic space group. This is in accordance with the antiferromagnetic ordering within and between the Fe³⁺O₆ chains. Fig. 47b combines the integrated intensities of the strong magnetic Bragg reflections (100)_m and (010)_m, as extracted from the neutron diffraction experiment and the susceptibility data. The susceptibility (magnetic moment) shows a maximum at 20.8 K and an inflection point at 17.5 K. The latter temperature is in agreement with the appearance of the magnetic reflections in neutron diffraction experiments [01R1].

8.1.4.1.3 Magnetization. Magnetic susceptibility**Fe_xMg_{1-x}SiO₃**

The magnetic susceptibility of ferrosilite (*x* = 1) shows two distinct peaks at *T_N* \cong 40 K and *T_N* = 8 K – Fig. 48 [88G2]. The first one corresponds to a paramagnetic to antiferromagnetic transition, whereas the second one represents a spin canting transition. The reciprocal susceptibilities, in the paramagnetic region, obey a Curie-Weiss law. A value of the paramagnetic Curie temperature Θ = 138 K, was determined from the χ vs. *T* curve in the temperature range 190...300 K. The magnetization isotherms at 4.2 and 25 K show an upward curvature and an inflection at around 4.5 T, indicating a spin-flip transition [85C2]. The above data are consistent with a ferromagnetic coupling of Fe²⁺ spins within an octahedral band, which in turn is antiferromagnetically coupled to neighbouring octahedral bands (see section 8.1.4.1.2). The intrachain exchange constant *J*₁ is positive and much larger than the interchain constant *J*₂; the behaviour is characteristic for a pseudo one-dimensional system.

The Néel temperatures, *T_N*, for Fe_{*x*}Mg_{1-*x*}SiO₃ orthopyroxenes decrease when the magnesium content is increased – Table 9. The samples with *x* \leq 0.4 did not show magnetic ordering in the temperature region above 1.7 K [69S2]. The susceptibility of Fe_{0.87}Mg_{0.13}SiO₃ along the *b*-axis shows an inflection point at *T_N* = 26(1) K, which is somewhat lower than the temperature *T_N* of FeSiO₃ – Fig. 49a [86W4]. The susceptibilities measured along the orthorhombic axes are quite different from each other, reflecting the strong anisotropy that results from the splitting of the ⁵D term of Fe²⁺ in a crystal field of overall orthorhombic symmetry – Figs. 49b and c. Below *T_N*, the susceptibility for *H* \parallel *b* decreases continuously, whereas for *H* \parallel *c* and *H* \parallel *a* increases slightly. This behaviour suggests that in the ordered state, the moments must be aligned along the *b*-axis. The magnetization isotherms for a single crystal in external fields along the directions *a* and *c* are a linear function of $\mu_0 H$ up to 5 T, whereas the curve for *H* \parallel *b* changes in slope above 1.0 T. Such behaviour is characteristic for a metamagnetic-type transition at a critical field *H_c*, where the antiferromagnetic ordering changes to parallel spin alignment – Fig. 49c. A similar behaviour was observed for FeSiO₃, the metamagnetic transition occurring at $\mu_0 H_c$ = 5 T [86W4]. The effective exchange constants inside one ribbon is zJ/k_B = 10.5 K and the magnetic coupling between Fe²⁺ ions in adjacent ribbons is $z'J'/k_B$ = -3.1 K both for *x* = 1.0 and 0.87. The ratio $z'J'/zJ$ = 0.3 is a value typical for a low-dimensional magnetic system. As mentioned already, it was suggested that in orthopyroxenes, a ferromagnetic coupling exists between the Fe species within a given ribbon formed by two M1

and M2 sites. However, some controversy remains concerning the nature of the dominant, long-range magnetic ordering [01E1]. The Fe^{2+} ions at the M1 sites exhibit low hyperfine fields, while much higher values were observed for the M2 sites. In [92P1] was reported that in $\text{Mg}_{0.9}^{57}\text{Fe}_{0.1}\text{SiO}_3$ orthopyroxene only 25 % of the Fe^{2+} ions at M2 take part in the magnetic ordering at 4.2 K, but the exact nature of the coupling has not been determined.

In [01E1] the magnetic behaviour of $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ clinopyroxenes was studied in order to analyze comparatively their properties with those of orthopyroxenes and also to obtain information about the nature of short-range magnetic interactions within the M bands, as well as of the long-range order between the ribbons. The temperature dependences of the magnetic susceptibilities, for $\text{P2}_1/\text{c}$ clinopyroxenes with $x = 1.0$ and 0.87 , are plotted in Fig. 50. In Table 9 are given some data obtained by analyzing the χ vs T curves. Generally spoken, the magnetic behaviour of $\text{P2}_1/\text{c}$ clinopyroxenes is similar to that of orthopyroxenes with similar (Mg,Fe) composition. The macroscopic magnetic results suggest ferromagnetic ordering of Fe^{2+} ions within ribbons consisting of two linear bands of M2 sites that enclose chains of M1 sites and antiferromagnetic coupling between neighbouring ribbons (see also section 8.1.4.1.4).

For magnetic properties of pyroxenes see also [82B1, 88C2, 89S2].

Hedenbergites, synthetic and natural

The Néel temperatures of $\text{CaFeSi}_2\text{O}_6$ hedenbergite is $T_N = 38$ K [85C2, 88G2]. The reciprocal susceptibility follows a Curie-Weiss behaviour at $T > 100$ K – Fig. 51. The positive value of Θ shows that the principal magnetic interactions are ferromagnetic involving Fe^{2+} in edge-sharing octahedra because the Fe-O-Fe superexchange bond angle is near 90° . The ferromagnetic M1 chains are coupled antiparallel by antiferromagnetic interchain interactions. Both the above studies [85C2, 88G2] show the moments to be in the (*ac*)-plane. In Fig. 52c are plotted the directions of magnetic moments in hedenbergite reported by various authors. An angle of 135° from the *c*-axis was proposed by [85C2]. A value of 45° from the *a*-axis was reported by [86W3]. In [97B1] was found nearly the same direction, 50° from *a* and $60(3)^\circ$ from *c* as in [86W3].

In $\text{CaFe}_{0.8}\text{Mg}_{0.2}\text{Si}_2\text{O}_6$ natural hedenbergite, a value $T_N = 35$ K was reported [86W3]. In this system the magnetic zig-zag chains formed by Fe^{2+} on M1 are diluted by ≈ 20 % Mg^{2+} ions thus lowering the T_N value as compared to pure hedenbergite. The magnetic moments, as in $\text{CaFeSi}_2\text{O}_6$, are aligned parallel to each other in the (*ac*)-plane. Magnetic measurements on $\text{Ca}_{0.99}\text{Fe}_{0.84}^{2+}\text{Mg}_{0.12}\text{Mn}_{0.04}\text{Si}_2\text{O}_6$ single crystal show that the direction of magnetic moments lie within the (*ac*)-plane, $45(2)^\circ$ from *a* and $60(2)^\circ$ from the *c*-axis, respectively [97B1]. At lower temperatures (4.2 K), a field induced magnetic transition can be seen at $\mu_0 H_c = 3.7$ T, when the field is applied along the easy direction – Fig. 52a. Outside of the easy direction, a stronger magnetic field is necessary to force the spin to flip. The effect, in general, broadens with increasing temperature until it disappears completely at T_N . The critical field, H_c , decreases with increasing temperature. The sharp kink in the temperature dependence of the magnetic susceptibility marks the antiferromagnetic ordering temperature, T_N – Fig. 52b. It is more visible in the easy direction (χ_{\parallel}), whereas it cannot be observed perpendicular to it (χ_{\perp}). The interchain ferromagnetic interactions occur via Fe-O-Fe superexchange as expected for edge-sharing M1 octahedron chain with Fe-Fe distances of 3.14 Å and is stronger than the antiferromagnetic interaction between neighboured M1-chains as evidenced by the positive Θ value.

Diopside – $\alpha\text{-Fe}_2\text{O}_3$

The magnetic properties of the diopside – Fe_2O_3 system were studied [83N1]. There is well pronounced rise in magnetization with increasing Fe content. Whereas Di – 3 % $\alpha\text{-Fe}_2\text{O}_3$ shows pure paramagnetic behaviour, Di – 7 % and Di – 20 % $\alpha\text{-Fe}_2\text{O}_3$ convert to superparamagnetism. The presence of light remanence for Di – 20 % $\alpha\text{-Fe}_2\text{O}_3$ indicates tendency towards ferromagnetism. A $\text{Ca}_{0.75}\text{Mg}_{0.75}\text{Fe}_{0.50}\text{Si}_2\text{O}_6$ sample shows a magnetization curve possessing a remanence. At 4.2 K the maximum magnetization is 0.5 emu in a field of 7 T.

$\text{CaCo}_{1-x}\text{Ni}_x\text{Si}_2\text{O}_6$

The temperature dependences of the magnetic susceptibilities and χT product for $\text{CaCo}_{1-x}\text{Ni}_x\text{Si}_2\text{O}_6$ solid solutions (space group $\text{C2}/\text{c}$) are plotted in Fig. 53. The Néel temperatures, T_N , increase with increasing Ni content from 9.75 K ($x = 0$) to 21.7 K ($x = 1.00$) – Table 9. For $x = 0$, the χT values slowly decrease between

300 and 50 K, and then a plateau ($\chi T \cong 2.5 \text{ emu K mol}^{-1}$) is observed between 50 and 25 K. Such behaviour may be related to the spin-orbit coupling effect for the Co^{2+} ion, that stabilizes a Kramers doublet ground state [96D3]. However, the χT value of $2.5 \text{ emu K mol}^{-1}$ appears to be higher than expected ($1.875 \text{ emu K mol}^{-1}$). Other effects, as a contribution of a ferromagnetic coupling between Co atoms inside the CoO_6 infinite chains, are therefore to be considered in this part of the curve. At lower temperatures, χT sharply decreases down to zero, in relation with antiferromagnetic interactions evidenced also by a sharp peak at 9.75 K. In the paramagnetic domain, the magnetic susceptibility follows a Curie-Weiss law with negative Θ value. Similar results are shown for the solid solutions with nickel. As the cobalt content decreases, the spin-orbit coupling plateau progressively vanishes from the χT curves. There are ferromagnetic interactions inside the MO_6 zig-zag chains that order antiferromagnetically at T_N . In case of $\text{CaNiSi}_2\text{O}_6$, the slight increase of the χT value from RT down to 30 K was related to ferromagnetic coupling inside the NiO_6 zig-zag chains which takes place by two superexchange pathways via oxygen O1 bridges.

Aegirine (acmite), aegirine (acmite) - diopside

The structure of aegirine (acmite), $\text{NaFeSi}_2\text{O}_6$, has a single zig-zag chain of edge-sharing octahedral M1 sites and sodium in eightfold-coordinated M2 sites (section 8.1.4.1.1). The direct Fe-Fe distance within the chains is 3.19 Å, whereas the separation of chains is 6.55 Å in the (*ab*)-plane although the shortest Fe-Fe distance between chains is 6.18 Å [89B1]. The structure is illustrated in Fig. 27a, while the position of M1 sites in the unit cell and their symmetry relationships of M1 are shown in Figs. 27b.

The thermal variations of reciprocal susceptibilities for $\text{NaFeSi}_2\text{O}_6$ (synthetic) and natural $\langle \text{Na}_{0.80}\text{Ca}_{0.01}\text{Mn}_{0.01} \rangle \{ \text{Fe}^{3+}_{0.74}\text{Ti}_{0.03}\text{Al}_{0.12}\text{Fe}^{2+}_{0.07} \} [\text{Si}_{1.99}\text{Al}_{0.01}]\text{O}_6$ acmites are given in Fig. 54A, while in Fig. 54B some magnetization isotherms are plotted. In Fig. 55 the thermal variations of reciprocal susceptibilities for $\text{AFFeSi}_2\text{O}_6$ ($A = \text{Li, Na}$) are plotted [88B1]. Both natural and synthetic acmites show predominantly antiferromagnetic exchange coupling although in the natural sample the antiferromagnetic exchange is weakened by the presence of some Fe^{2+} , presumably because the $\text{Fe}^{2+}\text{-Fe}^{3+}$ exchange is ferromagnetic. According to [89B1] the inter- and intrachain interactions are both antiferromagnetic and in competition. However, the structure implies that chain to chain coupling via intervening SiO_4 groups is dominant and overcomes exchange within the chain. Therefore exchange interactions were considered to occur via two oxygens, that is, four nonequivalent classes of Fe-O-Si-O-Fe paths (J'_{14} , J''_{14} , J'_{13} and J''_{13}) – Fig. 54C. J'_{14} couples moments 1 and 4 or the moments 2 and 3. The paths of this class are connected from cell to cell along $a + c$, i.e. they couple a moment 1 to two moments 4, one of which is $c/2$ above its z -level, the other $c/2$ below. The paths corresponding to J''_{14} make just the same connection, so that it is necessary to consider $J_{14} = J'_{14} + J''_{14}$. J'_{13} couples the moments 1(or 2) to two moments 3(or 4), and J''_{13} to two other moments 3(or 4), all at the same z -level. When the magnetic cell is the crystallographic cell, all moments 3, for instance, are equivalent, and we are left with three effective parameters, J_{12} , $J_{13} = J'_{13} + J''_{13}$ and J_{14} . The frustration is understood by considering, for instance, how moments 1, 2 and 3 interact together. They form triangles of antiferromagnetic interactions which cannot be satisfied simultaneously. Therefore, the weakest, J_{12} , of the three has to yield. The covalent character for the bonding in the SiO_4 group may account for its ability to act as a superexchange ligand. Transfer of electrons from the SiO_4 into the unoccupied spin down orbitals of an adjacent Fe^{3+} ion will lead to an excess of spin up electrons elsewhere on the group, hence antiferromagnetic coupling with another adjacent Fe^{3+} . Thus, acmite orders antiferromagnetically principally in a structure with ferromagnetic ferric chains. Exchange interactions are antiferromagnetic and frustrated, the dominant interactions being interchain coupling via an SiO_4 group. Acmite is therefore in this sense a quasi-one-dimensional Heisenberg antiferromagnet.

The temperature dependence of the magnetic susceptibility for **Ac₈₁Di₁₉ silicate** is plotted in Fig. 56 [88D1]. A value $T_N = 15(1) \text{ K}$ was shown. The negative Θ value and the cusp in χ vs. T indicates that the dominant superexchange interactions between the iron ions are antiferromagnetic. A model was considered [88D1] in which the antiferromagnetic interactions are expected for Fe^{3+} ions in edge-sharing octahedra and ferromagnetic interactions for Fe^{2+} in the same symmetry, because the Fe-O-Fe superexchange bond angle is near 90° , and the two neighbouring cations that share a common edge have a direct overlap of the half-filled d_{xy} (or d_{yz} , or d_{xz}) orbitals.

LiFeSi₂O₆

Magnetic susceptibility measurements revealed a distinct transition to collinear antiferromagnetic structure with the *c*-axis as easy direction of magnetization, at $T_N = 19.5(5)$ K – Fig. 57 [88D1, 98A1] – see also Fig. 55, or at 17.5 K [01R1]. Magnetic ordering in Li-aegirine was also observed by the ^{57}Fe NGR method below 20 K and by neutron diffraction below 15 K [98A1] or 17.5 K [01R1]. The magnetic susceptibility and ^{57}Fe NGR data indicate short-range or local magnetic ordering at slightly higher temperatures than the onset of complete 3-dimensional, long-range magnetic order at 17.5 K, as shown by neutron diffraction. The higher magnetic ordering temperature as compared to NaFeSi₂O₆ can be explained by its smaller Fe-Fe interchain distance of 5.31 Å, as compared to 5.34 Å in case of NaFeSi₂O₆. The expansion of the structure is caused by the substitution of the smaller Li-ion by the larger Na-ion in the M2 sites accompanied by an increase of the coordination number from 6 to 8 [88B1].

ATiSi₂O₆ (A = Li, Na)

The temperature dependences of the magnetic susceptibilities for NaTiSi₂O₆ and LiTiSi₂O₆ are plotted in Fig. 58a, b [02I1]. The most significant feature of the $\chi_m(T)$ curves is a gaplike behavior. In case of NaTiSi₂O₆, a Curie-Weiss dependence was shown in the high-temperature range. A sharp decrease of magnetic susceptibilities was observed below 210 K. The $\chi_m(T)$ increases again below 60 K. This increase was attributed to the presence of magnetic impurities. By assuming an impurity with $S = 1/2$, the concentration of a possible magnetic impurity was estimated to be ≈ 0.5 mol %. The $\chi_m(T)$ values, after subtracting this contribution, are shown in inset of Fig. 58a. It can be seen that $\chi_m(T)$ for impurity corrected susceptibilities starts to decrease at 210 K and becomes temperature independent below 60 K. The constant value of $\chi_m = 6 \cdot 10^{-5}$ emu/mol at low T is comparable to the magnetic susceptibility at the ground state in spin-gap systems with $S = 1/2$. The rough estimate for the spin-gap value was obtained by fitting $\chi_m(T)$ in a low-temperature range to the relation $\chi_m = \alpha \exp(-\Delta/k_B T) + \chi_0$, where α is a constant value corresponding to the dispersion of excitation energy, Δ is the spin gap and $\chi_0 = 6 \cdot 10^{-5}$ emu/mol is a constant term attributed to the Van Vleck paramagnetism and diamagnetism of core electrons. Values $\alpha = 5.4 \cdot 10^{-3}$ emu/mol and $\Delta/k_B \approx 500$ K were obtained. In the higher temperature range, $\chi_m(T)$ exhibits a Curie-Weiss behavior but deviates from this dependence at $T < 400$ K. A better fit of experimental data was obtained by the Bonner-Fisher relation [64B1] for the $S = 1/2$ antiferromagnetic Heisenberg linear chain. The best fit was shown for an average g factor $g = 2$ and intrachain exchange integral $J/k_B = 295$ K. A broad peak of heat capacity was observed at the temperature roughly corresponding to that of the spin-gap opening [02I1] (see section 8.1.4.1.7). The magnetic transition is similar to the spin-Peierls one. The most significant feature is that the transition occurs at a temperature higher than that at the maximum point of the Bonner-Fisher curve. This means that the short-range magnetic correlations within the chain are not fully developed and the intrinsic magnetoelastic instability of an 1D system cannot be considered as a driving force for the transition. In order to analyse this matter, the crystal structure was studied in the low-temperature range. It was shown that the phase transition at 210 K is accompanied by a structural change and spin singlet formation [03N1]. The crystal structure changes to the triclinic one at low temperatures. There exist two crystallographically independent sites for Ti – Fig. 58c. This indicates the formation of dimers, which is consistent with the spin singlet ground state. The alteration of Ti-Ti distance starts at $T_c \approx 210$ K and gradually increases with decreasing temperature, indicating the gradual development of the formation of $\text{Ti}^{3+}\text{-Ti}^{3+}$ single pairs.

The magnetic susceptibility for LiTiSi₂O₆ as function of temperature follows a similar behavior as for NaTiSi₂O₆ – Fig. 58b. A transition at $T_c = 230$ K was shown. Some extra anomalies in $\chi(T)$ were attributed to the presence of impurity phases.

The magnetic properties of NaTiSi₂O₆ were further theoretically analysed [04H2]. Although the magnetic transition reminds of a spin-Peierls one [02U1], the magnetic susceptibility shows an unusual temperature dependence above T_c , which deviates from that of other spin Peierls compounds. In spin-Peierls systems, the dimerization is caused by the magnetoelastic coupling, and therefore the transition occurs when short-range spin correlations develop enough to drive the lattice dimerization. This development of spin correlations is manifested in a broad peak of the magnetic susceptibility above T_c , and the peak temperature gives a rough estimate of the spin exchange energy scale. Contrary to this conventional behaviour, the magnetic susceptibility of ATiSi₂O₆ silicates, going from high temperatures, increases as temperature decreases, and suddenly drops at T_c without a clear formation of the broad peak. This suggests a breakdown of the simple spin-Peierls picture. In order to

describe this peculiar transition to the singlet state, the importance of the t_{2g} orbital degree of freedom has been pointed out [02I1, 04K1] – Fig. 40b. It was proposed theoretically [99K1] that the orbital ordering may modify effective spin exchange interactions and induce the spin-singlet formation. This mechanism was considered in analyzing the magnetic behaviour of ATiSi_2O_6 ($A=\text{Na, Li}$) systems [04H2, 04K1, 04K2]. Thus, in [04K2] was shown that the t_{2g} orbitals of Ti^{3+} ions dominate the exchange and fluctuations and it was argued that the phase transition in $\text{NaTiSi}_2\text{O}_6$ can be regarded as an orbital analogue of the spin-Peierls phase transition. The Raman scattering study [04K1] revealed the existence of phonon anomalies at T_c and a large phonon broadening in the room temperature spectra of $\text{NaTiSi}_2\text{O}_6$. The microscopic orbital-spin model [04K1] shows that the difference between $S=1/2$ and $S\neq 1$ pyroxenes originates from a unique interplay between electronic anisotropy (quasi-one dimensional) and t_{2g} orbital degeneracy, and it was suggested that the quasi-one dimensional dynamical Jahn-Teller phase of $\text{NaTiSi}_2\text{O}_6$ exhibits a spontaneous breaking of the translational symmetry into a dimerized orbital ordered state with a spin-gap due to the formation of spin valence bonds. By using a density functional approach, in [04P1] was found that the electronic structure of $\text{NaTiSi}_2\text{O}_6$ with mixed antiferromagnetic-ferromagnetic order is favorable in the ground state at low temperature. Their model includes the ferromagnetic ordering of spins inside Ti-Ti crystallographic dimers in the low-temperature phase of $\text{NaTiSi}_2\text{O}_6$ and antiferromagnetic ordering between them. In [04H2], an effective spin-orbital-lattice coupled model in the strong correlation limit was derived for a quasi-one-dimensional spin $-1/2$, with explicitly taking into account the t_{2g} orbital degeneracy and the model was investigated by numerical simulation as well as the mean-field analysis. An interplay between orbital and spin degrees of freedom occurs. Although both orbital and spin correlations are of antiferromagnetic type and compete with each other at high temperatures, the development of AF spin correlations with decreasing temperature yields a sign change of orbital correlations from antiferro- to ferro-type. After the spin change, the ferro-type orbital correlations grow as compared to the antiferro-type spin correlations, and finally induce the spin-singlet formation with a dimerization. As a result of this interplay, the system undergoes a finite temperature transition to the spin-dimer and orbital-ferro-ordered phase concomitant with the Jahn-Teller lattice distortion. The numerical results for the magnetic susceptibility reproduce the experimental data. The results reveal that the Jahn-Teller energy scale is small and the orbital and spin exchange interactions play a decisive role in describing the magnetic properties of the $\text{NaTiSi}_2\text{O}_6$ system.

AVSi_2O_6 ($A = \text{Li, Na}$)

The temperature dependences of the magnetic susceptibilities for LiVSi_2O_6 and NaVSi_2O_6 are plotted in Fig. 59 [04V1]. Broad maxima at a temperature T_M , characteristic for a quasi-one-dimensional magnetic compound, are shown. The maxima indicate the formation of a regime of short-range correlations within the chains. At $T < T_M$, the $\chi(T)$ dependences bend at certain temperatures T_N which can be seen as sharp peaks in $d\chi/dT$. The weak up turns in $\chi(T)$, at lowest temperatures, are due to a small amount of magnetic impurities and deviations from stoichiometry [04V1]. The temperature of the broad maximum, T_M , is related to the value of the intrachain exchange interaction parameter J_{\parallel} : $T_M = 1.35 J_{\parallel}$ [01D1]. The value of exchange interaction between the chains $J_{\perp} = T_N/1.28 n [\ln(5.8J_{\parallel}/T_N)]^{1/2}$, where n is the number of nearest neighbouring chains ($n = 4$ in the present case). The values $J_{\perp}/J_{\parallel} = 0.029$ for $A = \text{Li}$ and 0.061 for $A = \text{Na}$ are characteristic for “one-dimensionality” of the magnetic subsystem. When substituting Na for Li, the values of the interchain exchange interactions, J_{\parallel} , increase while the values of interchain exchange interactions, J_{\perp} , do not vary significantly. Thus, the quasi-one-dimensional character of the LiVSi_2O_6 is more pronounced than of the Na-based system.

ACrSi_2O_6 ($A = \text{Li, Na}$)

The temperature dependence of the magnetic susceptibilities for $\text{NaCrSi}_2\text{O}_6$ is plotted in Fig. 60 [04I1]. Above 10 K the $\chi(T)$ follows a Curie-Weiss law. An anomaly at $T_N = 3.4$ K, identified as Néel temperature, indicates a long-range antiferromagnetic order. In $\text{LiCrSi}_2\text{O}_6$ a value $T_N = 11$ K was obtained [04I1].

Analyzing the magnetic behavior of $\text{AM}^{3+}\text{Si}_2\text{O}_6$ with $M = \text{Ti, V, Cr}$ and $A = \text{Na and Li}$ it can be concluded that the temperature of the broad maxima, T_M , where short-range magnetic correlation within the chain is fully developed, decreases with increasing the number of d electrons (d^n) or spin number increases. Thus, in $\text{NaM}^{3+}\text{Si}_2\text{O}_6$ values $T_M = 186$ K ($\text{Ti} = d^1$), 53 K ($\text{V} = d^2$) and less than 3 K ($\text{Cr} = d^3$) were determined – Table 9. The T_N , which reflects mainly interchain interactions, also decreases with increasing d^n , although the T_N values for Ti-based compounds cannot be estimated because of the spin-Peierls like transition far above T_M . For fixed d^n , both T_M and T_N are higher in the Li-based compounds than in the Na ones.

8.1.4.1.4 Nuclear gamma resonance (NGR) data

$\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$

A large number of studies were performed by the ^{57}Fe NGR method on $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ orthopyroxenes [67E2, 68V1, 69H1, 69R1, 69S1, 71B3, 71G1, 80S2, 86R1, 86S1, 86S2, 86S3, 86W4, 87R1, 87S2, 88S4, 91C1, 92P1, 93L1, 93S4, 93V1, 94V1, 94Y1, 01V1], clinopyroxenes [98A3, 00E1, 01E1] or perovskite [92F1, 92J1, 92M2, 94F2].

Some ^{57}Fe NGR spectra of orthopyroxenes are shown in Fig. 61. In the paramagnetic region, the spectra were fitted admitting the presence of two doublets – Fig. 61d. The doublet having the higher value of the isomer shift (δ) was attributed to Fe^{2+} in M1 octahedral site and the inner doublet to Fe^{2+} in the more distorted octahedral site, M2. The relative weak value of the quadrupole splitting $\Delta Q(\text{M2})$ indicates a strong contribution of the lattice term to the electric field gradient, V_{zz} , and thus it reflects the important distortion of the M2 oxygen octahedron. Unlike FeSiO_3 , where the intensities of the doublets are equal, in $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ OPx, a higher intensity of the M2 doublet relative to the M1 site was observed. This was ascribed to a preferred occupation of Fe^{2+} in M2 site [87R1] – see section 8.1.4.1.1. On cooling the sample from 300 K to 77 K, the quadrupole splittings of the Fe^{2+} in M1 increased by 24.4 % and 31.1 %, whereas for Fe^{2+} in the M2 site, ΔQ increased by 9.5 % and 9.6 % for OPx with $x = 0.12$ and 0.20 , respectively [01V1] – Fig. 62. The stronger temperature variation of ΔQ for Fe^{2+} in the M1 site reflects a small separation of the lowest crystalline field states and the weak temperature dependence of that in the M2 site is an indication of the unusually larger separation of the $^5\text{T}_{2g}$ level [69S2, 86S2, 86W4, 87R1, 93V1, 01V1]. According to [87R1], in the strongly distorted M2 site the orbital levels $|d_{xy}\rangle$, $|d_{yz}\rangle$, $|d_{zx}\rangle$ are strongly splitted by the low-symmetry crystal field. The lowest crystal field level might be an orbital singlet, widely separated from the first excited level, (by $\approx 1000 \text{ cm}^{-1}$). In the more symmetric M1 site, the orbital levels are less separated ($100 \dots 200 \text{ cm}^{-1}$) giving rise to a temperature dependent population of the level and hence to a thermal variation of ΔQ . The ^5D level scheme for Fe^{2+} in the M2 site was calculated [93V1]. Using this scheme, the T -dependences of ΔQ for $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ OPx with $x = 0.05$ and 0.27 were satisfactorily described. The lattice contribution to V_{zz} has most probably the opposite sign of the valence contribution. For the Fe^{2+} in M1 site the same approach leads to the conclusion of a predominantly trigonal compression of the M1 site in OPx, yielding a negative sign of the valence contribution to V_{zz} , whereas the lattice one has probably the same sign as the valence contribution. The first orbital level splitting accounting for the spin-orbit interaction, was found to be higher ($>400 \text{ cm}^{-1}$) than suggested ($<200 \text{ cm}^{-1}$) by [87R1]. The covalency factor, α^2 , for the M2 sites is larger by ≈ 10 % as compared to the corresponding value in M1. The electronic energy level pattern and the corresponding wave functions were obtained for $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ OPx with $x = 0.12$ and 0.20 [01V1]. The energy levels diagram of Fe^{2+} at the M2 site agrees with optical absorption spectra resulting mainly from Fe^{2+} at the M2 site. There seems to be small variations of eigenvalues and eigenfunctions with different Fe^{2+} concentrations. The ligand field energy values increase with dilution of Fe^{2+} in the M2 site, which it strongly prefers. Ligand field stabilization seems to be the reason for the strong preference of Fe^{2+} for the distorted octahedral M2 site in OPx. The ΔQ values of Fe^{2+} at the M2 site show very little variation with composition – Fig. 62. We note also that the linewidths for Fe^{2+} doublets of the M1 and M2 sites increase on cooling. The increase, when decreasing T from 300 to 77 K, is by 39.2 % and 14.6 % for $x = 0.20$ sample and 38.2 % and 14.4 % for $x = 0.12$ [01V1], which is an indication for the relaxation effects found generally in dilute silicate minerals with $x \leq 0.4$ [69S2, 86S1].

The ^{57}Fe NGR spectra of FeSiO_3 (OPx), at low temperatures ($T < T_N$), were fitted with two different hyperfine magnetic fields, B_{hf} , which were assigned to Fe^{2+} in the octahedrally-coordinated M1 and M2 sites, respectively – Fig. 61. We note that the assignment of the hyperfine field by [86R1, 86W4], now accepted, was opposite to the previous one [69S2], where the larger hyperfine field was associated with larger isomer shift, δ , and quadrupole splitting, ΔQ . The different B_{hf} values – Table 10 – were attributed to large difference in the orbital momentum of Fe^{2+} in the M1 and M2 sites.

The ^{57}Fe NGR spectra of $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ OPx are more complex than those of ferrosilite. Considering the evolution of the spectra for a $x = 0.87$ sample – Fig. 61b – between 10 and 1.6 K, one can rule out the presence of relaxation effects. The spectra were analysed as a distribution of the hyperfine fields – Fig. 61c [87R1]. As a main feature of the hyperfine field distribution law, $P(B_{\text{hf}})$, one finds that there are two well separated groups with principal maxima, $B_{\text{hf}}^{\text{M1}} = 6.8 \text{ T}$ and $B_{\text{hf}}^{\text{M2}} = 31 \text{ T}$ which closely correspond to the hyperfine fields associated with the M1 and M2 sites in FeSiO_3 , respectively. The maximum of the high field group (M2) is accompanied by an important shoulder and the distribution $P(B_{\text{hf}})$ is much more extended for the M2 site than

for the M1 site. The extension of $P(B_{\text{hf}})$ at M2, as compared with the M1 site, can be explained by their local environment effects inside the ribbons and the preferential occupancy of the Mg^{2+} ions in the M1 sites [86W4, 87R1]. Considering the nearest neighbours (NN), a Fe^{2+} ion located on the M1 site is surrounded by three Fe^{2+} ions on M2 sites and by two cations on M1 sites, which can be either Mg^{2+} or Fe^{2+} . Three types of geometrical configurations with 0, 1 or 2 Mg^{2+} ions can be present. A Fe^{2+} ion located on the M2 site can have up to 3 Mg^{2+} ions as NN located on M1 sites inside a ribbon. In the second cationic environment one finds two M1 sites belonging to an adjacent ribbon. The specific neighbourhood of Fe^{2+} in M2 leads to the observed broadening of the hyperfine field distribution around the value of 31 T. In order to explain the extension of $P(B_{\text{hf}})$ at M2, [87R1] inferred that the Fermi contact term of $P(B_{\text{hf}})(\text{M2})$ is strongly reduced by the presence of Mg^{2+} ions in NN of Fe^{2+} . The reduction of $B_{\text{hf}}(\text{M2})$, when the Mg^{2+} content increases in the M1, leads to a negative sign for $B_{\text{hf}}(\text{M2})$. The sign of B_{hf} can be negative or positive depending whether the negative Fermi contact term, B_{F} , and the positive orbital term, B_{O} , is dominating. Due to the fact that B_{F} (dominant) is reduced by substitution of nonmagnetic ions, this leads to a decrease of B_{hf} . This is not obvious for the M1 site where the distribution is less extended and more symmetric. For M1, the orbital term is of the same order of magnitude as the Fermi contact term [86R1].

The temperature dependences of the ^{57}Fe hyperfine fields for M1 and M2 sites in a FeSiO_3 sample and the corresponding mean values $\langle B_{\text{hf}}(\text{M1}) \rangle$ and $\langle B_{\text{hf}}(\text{M2}) \rangle$ in $\text{Fe}_{0.87}\text{Mg}_{0.13}\text{SiO}_3$ are plotted in Fig. 63. The hyperfine fields of Fe^{2+} in the M1 sites are almost saturated at 4.2 K, whereas the B_{hf} values, at the M2 sites, seem to be not completely saturated at this temperature. This behaviour was explained by considering that the effective magnetic exchange interaction relative to Fe^{2+} in M2 sites is much smaller than that of Fe^{2+} in M1 sites, due to the different number and distances of magnetic neighbours.

An analysis of the electric field gradient (EFG) at M1 and M2 sites was performed on natural orthopyroxene $(\text{Fe}_{0.008}\text{Mg}_{0.992})_{\text{M1}}(\text{Fe}_{0.132}\text{Mg}_{0.868})_{\text{M2}}\text{Si}_2\text{O}_6$ at 78 K and 295 K [88S4]. For the M2 site, V_{zz} is positive and its direction is about parallel to the (bc) -plane with an angle of $25(3)^\circ$ to the c -axis. A value $\eta = 0.20(7)$ was determined. The data obtained for the V_{zz} tensor at the M1 site of Fe^{2+} are less accurate. V_{zz} at the M1 site may be assumed to be about parallel to the $[111]$ direction. In case of FeSiO_3 , at 5 K, it was found that the signs of V_{zz} are positive at both M1 and M2 positions [86W3]. According to [88S4], in orthoenstatite, the sign is positive for M2 at 295 K, and probably also positive for M1 at 78 K. Thus, it was assumed that the sign at M2 does not change in orthorhombic $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ system in the whole range of composition, between 4 K and 295 K. The situation is more complex for the less distorted M1 position since here, ΔQ depends critically on temperature and, moreover, in FeSiO_3 , η is larger ($\eta = 0.4$ at 4 K) than at M2.

The study of hypersthenes (enstatite-ferrosilite) $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ with $x = 0.2 \dots 0.4$ shows that at liquid-helium temperatures, the electronic spins of Fe^{2+} ions relax slowly under a situation where the spin-lattice relaxation is almost completely suppressed and the spin-spin relaxation remains the dominant process [86S1, 87S2]. The observation of slow spin-spin relaxation for Fe^{2+} systems is quite uncommon, because the spin-lattice relaxation rate usually remains fast even at very low temperatures [86S1]. Later on, [87S2] showed that in various orthopyroxenes, the magnetic relaxation of paramagnetic Fe^{2+} ions, at low temperatures, proceeds through spin-spin interaction. The orthopyroxenes appear to provide a range of lattices where slow spin-spin relaxation can be observed with or without the presence of an external magnetic field. In case of $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$, the ^{57}Fe NGR spectrum, at 4(1) K, shows the onset of magnetic ordering – Fig. 64 [92P1]. The spectrum was interpreted in terms of three sites: one with a magnetic hyperfine relaxation combined with a static quadrupole interaction and two sites with pure quadrupole interaction, the last two having similar hyperfine parameters as those obtained at 70 K. The fact that the asymmetry parameter $\eta \equiv 0$ (and consequently $\phi \equiv 0$), implies a quasi threefold symmetry around the magnetically split Fe^{2+} , with moments tilted by $12(7)^\circ$ relative to the symmetry axis. These results are similar to those mentioned above by [86S1, 87S2]. The low Fe concentration of the above sample implies that spin correlations must extend over unit-cell dimensions ($\approx 5\text{\AA}$).

The ^{57}Fe NGR method was used to study also the iron distribution in M1 and M2 sites, their valence states, local geometry and chemical bonding of the coordination polyhedra of iron in the crystal structure [67E2, 68V1, 69H1, 71B1, 71B3]. As mentioned above, in $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ OPx, the Fe^{2+} ions show a rather strong preference for the more distorted M2 site [67E2, 68V1, 69S2]. This behaviour is in agreement with an X-ray diffraction study of $\text{Mg}_{0.93}\text{Fe}_{1.07}\text{Si}_2\text{O}_6$ orthopyroxene from a metamorphic rock which shows that Mg^{2+} and Fe^{2+} are ordered, Fe^{2+} preferring the M2 site. Generally, Fe^{2+} site occupation shows a high degree of ordering in orthopyroxenes. Heat treatment of the sample with $x = 0.532$, at 1000°C yields considerable Mg-Fe disorder [67E2].

A comparative analysis of the Fe-Mg distribution determined by X-ray diffraction and ^{57}Fe NGR method over the M1 and M2 octahedral sites in natural orthopyroxenes was performed [92S5]. The results obtained by the two methods are in good agreement for Fe/Mg intermediate compositions, provided that ^{57}Fe NGR data were thickness corrected. For Fe-poor and Al-rich samples, the results diverge, XRD gives a more ordered Fe/Mg distribution than ^{57}Fe NGR data with up to 0.05 more Fe atoms per formula unit in the M2 position. The thickness effect on ^{57}Fe NGR data in ordered orthopyroxenes cause considerable distortion of the spectra resulting in an underestimate of the degree of ordering. The Fe distribution obtained by ^{57}Fe NGR data can be corrected by extrapolation to zero thickness.

The ^{57}Fe NGR study on $\text{Fe}_{0.55}\text{Mg}_{0.45}\text{SiO}_3$ shows that after electron irradiation with 2 MeV, in addition to the two doublets characteristic for unirradiated sample, a third doublet was observed with $\delta = 0.91$ mm/s, $\Delta Q = 2.19$ mm/s, at the expense of Fe^{2+} in M2 site [80S2]. The third doublet has been found to disappear exponentially with the time that has elapsed after the end of the irradiation. Similar results were obtained in $\text{Fe}_{0.88}\text{Mg}_{0.12}\text{SiO}_3$ orthopyroxene [80S2]. The $\text{Fe}_{0.14}\text{Mg}_{0.86}\text{SiO}_3$ sample implanted with 70 keV ^{57}Fe ions was also studied by ^{57}Fe NGR [86S2]. The dose of implants was $2 \cdot 10^{16}$ ions/cm² resulting in the average concentration in implanted layer (about 700 Å) of about 3 at %. The samples were annealed for 3 h in vacuum in steps of 100°C up to 1000°C. Only 30 % of implanted ^{57}Fe ions substitute, during the implantation, the Mg cations. At elevated temperatures, a part of Fe ions is again replaced by Mg. In as-implanted samples the most favorable states of Fe are the paramagnetic precipitations. In the 500 to 700°C temperature range, a migration of the Fe impurities within the implanted layer takes place, leading to the growing of the magnetic iron particles. Above 700°C, a reverse process begins, metallic iron dissolves in the crystal. This is joint with a long-range diffusion into the bulk. Such a fast diffusion, at rather moderate temperature, is in agreement with the quite low activation energies for (Mg,Fe) cation ordering and disordering over M1-M2 sites in pyroxenes [69V1]. The investigated samples may be compared with lunar ones where pyroxenes are one of the main constituents. The minerals are exposed to permanent iron implantation of solar wind, leading to increased abundance of some elements on the surface. In particular, the degree of iron enrichment on lunar sample surface is in rough agreement with the solar wind hypothesis of its origin [76Z1]. In lunar samples, especially in the light dust, the metallic precipitates, mainly magnetic but also paramagnetic, were found [70H1]. The analogy is limited. For example, in lunar samples, and particularly in lunar pyroxenes, Fe^{3+} as unusual valence state of iron, although expected, is virtually absent [70M3]. On contrary, in investigated specimens by [86S2], these are substantial.

The $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ **clinopyroxenes** (space group P2₁/c) were also studied by the ^{57}Fe NGR method [98A3, 00E1, 01E1]. The low-temperature ^{57}Fe NGR spectra for some CPx are plotted in Fig. 65 [01E1]. These were analysed by considering local environment effects. The magnetic ^{57}Fe NGR spectra were refined using a full hyperfine interaction Hamiltonian approach, assuming different Fe^{2+} - Mg^{2+} NNN configurations – Table 10. In case of $\text{Mg}_{0.91}\text{Fe}_{0.09}\text{SiO}_3$, the spectra at 4.2 K and 0.3 K were fitted with a superposition of two quadrupole doublets corresponding to M1 and M2 sites, respectively, and one magnetic component ascribed to the M2 site. Similar as for $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$ OPx [92P1], the existence of spin correlations was suggested to extend over unit-cell dimensions. The ΔQ values of the magnetic components and of the non-magnetic M2 components are equal within experimental errors indicating that both magnetic interactions and ordering occur at the M2 site. The different strengths of the M1 and M2 hyperfine fields can be related to different ^5D electronic level schemes, as determined from paramagnetic spectra [00E1].

The paramagnetic ^{57}Fe NGR spectra of $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ CPx consist of one doublet produced by Fe^{2+} ions at an almost regular octahedral M1 site and a second doublet at a more distorted octahedral M2 site – Fig. 66 [00E1]. The temperature dependences of the Fe^{2+} center shift, for M1 and M2 sites, in samples with $x = 1.0$ and $x = 0.19$ are plotted in Fig. 67. The δ vs T curve were fitted by an equation derived from the Debye model for the lattice vibrations: $\delta(T) = \delta_i + \delta_{\text{SOD}}(T)$ where δ_i is the intrinsic isomer shift, considered to be constant, and δ_{SOD} the second-order Doppler shift. The intrinsic isomer shift, δ_i , of M1 is slightly larger compared to δ_i of M2. At the M1 site, a small increase of δ_i is observed with increasing Fe content whereas δ_i at M2 decreases along composition – Fig. 68. The uniform expansion of the M1 octahedron by substitution of Mg^{2+} by the larger Fe^{2+} ion [98A3] results in a decrease of electron density at the Fe nucleus and hence in an increase of the δ_i . The larger distortion of the M2 octahedron with increasing Fe content causes the valence electron density to increase and δ_i to decrease. The latter effect is more prominent than the former one. The quadrupole splitting, ΔQ , of Fe^{2+} ion is mainly due to its non-spherical 3d electron shell. Distortion from octahedral site symmetry removes the threefold degeneracy of the lower t_{2g} and the twofold degeneracy of the upper e_g orbitals of the 3d⁶ (^5D)

electrons. The ΔQ values suggest that both Fe^{2+} sites have a singlet electronic ground state. The analysis of the paramagnetic spectrum of clinopyroxene with $x = 0.19$ in a field of 6 T – Fig. 66 – shows a further distortion from axial symmetry. Within the crystal-field approach, the non-axial site deformation results in two excited electronic states separated by energies Δ_1 and Δ_2 from the singlet ground state of the low-lying t_{2g} orbital. The Δ_1 and Δ_2 values were obtained by fitting ΔQ vs T curves. The Δ_1 values of M1 are not significantly affected by the composition, whereas the Δ_1 ones at M2 show a small decrease with increasing Fe content. The energy gap for the first excited state at M2 ($\approx 930 \text{ cm}^{-1}$) is approximately twice the value for M1 ($\approx 430 \text{ cm}^{-1}$). The energies of second excited states at M2 are relatively high ($\approx 2000 \text{ cm}^{-1}$). Consequently, the thermal population of these states is low. The quadrupole splitting ΔQ , at 40 K, for the M1 site increases with increasing Fe content – Fig. 68b. The geometry of the M1 site is invariant with compositional changes, whereas that of the M2 site is determined by rotations of tetrahedral chains [95C1]. The contribution of the valence term dominates as compared to the lattice contribution to ΔQ , the latter acting in opposite sense. At the more distorted M2 site, the influence of the lattice term is more important than at the more regular M1 site. This explains the observed trend as shown in Fig. 68b [00E1].

A review of the ^{57}Fe NGR studies in clinopyroxenes was presented in [03D3]. Accordingly, the enstatite-ferrosilite spectra recorded at temperatures between 0.3 K and 4.2 K are adequately described taking into account a discrete number of components corresponding to the possible next-nearest neighbour (NNN) configurations of both M1 and M2 sites. The M2 hyperfine fields are considerably higher than those for M1. For both sites the strengths of the hyperfine field depend on the NNN configuration. The M2 hyperfine fields decrease with increasing Mg content, while for M1 no clear tendency is observed.

The effect of Fe on the crystal structure of MgSiO_3 **perovskite** has been studied by ^{57}Fe NGR spectroscopy [91J1, 92F1, 92J1, 92M2, 94F1, 97M2, 98M1, 00L2]. For $\text{Mg}_{0.90}\text{Fe}_{0.10}\text{SiO}_3$ perovskite, synthesized in a diamond-anvil cell by laser heating, it was proposed that Fe^{2+} substitutes for Si in the octahedral site [87J1, 92J1], thereby requiring some Si to be in the larger and more distorted polyhedral sites. This is contrary to X-ray diffraction data on $(\text{Mg},\text{Fe})\text{SiO}_3$ perovskite synthesized in a multianvil apparatus [90K1, 90P2]. In [92M1] was shown that the amount of Fe^{3+} in $(\text{Fe},\text{Mg})\text{SiO}_3$ perovskite can be determined unambiguously from the area difference between high and low-velocity components, but the location of Fe^{3+} in the perovskite structure is difficult to resolve due to the lack of constraint on the hyperfine parameters (δ , ΔQ). The spectra of $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ perovskites with $x = 0.05$ and 0.10 were recorded at temperatures from 30 K to 450 K [94F1]. The spectra were analysed by two methods. In the first case the spectra were fitted with two Fe^{2+} doublets and one Fe^{3+} doublet. In this analysis there were systematic deviations of computed curves as compared to experimental data. Then, the spectra were fitted with four quadrupole split doublets – Fig. 69 and Table 10 – two Fe^{2+} resulting from different local configurations, one to Fe^{3+} and one to Fe^{n+} , the latter with ΔQ and δ values intermediate between those assigned to Fe^{2+} and Fe^{3+} . The relative intensity of the Fe^{n+} doublet increases with increasing temperature, indicative of mixed-valence states that result from a thermally activated electron-delocalization process – Fig. 70. This is followed by a corresponding decrease in the intensity of cumulative Fe^{2+} and Fe^{3+} absorptions. The broad absorption was attributed to thermally activated Fe^{2+} - Fe^{3+} electron delocalization [94F2]. The hyperfine parameters of Fe^{3+} were consistent with octahedral coordination – Fig. 70. Fe^{2+} in the structure was assigned to the distorted eight- to twelvefold coordination polyhedra. According to [94F2] the electron exchange most likely occurs between face-sharing Fe^{3+} -bearing octahedra and distorted Fe^{2+} -bearing polyhedra in the perovskite structure. In [92M2, 98M1] the ^{57}Fe hyperfine parameters in $\text{Fe}_{0.05}\text{Mg}_{0.95}\text{SiO}_3$ perovskite were also analyzed. A model with a quadrupole splitting distribution for Fe^{2+} and Lorentzian line shapes for Fe^{3+} and Fe^{n+} was used [98M1]. The calculated average valence in rapid electron exchange that occurs between Fe^{2+} and Fe^{3+} from hyperfine parameters was 2.50(7). The presence of two Fe^{2+} doublets in the ^{57}Fe NGR spectra may arise from differences in the next neighbour environments in the 8–12-coordinated sites [92M2, 94F1, 97M2]. The site occupancy of Fe^{3+} is less clear. Some studies suggest that Fe^{3+} may occupy the octahedral sites or both cation sites in silicate perovskite according to coupled substitutions: $^{[6]}\text{Fe}^{3+} + ^{[8-12]}\text{Fe}^{3+} \rightarrow ^{[8-12]}\text{Mg}^{2+} + ^{[6]}\text{Si}^{4+}$ [91H1, 92M2, 94F1, 98M1]. In [95K1] the ability of different cations to substitute into the two sites of perovskite structure was evaluated based on the difference in size between the sites and ionic radius. The presence of Fe^{2+} for 8–12-coordinated sites was explained by the similarity in size. According to their calculation, Fe^{3+} is 13% too large for the octahedral site but only 5% too small for the 8–12-coordinated site, implying that Fe^{3+} should be more stable in the 8–12-coordinated site, based on size consideration alone. There are also other factors, which stabilize Fe^{3+} in octahedral site, this being sensitive to changes in p , T , oxygen

fugacity and/or composition. Thus, in case of samples prepared at minimum oxygen fugacity, f_{O_2} , stability limit, Fe^{3+} occupies only octahedral sites, while for higher f_{O_2} -values, Fe^{3+} appears to occupy both sites in the perovskite structure [92M2, 98M1]. The electronic environment of the Fe nuclei in $Fe_xMg_{1-x}SiO_3$ perovskites with $x = 0.05$ and 0.1 have been studied up to 120 GPa and 75 GPa, respectively, at RT, by using ^{57}Fe NGR method [05J1]. The results were explained in the framework of a “three-doublet” model, which assumes two Fe^{2+} -like sites and one Fe^{3+} -like site that were distinguishable by the hyperfine fields at the location of the Fe nuclei. At low pressures, $Fe^{3+}/\Sigma Fe \cong 0.40$ for both samples. At pressures extending into lowermost mantle the fraction of Fe^{3+} remains essentially unchanged, indicating that pressure alone does not alter the valence states of iron. The quadrupole splittings of all Fe sites first increase with increasing pressure, which suggest an increasingly distorted (noncubic) local iron environment. At $p > 40$ GPa ($x = 0.1$) and $p > 80$ GPa ($x = 0.05$), the quadrupole splittings are relatively constant, suggesting an increasing resistance of the lattice against further distortion. Around $p = 70$ GPa, a change in the volume dependence of the isomer shift could be indicative of the endpoint of a continuous transition of Fe^{3+} from high-spin to low spin state [05J1].

The temperature dependence of the center shifts in $Fe_{0.05}Mg_{0.95}SiO_3$ perovskites were fitted considering the Debye model, with characteristic lattice temperatures $\Theta_M(Fe^{2+}) = 365(52)$ K and $\Theta_M(Fe^{3+}) = 476(96)$ K [98M1].

CaFe_xMg_{1-x}Si₂O₆

The $CaFe_xMg_{1-x}Si_2O_6$ silicates were studied both for compositions rich in hedenbergite end member, as well as the diopside rich side. In the first part we analyse the data obtained for samples having high iron content and then the diopside side.

In ideal hedenbergite, $CaFe^{2+}Si_2O_6$, Ca^{2+} cations occupy the strongly deformed M2 polyhedra with eightfold O atom coordination, whereas the more regular octahedral M1 sites contain Fe^{2+} . In principle, hedenbergite should give rise to a ^{57}Fe spectrum with a single well-resolved quadrupole doublet, at temperatures $T > T_N$ [84A1, 86S3, 00R1, 00T1]. Since naturally occurring hedenbergite is almost never ideal in composition, fluctuations in the chemical environment of the ^{57}Fe probes and/or the presence of ferric ions will produce additional subspectra. Consequently, the spectra of natural samples were decomposed into several quadrupole doublets, Fe^{2+} at M1 sites [71B1, 84A1, 86S3, 00R1, 00T1], Fe^{2+} at M2 sites [71B1, 73D3] and Fe^{3+} at M1 sites [82D3, 84A1, 00R1]. For example, the natural diopside – hedenbergite series having C2/c-type structure show spectra containing a single doublet assigned to Fe^{2+} in the M1 position [71B1]. For a sample containing actinolite present as impurity, in addition to Fe^{2+} in M1 site, two small doublets were attributed to Fe^{2+} in M2 and, in addition, M1 positions in actinolite. The effects of the non-uniform NNN configurations were more recently considered in analyzing the spectra [03E1, 03E2]. As already shown in case of aluminous orthopyroxenes [83S4] or synthetic P2₁/c Mg-Fe clinopyroxenes, NNN interactions play an important role in affecting the ^{57}Fe hyperfine parameters. In [03E1, 03E2] the spectra of two hedenbergites^{10, 11)} (for compositions see footnotes of Table 3) were analysed. The ^{57}Fe NGR spectra were interpreted in terms of two model-independent quadrupole-splitting distributions (QSD), one for Fe^{2+} and one for Fe^{3+} . Results of the fitting procedure for sample¹¹⁾, at $T > T_N$, are given in Fig. 71a. The spectral contribution of Fe^{3+} is small; for hedenbergite¹⁰⁾ (for footnote see Table 10) this is 0.02 and hence its parameters are ill defined. The Fe^{2+} QSD profile for hedenbergite¹¹⁾ shows a predominant contribution and one or two additional minor satellite peaks. The origin of these satellites was attributed to different configurations of the more distant M1 neighbours. The maximum probability values for ΔQ are listed in Table 10. The Fe^{3+} component was suggested to be partly due to an oxide layer covering the hedenbergite grains and partly to Fe^{3+} at the octahedral site in the hedenbergite structure.

The effects of an external field on the ^{57}Fe NGR spectra were analysed [86S3, 03E1, 03E2]. In [86S3] two hedenbergites were studied at $4.2 \leq T \leq 295$ K in applied fields of 4.5...7 T. For the sample with composition $Ca_{0.97}Mn_{0.17}Fe_{0.79}Mg_{0.06}Al_{0.01}Si_{2.00}O_{6.01}$, a negative sign for V_{zz} and an asymmetry parameter $\eta \cong 0.6$ was obtained at 295 K. For $Ca_{0.96}Mn_{0.02}Fe_{0.66}Mg_{0.31}Al_{0.06}Si_{1.99}O_{6.02}$, at 295 K a negative V_{zz} and $\eta = 1.0$, and at 78 K a positive V_{zz} and $\eta = 0.3$ were found. For the former sample, the largest value for the field reduction occurs along the principal axis of EFG, namely Z and for latter one along the Y -axis. The ^{57}Fe NGR spectra for hedenbergites^{10, 11)} in a field of $\mu_0 H = 6$ T are plotted in Fig. 71b for $80 \leq T \leq 290$ K. For Fe^{2+} species in a non-cubic environment, an anisotropic field reduction due to spin polarization [76V1] was considered. The field reductions $H \parallel X$, $H \parallel Y$, $H \parallel Z$ are listed in Table 10. The principal components of the EFG V_{zz} for sample¹¹⁾ was determined to be positive and the asymmetry parameter was $0.70 \leq \eta \leq 0.80$. Considering the discrepancy between the calculated

and the experimental applied field ^{57}Fe NGR spectra, the results for hedenbergite¹⁰⁾ were assumed to be somewhat less accurate. The ^{57}Fe NGR study on small single crystals of $\text{CaFe}_{0.54}\text{Mg}_{0.46}\text{Si}_2\text{O}_6$ allowed the determination of the electric field gradient and mean square displacement tensors for Fe^{2+} at the M1 site [00T1]. Each tensor has in common, as required by crystal symmetry, the twofold axis of the monoclinic unit cell, but the principal directions of the two tensors, in the perpendicular plane are non-coincident. A negative V_{zz} value was obtained. The asymmetry parameter was $\eta = 0.97$. As shown above, the data obtained by different authors are to some extent in disagreement. The sign of V_{zz} was reported to be either positive or negative and a reversal of that sign at some temperature is possible. According to [03E1], when $V_{zz} > 0$, the largest value of the field reduction is that along the Y -axis of the principal-axes frame of the EFG, while if $V_{zz} < 0$, $H \parallel Z$ seems to be the highest. The reason for this behaviour is not clear, but the composition can play an important role.

The temperature dependence of the center shift, $\delta(T)$, was analysed considering contributions arising from the s -electron density at the ^{57}Fe nucleus (δ) which is weakly T -dependent [72P1] and of second-order Doppler shift (δ_{SOD}) which is significantly temperature dependent. For temperatures $T < 600$ K values of the lattice temperatures $\Theta_M = 330(20)$ K and $370(20)$ K were determined for sample¹⁰⁾ and ¹¹⁾, respectively. At $T > 600$ K, the determined Θ_M values were $420(20)$ K and $490(20)$ K, respectively [03E1]. The temperature dependences of the quadrupole splittings, ΔQ – Fig. 71c, have been analysed by using crystal field theory. Two approaches have been applied to evaluate the crystal field. In both cases the crystal field Hamiltonian included the spin-orbit coupling. The first model emanates from the approximate and simplified symmetry of the ferrous sites, whereas the second takes into account the real symmetry of the sites, thus leading to a point charge calculation. The temperature dependences of the ΔQ and η could be satisfactorily described using the latter approach (solid lines in Fig. 71c) [03E1].

The ^{57}Fe NGR spectra of hedenbergites were studied also in the low-temperature range in order to obtain information on their magnetic behavior. These properties are determined by crystal structure and composition. For a $C2/c$ -type structure, the $\text{Fe}^{2+}(\text{M1})$ octahedra and $\text{Ca}^{2+}(\text{M2})$ polyhedra share edges to form laterally continuous sheets that lie parallel to the c -axis. The sheets include zig-zag chains of M1 sites sandwiched between two linear chains of M2 sites and alternate with SiO_4 tetrahedral layers along $a \sin \beta$ [80C1]. The linear chains of distorted M2 polyhedra are completely occupied by diamagnetic Ca^{2+} ions. The Fe^{2+} ions are located in zig-zag chains of more regular M1 octahedra which are “diluted” by diamagnetic ions (mostly Mg^{2+}). The magnetic studies [85C2, 86W3, 88G2, 88R1, 99H1, 03E2] suggested that a ferromagnetic coupling exists between the Fe species within a particular M1 chain and the long-range magnetic ordering between M1 chains is antiferromagnetic. The positive Θ values show that the ferromagnetic intrachain interaction, which occurs via Fe-O-Fe superexchange, is stronger than the antiferromagnetic interchain interaction, the latter occurring via intervening SiO_4 groups [85C2, 88R1, 97B1]. In [99H1] was suggested that for a strongly diluted sample (40% Mg), the interchain antiferromagnetic coupling might vanish.

Some controversy exists concerning the Fe^{2+} spin direction. According [88G2], the space group $C2/c$ allows for two different orientations of spins, i.e. perpendicular or parallel to the b -axis; which is the only (twofold) symmetry axis of the M1 sites. On the basis of neutron diffractions studies concluded that the magnetic moments are lying in the (ac) -plane (i.e. \perp to b -axis) making an angle of 45° with a -axis [86W3]. In [97B1] was suggested from susceptibility measurements on a s.c. that the spins lie in the (ac) -plane, while in [99H1] was reported that the Fe^{2+} spin direction is in the (ab) -plane, on the basis of susceptibility measurements.

The magnetically split ^{57}Fe NGR spectra were analysed for a synthetic [85C2] and natural [86S3, 87S3] hedenbergite. They obtained single ^{57}Fe hyperfine fields, B_{hf} , of 18.8 T and 17.5 T, respectively, at 4.2 K. Angles of 135° [85C2] and 45° [86W3] between c -axis and spins were reported. According to [85C2] the hyperfine field makes an angle of $74(5)^\circ$ with the principal Z -axis of the EFG: Since this is close to perpendicular to the Z -axis of the EFG, the presence of an orbital ground state with hard axis anisotropy is suggested. The positive small field asymmetry parameter indicates an effective tetragonal distortion of the M1 site from cubic symmetry. According to [85C2] the hard axis may correspond to the O1A2-O1B2 diagonal of the octahedron which is perpendicular to b . For a natural hedenbergite it was found that η depends critically on temperature between 5 K and 445 K [86S3, 87S3]. A reversal of the sign of V_{zz} at about 295 K, from positive at lower temperatures to negative at higher temperatures, was shown. The assumption of split d_{xz} , d_{yz} doublets, as the ground state of Fe^{2+} , was suggested. At 4.2 K, it was shown that M is collinear to B_{hf} , i.e. roughly perpendicular to the Z -axis of the EFG.

For a natural magnesian hedenbergite with composition $\text{Ca}_{0.96}\text{Fe}_{0.82}\text{Mg}_{0.19}\text{Mn}_{0.02}\text{Si}_2\text{O}_6$, a discrete distribution of six hyperfine field components, which were related to the possible Fe^{2+} - Mg^{2+} NN configurations surrounding the Fe^{2+} ion was accounted for in order to describe the low-temperature ^{57}Fe NGR spectra [88R1]. The six patterns are the results of the probabilities of random distribution of Mg^{2+} and Fe^{2+} in the zig-zag chains of M1 sites which include second cationic neighbourhood. In [99H1] magnetically split ^{57}Fe NGR spectra were measured for $\text{CaFe}_{1-x}\text{Mg}_x\text{Si}_2\text{O}_6$ ($x = 0 \dots 0.5$) at 7 K. For samples with $x > 0.2$, the coexistence of a paramagnetic and magnetic ordered component was reported, the lattice showing a distribution of B_{hf} values, which reflects, according to the authors, the coexistence of paramagnetic and ferromagnetic clusters. In [97B1] was claimed that the ^{57}Fe NGR spectra for magnesian-hedenbergite, collected at 5 K, exhibit relaxation phenomena. Low-temperature ^{57}Fe NGR spectra for hedenbergite¹⁰⁾ (for footnote see Table 10) are plotted in Fig. 72a [03E2]. The hyperfine fields, B_{hf} , were refined using a superposition of two model-independent distributions, one for the dominant Fe^{2+} component and one for the weak Fe^{3+} contribution, the positions of the eight absorptions and their intensities for each composing elemental subspectrum being determined by diagonalization of the hyperfine interaction Hamiltonian. The maximum probability saturation hyperfine fields for Fe^{2+} were found to be 18 T and 18.5 T for samples¹⁰⁾ and ¹¹⁾, respectively. For both hedenbergites, the Fe^{2+} asymmetry parameter η of the electric field gradient is quite large $\eta = 0.7 \dots 0.8$, regardless of temperature. The orientation of the Fe^{2+} hyperfine field in the EFG principal axis frame is ($\theta \cong 85^\circ$, $\varphi = 38^\circ$) and is not affected by the temperature. The polar angle $\theta = 85(5)^\circ$ is close to $74(5)^\circ$ reported by [85C2]. Hence, the direction of the field is nearly perpendicular to the EFG's principal component, which likely lies along the c -axis. This remark is in reasonable agreement with [85C2]. A weak component (4%), with a hyperfine field $B_{\text{hf}} = 54.7(5)$ T was found. The Fe^{3+} ions were attributed to M1 sites as in case of the paramagnetic spectra [03E1]. The probability profiles of B_{hf} – Fig. 72a – do not exhibit any fine structure and hence provide no indication whatsoever that discrete hyperfine components are present or can be resolved. Thus, these profiles are indicative that a quasi-continuous distribution of hyperfine fields governs the line shape of ^{57}Fe NGR spectra.

According to [03D3] the spectra of the hedenbergite sample, at temperatures between 4.2 K and $T_N \cong 33$ K, are best described by a model-independent hyperfine-field distribution (HFD), especially those at the higher temperatures. The distribution at low temperatures is narrow and close to symmetric. The average hyperfine field at 4.2 K ($B_{\text{hf}} \cong 18$ T) is higher than the fields at the M1 sites in Fs-En samples ($B_{\text{hf}} \cong 8.3$ T for ferrosilite end member). Analysing the literature it was concluded that some of the derived hyperfine parameters disagree and the discrepancies were attributed due to different fitting procedures. The temperature dependence of the hyperfine field suggests a rectangular 2D-Ising type behaviour.

The ^{57}Fe NGR spectrum of hedenbergite¹⁰⁾ in a field of 6 T at $T = 4.2$ K is plotted in Fig. 73 [03E2]. An obvious difference with respect to the zero field spectrum is the appearance of shoulders outward the outer absorption lines. Apart from the appearance of the shoulders, the line shapes are similar to those obtained in zero field spectrum. This implies that the applied field does not disrupt the magnetic ordered pattern, as previously reported for other samples [85C2, 88R1, 97B1] and consequently the magnetic anisotropy is quite strong. The spectra in an external field were described by a two-parameter distribution model, taking into account distributions for the magnitude and the orientation of the hyperfine field with respect to the external field. The parameters obtained by fitting the spectra are listed in Table 10. The maximum probability hyperfine field $B_{\text{hf}}(\text{max})$ is 16.8(5) T for sample¹⁰⁾ and 17.3(5) T for hedenbergite¹¹⁾. Both values are lower than those obtained from zero field ^{57}Fe NGR spectra. This lowering could imply that the external field induces an additional contribution to the hyperfine field or that it slightly affects the 3d wave functions of the probe Fe^{2+} cations [03E2].

The temperature dependences of the hyperfine fields (for $H = 0$) are shown in Fig. 72b. A point charge approach and a two-dimensional rectangular Ising model were used to analyze the experimental data [03E2]. The two-dimensional rectangular Ising model, considering that the interchain and intrachain magnetic exchange interactions are of similar magnitude, describe better the experimental $B_{\text{hf}}(T)$ values.

The ^{57}Fe nuclear forward scattering (NFS) of synchrotron radiation, and the use of diamond anvils with helium as pressure medium, allowed to study the electronic state of Fe^{2+} in the chain silicate hedenbergite, $\text{CaFeSi}_2\text{O}_6$, up to $p = 68$ GPa [99Z1]. The ΔQ values, determined from the time spectra at low pressures, are in good agreement with the linear dependence of δ and ΔQ on pressure for $0 \leq p \leq 4$ GPa and show a discontinuity at 4.6 GPa. The time spectra, at 53.3 GPa and 68 GPa, revealed a significant difference in their shapes. By fitting the RT spectra using an Hamiltonian for the general case of mixed electrostatic and magnetic interactions, $B_{\text{hf}} =$

6.6(5) T, $\Delta Q = 1.2(2)$ mm/s, $\eta = 0.6(2)$ and the angle θ between B_{hf} and V_{zz} of $\theta = 30(10)^\circ$ were obtained. The angle φ between the projection of B_{eff} on the XY -plane was constrained to be $\varphi = 0$. These data revealed a reversible phase transition from the paramagnetic phase at low pressure to the magnetic phase at high pressure. If this interpretation is correct, T_N of hedenbergite depends critically on pressure [99Z1]. The ^{57}Fe NGR spectra of $\text{CaFe}_x\text{Mg}_{1-x}\text{Si}_2\text{O}_6$ silicates with $0.6 \leq x \leq 1.0$ were studied at ambient temperature (293 K) and pressures up to 10 GPa [92Z1]. The spectra consist of a single doublet which was assigned to Fe^{2+} at the octahedrally-coordinated M1 sites. The δ and ΔQ values decrease with increasing pressure. They exhibit a discontinuity between 3.8 and 4.3 GPa, as in case of $\text{CaFeSi}_2\text{O}_6$, indicating a reversible phase transition of first order – Fig. 74. At constant pressure, the values of δ are independent of the Fe/Mg ratio, whereas ΔQ values decrease with decreasing Fe/Mg ratio. A change in δ with pressure below 4 GPa results mainly from variations of Fe^{2+} valence orbitals. The variation of ΔQ is due to changes in the distribution of the $3d^6$ electron over the d_{xy} , d_{xz} , d_{yz} levels related to a change in pseudoaxial distortion. The variations of δ and ΔQ , above 4 GPa, were attributed to changes in overlap between Fe^{2+} and ligand orbitals. The decrease in ΔQ as function of Fe/Mg ratio, at constant pressure, results mainly from the change in geometry of the M1 octahedra occupied by Fe^{2+} . In [97Z1] was shown that neither any significant discontinuity in the unit cell, nor any abrupt change in bond lengths angle was observed in X-ray diffraction studies as function of pressure. The discontinuity in hyperfine parameters of Fe^{2+} coincides with the crossover of the two longest bond lengths in both the CaO_{6+2} and FeO_6 polyhedra at about 4 GPa. There is also a change in the compressibilities of the two shortest bond lengths in the SiO_4 tetrahedron at about 4 GPa.

The Fe-containing diopsides have been also studied by the ^{57}Fe NGR method [71B1, 71H1, 71W2, 82D3, 83N1, 89S4, 89S5, 96D1, 02D1, 03D1]. In [71B1] the ^{57}Fe NGR spectra for a natural diopside having composition $\text{Ca}_{1.01}\text{Fe}_{0.05}\text{Mg}_{0.94}\text{Si}_2\text{O}_6$ were reported. They observed, at 295 K, a single Fe^{2+} quadrupole doublet with $\delta = 1.17$ mm/s and $\Delta Q = 1.89$ mm/s. For a synthetic sample with Fe content $x = 0.02$, at 295 K, a ferrous quadrupole doublet was similarly found with $\delta = 1.17$ mm/s and $\Delta Q = 1.85$ mm/s [82B3]. In both studies the doublet was attributed to Fe^{2+} at the M1 site. As already mentioned, in magnesian hedenbergite $\text{Ca}_{0.95}\text{Mg}_{0.20}\text{Fe}_{0.85}\text{Si}_2\text{O}_6$ two ferrous doublets were ascribed to $\text{Fe}^{2+}(\text{M1})$ and $\text{Fe}^{2+}(\text{M2})$, the latter with an abundance of 0.07 apfu [71B1]. In [71W2] two Ca-deficient Di – Hd were examined. Two doublets were found, in agreement with [71B1]. The shortcoming in the fit procedure in the above reports was attributed to the fact that both Fe sites are actually composed of several distinct components arising from non-uniform chemical environments of the probe nuclei [73B1]. Ferrian diopsides have been analysed by the ^{57}Fe NGR method [71H1, 83N1, 89S4, 89S5, 96D1, 98R1] as well as Fe-aluminum diopsides, formerly called “fassaite” [77M2, 83S4, 97K1, 02D1]. The model-independent quadrupole splitting distribution (QSD) procedure [94V2] was used particularly for the latter species. Three natural diopsides with iron content 0.01, 0.06 and 0.3 apfu were studied by [03D1]. A superposition of two Fe^{2+} doublets (at M1 and M2) and one weak Fe^{3+} doublet provided adequate analysis of the ^{57}Fe NGR spectra. The fraction of Fe^{3+} seems to increase when increasing the total iron content. The coordination of the ferric ions could not be inferred, but the observed line broadening of the Fe^{3+} doublet indicates that they possibly substitute at both M1 and M2. The Fe^{2+} ions have strong preference for the M1 site. For the diopside with $x = 0.3$, a spectrum at 80 K, in an applied field $\mu_0 H = 6$ T, was recorded to determine the signs and the asymmetry parameters of the EFG. The signs are all negative and the asymmetry is large ($\eta \approx 0.9$), implying that an additional distortion is superimposed on the trigonal compression of the polyhedra. An anisotropic field reduction was shown – Table 10. The reductions are due to spin polarization of the probe nuclei's s-electron cloud by external field and are proportional to the corresponding components of the magnetic susceptibility tensor [67J1]. The center shifts, δ , for the two Fe^{2+} sites are equal within experimental error limits. From their temperature variations, values of lattice temperature $\Theta_M = 350(10)$ K were determined for both sites. [03D1]. The temperature variations of the ferrous quadrupole splitting show the importance of spin-orbit coupling. The $\Delta Q(T)$ values were calculated from thermal populations of the 25 electronic levels within the ^5D term. The energies of these levels were determined by diagonalization of the complete crystal-field Hamiltonian. The point charge approach which takes into account the real point symmetry of the M1 and M2 lattice sites and the effective charges of the various cations and anions, in the diopside unit cell, were considered. The lattice contribution to the EFG and the spin-orbit coupling were included. This type of analysis describes the data for M1 sites. The analyses for M2 sites were less successful [03D1]. In [02D1] $(\text{Ca}_{0.98}\text{Na}_{0.03})(\text{Mg}_{0.68}\text{Fe}_{0.07}^{2+}\text{Fe}_{0.03}^{3+}\text{Al}_{0.16}\text{Ti}_{0.04})(\text{Si}_{1.77}\text{Al}_{0.23})\text{O}_6$ diopside was studied by the ^{57}Fe NGR method. The presence of both Fe^{2+} and Fe^{3+} ions was found. Both exhibit a broad quadrupole-splitting distribution, indicating widely fluctuating chemical and structural environments for the probe Fe nuclei. The numerical analysis based

upon a shape independent distribution fitting, using superposition of the ferrous and ferric QSD with single, but different center shift values for each of the two iron valence states were found to describe adequately the experimental line shapes – Fig. 75. The two maxima in the ferric $P(\Delta Q)$ distributions might indicate the presence of Fe^{3+} in two different M1 sites, related to the Al- for Si substitution and that additional broadening of the individual components results from different cation configurations in the next-nearest neighbour shells. Considerations to relate the Fe^{2+} quadrupole-splitting distributions to structural properties were not attempted [02D1].

In [69V1] the pressure effect on the distribution of Fe^{2+} between M1 and M2 in orthopyroxenes in the range of 0.72 to 1.82 GPa was studied. Fe^{2+} was found to be ordered in M1 at elevated pressures. The polyhedral volume of M1 and M2 in diopside were compressed under high pressure (≈ 5.3 GPa) [81L1, 96H2] resulting in congruent behavior of M1 and M2, which subsequently influenced the distribution of Fe^{2+} between M1 and M2. In [85D2] was shown that increasing ordering of Fe^{2+} in M2 increased the unit-cell volume and vice versa. This implies that a disorder tendency at elevated pressure that resulted from a decrease of unit-cell volume has a greater effect on the distorted, bigger M2 than on M1 sites [94H2]. Therefore, like the temperature effect that resulted in more disorder of Fe^{2+} - Mg^{2+} partitioning between M1 and M2 sites, the effective increases in the pressure will make the M2 site more regular and closer to M1. This will thereby cause more Fe^{2+} to occupy M1, provided that the thermal effect is not significant. The study of temperature induced partitioning of Fe^{2+} - Mg^{2+} between M1 and M2 [69V1] showed that the Fe^{2+} content on the M1 site in $\text{Ca}_{0.04}\text{Na}_{0.05}\text{Mg}_{1.968}\text{Fe}^{3+}_{0.013}\text{Fe}^{2+}_{0.13}\text{Al}_{0.008}\text{Si}_{1.932}\text{O}_6$ should be less than 35% of total Fe^{2+} at its metamorphic temperature, if no pressure effect was present. The high pressure (4.0...6.0 GPa) induced more Fe^{2+} occupancy of the M1 site. This feature is different from the low p - T orthopyroxenes in which Fe^{2+} generally favored M2 sites [70C1, 78A2, 89D2]. In [05L1] was evidenced by the ^{57}Fe NGR method that Fe^{2+} in clinopyroxenes with low Na+Ca contents in their M2 sites shows pressure induced occupation in the M1 site.

The ^{57}Fe NGR method was used to analyse the hyperfine parameters in $\text{CaMg}_{1-x}\text{Fe}^{3+}_x\{\text{Si}_{2-x}\text{Fe}^{3+}_x\}\text{O}_6$ ferridiopsides [67D1, 70D1, 71H1, 73D3, 96D1, 98R1]. In [71H1] the spectra were decomposed in two prominent Fe^{3+} components and a rather weak, but not fitted Fe^{2+} component. The authors assigned the Fe^{2+} doublet to the octahedral M1 site and the two Fe^{3+} doublets to the M1 and the tetrahedral sites, respectively. In [96D1] the analysis of synthetic ferridiopsides in the temperature range 80...300 K was reported. The spectra were fitted with three Lorentzian shaped quadrupole doublets which were assigned to Fe^{2+} on M1, Fe^{3+} on M1 and on the tetrahedral sites. The same decomposition of the spectra was performed by [98R1]. A markedly high amount of Fe^{2+} was found in diopside-rich samples synthesized at high temperature, which decreases with both decreasing synthesis temperature and increasing ferri-Tschermak's component. The isomer shift of $^{44}\text{Fe}^{3+}$ increases distinctly with the Fs component as a consequence of increasing mean T-O bond length – Fig. 76. The isomer shifts of Fe^{3+} and Fe^{2+} on octahedral sites are rather insensitive to changes in composition, in contrast to quadrupole splitting of all three components. The negative correlation of quadrupole splitting versus Fs content of Fe^{3+} on the tetrahedral and on the octahedral sites – Fig. 76 – can be interpreted as decreasing Fe polyhedral distortion as the Fs content is increased, whereas the increase of Fe^{2+} quadrupole splitting is a sign of increasing distortion of the Fe^{2+}O_6 octahedra in Fe^{3+} rich diopside [98R1].

The assignment of the doublets and the interpretation of area ratios were analyzed in the $\text{CaFe}_2\text{SiO}_6 - \text{FeSiO}_3$ system with the hypothesis that a distinct doublet arises from each of the four different types of NNN configurations of the iron cations in the site M1 [73D3]. The four types arise from random distribution of calcium and iron in M2 site. The M1 site, because of its lowest distortion, is very sensitive to small changes in its environment, hence there are several doublets for the different NNN configurations. Variation in quadrupole splitting of the distorted M2 site, though less pronounced than that of M1, probably represents larger structure variations, because of high distortion, quadrupole splitting is less sensitive to small changes.

For ^{57}Fe NGR study of hedenbergite – ferrosilite series see also [67D1, 70D1].

$\text{CaMgSi}_2\text{O}_6 - \alpha\text{-Fe}_2\text{O}_3$

The relative high Fe concentrations in the unfired mixtures of $\text{CaMgSi}_2\text{O}_6$ (diopside) and $\alpha\text{-Fe}_2\text{O}_3$ (hematite) suggest that the obtained product, after sintering at 1170°C, consists of a mixture of ferridiopside and hematite, the contribution of the latter becoming more and more important as the starting Fe content increases. The limit solubility of $\alpha\text{-Fe}_2\text{O}_3$ in $\text{CaMgSi}_2\text{O}_6$ has been analysed [69H3]. In [91V1] the phases formed by synthesizing ferric diopsides with iron contents exceeding the solubility limit were studied by the ^{57}Fe NGR method.

CaMgSi₂O₆ – CaFeSi₂O₆ – CaMnSi₂O₆

The analysis of ⁵⁷Fe NGR spectra of the natural diopside – hedenbergite – johannsenite join shows the presence of Fe²⁺ and Fe³⁺ [99C3]. The subspectrum with higher quadrupole splitting has been attributed to Fe²⁺ in the octahedral site M1 and secondly to Fe³⁺ on M1 or to another iron phase. The quadrupole splittings for Fe²⁺ are distributed in a narrow range of values. The distortion of the M1 octahedron was correlated with the ratio Mn/Fe and the quadrupole splitting of Fe³⁺.

In natural hedenbergite, Hd₈₄Di₁₂Jo₄, the ⁵⁷Fe NGR spectra at 77 K and RT were fitted with one doublet [97B1]. This is typical for Fe²⁺ in octahedral oxygen environment, i.e. the M1 site – Table 10. At 5 K, a magnetic six-line spectrum of Fe²⁺ is fully developed and the parameters determined by fitting the experimental data are typical for Fe²⁺ in the magnetically ordered state. The onset of magnetic ordering is observed below 27.5 K.

CaMgSi₂O₆ – CaFeAlSiO₆

In the CaMgSi₂O₆–CaFeAlSiO₆ system, different points of view were expressed concerning the effect of pressure on the ordering of ferric iron and aluminium between octahedral (M1) and tetrahedral (T) sites in the clinopyroxene structure. According to [73O3], the content of ferric iron on octahedral site is increased and that of the tetrahedral site is decreased at 2 GPa and 800°C as compared to the site occupancy of ferric iron in clinopyroxene crystallized at atmospheric pressure. Later on, [97A1] has shown by the ⁵⁷Fe NGR method that the occupancy ratio Fe³⁺(M1)/Fe³⁺(T) is 92/8 to 85/15 – Table 10. This ratio does not depend on pressure and is slightly dependent on temperature and sample formation. We note that in [81K2] was suggested that the Fe³⁺ distribution in M1 and T sites depend on temperature.

CaFe³⁺Ga³⁺SiO₆ – CaGa³⁺SiO₆

In 0.9CaFe³⁺Ga³⁺SiO₆–CaGa³⁺SiO₆ pyroxene, the Fe³⁺(M1)/Fe³⁺(T) ratio determined by ⁵⁷Fe NGR is 65/35 [97A1]. For CaSc³⁺AlSiO₆, CaFe³⁺AlSiO₆, 0.9CaFe³⁺GaSiO₆ – 0.10CaGa₂Si₂O₆ and CaAl₂SiO₆ clinopyroxenes, the site occupancies of Sc³⁺, Fe³⁺, Ga³⁺ and Al³⁺ ions in the M1 and T sites were correlated with the ionic radius ratio between larger M³⁺ cations and the smaller ones. If the ionic radius of the larger M³⁺ cation is R_L and of the smaller one is R_S in the M1 site, then the correlation between the occupancy of larger M³⁺ cation (y) and the ratio $x = R_L/R_S$ in the M1 site is given by $y = -249.46x^2 + 710.27x - 405.69$. This relation has been proposed to estimate the site populations of M³⁺ cations in the M1 and T sites [97A1].

Rhodonite

The ⁵⁷Fe NGR spectra of rhodonite¹⁶⁾ (for footnote see Table 10) were analyzed considering the presence of five doublets [75D1]. All the iron is in ferrous state. Most of iron is located in octahedrally- coordinated M1, M2 and M3 sites. The Fe²⁺ ions show a small preference for the near five-coordinated M4 site and little iron enters the seven-coordinate M5 site.

Ferrobustamite

In ferrobustamite, Ca_{0.816}Fe_{0.152}Mn_{0.032}SiO₃, the following intracrystalline exchange reaction was confirmed by intensity measurements of ⁵⁷Fe NGR spectra: Fe(M3) + Ca(M1,M2) = Fe(M1,M2) + Ca(M3) [79Y2]. At low temperatures, Fe²⁺ preferentially occupied the M3 site and secondly the M1 and M2 sites. Disorderness of cation distribution proceed as the heating temperature was raised – Fig. 77 [79Y2]. The activation energy for Fe²⁺-Ca²⁺ exchange in the M1, M2 and M3 sites is 27.61 kcal for the disordering process and 18.45 kcal for the ordering process.

Ca_{0.30}Mg_{0.74}Fe_{0.96}Si₂O₆, pigeonite

The Ca_{0.30}Mg_{0.74}Fe_{0.96}Si₂O₆ pigeonite, from Ibitira meteorite, was studied by ⁵⁷Fe NGR [91C1]. The maximum occupancy of Fe²⁺ at the M2 site, that is the maximum degree of order, can be described by (Fe_{0.70}Ca_{0.30}) at the M2 site and (Mg_{0.74}Fe_{0.26}) at the M1 site. Comparing this with the actual occupancy determined experimentally (Mg_{0.06}Fe_{0.64}Ca_{0.30}) at the M2- and (Mg_{0.68}Fe_{0.32}) at the M1-site, it was concluded that the distribution is close to the maximum degree of cation order. The experimental results yield a disordering parameter p = 0.04. According

to [71D1] the chemically homogeneous pyroxenes, shocked under controlled conditions at very high pressures, were highly disordered. The lunar pigeonites from Apollo 12 and 14 were also analyzed by ^{57}Fe NGR [72G1]. Cation order determined in two pigeonites is high, the K_D values being 0.086 and 0.030, respectively.

Aegirine, $\text{NaFeSi}_2\text{O}_6$

The synthetic and natural aegirines were studied by ^{57}Fe NGR [70O1, 88B1, 88D1, 89B1, 98D1, 04S1]. At low temperatures, both natural and synthetic samples are magnetically ordered. The resonance lines of the magnetic hyperfine spectra for natural samples are very broad. This is due to somewhat different compositions, as for example $(\text{Na}_{0.80}\text{Ca}_{0.01}\text{Mn}_{0.01})(\text{Fe}_{0.74}^{3+}\text{Ti}_{0.03}\text{Al}_{0.12}\text{Fe}_{0.07}^{2+})(\text{Si}_{1.99}\text{Al}_{0.01})\text{O}_6$, as compared with the ideal sample, and implies local environment effects [89B1]. A reasonable fit was obtained with one sextet, at 1.5 K, for a synthetic sample – Table 10. From the temperature dependences of hyperfine fields, Néel points of 8 K and 6 K were estimated for the synthetic and above mentioned natural samples, respectively [89B1]. In [88B1] was reported for a synthetic crystal that the asymmetric quadrupole doublet at 15 K is replaced by a broad six-line pattern combined with a paramagnetic peak at 12.5 K. With decreasing temperature the six-line spectrum gains intensity with narrowing linewidths over the residual paramagnetic peak, which has completely disappeared at 6.5 K. At room temperature, a doublet is present, typical for Fe^{3+} in sixfold oxygen coordination, i.e. the M1 sites. A magnetically split ^{57}Fe NGR spectrum for a synthetic aegirine was analysed at 5 K [88B1]. They obtained a hyperfine field $B_{\text{hf}} = 46.1$ T, however with a tremendous broadening of the Lorentzian lines. For a natural sample, at 2 K, three sextet components were considered with B_{hf} values in the range 42.4...46.2 T, with reasonable linewidth [88D1].

According to [03D3] the lineshape of the 4.2 K ^{57}Fe NGR spectrum of aegirine is characteristic for a broad hyperfine field distribution for the Fe^{3+} cations at M1 sites. Fitting the spectrum with a superposition of a ferrous and a ferric HFD revealed three major Fe^{3+} contributions ($\cong 28.7$, 37.6 and 4.68 T). These fields are low because the relatively high value of the reduced temperature is $T/T_N \cong 0.4$. The presence of these three distinct components is in disagreement with the NNN models.

The natural aegirine, $\text{Na}_{1.06}\text{Ca}_{0.06}\text{Mg}_{0.04}\text{Fe}_{1.01}\text{Al}_{0.06}\text{Si}_{1.91}\text{O}_6$, was studied by ^{57}Fe NGR in a field of $\mu_0 H = 6$ T [98D1]. The paramagnetic spectra were fitted with four symmetrical doublets. One ferric and two weak ferrous doublets were attributed to iron located in M1 sites [98D1]. The fourth component indicates a ferric state in tetrahedral coordination – Table 10 and Fig. 78a. The ^{57}Fe NGR spectra at 80 K and 277 K, in an applied field of $\mu_0 H = 6$ T, are plotted in Fig. 78b, c. At 80 K, only one ferric and one ferrous doublet were considered, due to the lack of a sufficient fine structure. At 277 K, the spectrum was fitted with four components. At higher temperatures the lineshape displays better resolved feature than at 80 K, consequence of the field reduction due to spin polarization. The asymmetry parameter for $\text{Fe}^{3+}(\text{M1})$ was $\eta = 0.8...1.0$ at 80 K and $\eta = 0.85$ at 277 K [98D1]. The large magnitude of the asymmetry parameter at the $\text{Fe}^{3+}(\text{M1})$ implies that the geometry of these sites is strongly deformed from axial one [98D1]. At 4.2 K, the ^{57}Fe NGR spectrum was fitted by considering two model-independent magnetic hyperfine field distributions (MHFD) – one for Fe^{3+} and one for Fe^{2+} – Fig. 78d. This means that the obtained quantities for Fe^{3+} will refer to the M1 sites, while those for Fe^{2+} will be the average values for the two M1 sites (as evidenced in the paramagnetic range). The distribution referring to Fe^{3+} is multimodal and can be described by a superposition of six Gaussian curves. The maxima centered at 2.3 T and 12.2 T were artifacts of the fitting procedure. The four remaining maxima at 19.8, 28.7, 37.6 and 46.8 T can be attributed to different NN configurations. The center shifts for the four sites show a temperature variation described by $\delta(T) = \delta_i + \delta_{\text{SOD}}(T)$, where the intrinsic isomer shift, δ_i , is weakly dependent on T as a result of the thermal expansion of the lattice. The second-order Doppler shift, δ_{SOD} , and its temperature dependence is determined by the lattice-vibrational spectrum and can be calculated using the Debye approximation [91D1]. The lattice temperatures, Θ_M , and δ_i values thus determined are $\Theta_M = 540$ K, $\delta_i = 0.64$ mm/s for $\text{Fe}^{3+}(\text{M1})$, and $\Theta_M = 380$ K, $\delta_i = 1.38$ mm/s for $\text{Fe}^{2+}(\text{M1})$ having larger quadrupole splitting. The temperature dependences of the quadrupole splittings are weak for both Fe^{3+} species. The $\Delta Q(T)$ values for $\text{Fe}^{2+}(\text{M1})$ (with higher ΔQ) were analysed considering a point charge model [93V1]. For the other $\text{Fe}^{2+}(\text{M1})$ doublet, the scatter of data was rather high. The data were qualitatively discussed by considering a thermally activated electron-hopping process involving pairs of $\text{Fe}^{2+}\text{-Fe}^{3+}$ cations on adjacent M1 sites or that a part of ferrous ions flip from one configuration to the other when the temperature changes.

The ^{57}Fe NGR method was further used to determine the distribution of iron ions in lattice sites in order to correlate with electrical conductivity [04S1].

Aegirine – hedenbergite, $\text{NaFe}^{3+}\text{Si}_2\text{O}_6 - \text{CaFe}^{2+}\text{Si}_2\text{O}_6$

In the solid solution series of the $\text{NaFe}^{3+}\text{Si}_2\text{O}_6 - \text{CaFe}^{2+}\text{Si}_2\text{O}_6$, Fe^{2+} and Fe^{3+} occupy the crystallographically equivalent sixfold-coordinated M1-positions, which form chains parallel to the *c*-axis via common edges. The ^{57}Fe NGR spectra, at 77 K and RT, for $\text{NaFeSi}_2\text{O}_6 - \text{CaFeSi}_2\text{O}_6$ consist of a predominant Fe^{3+} doublet with ΔQ at RT increasing from 0.29 mm/s for the Na end member to 0.46 mm/s for 20Na-80Ca composition [82D3]. With increasing Ca content, this doublet was found to become more and more asymmetrically broadened. In addition, two weaker Fe^{2+} doublets were resolved and attributed to two distinct M1 sites. With the increase in temperature, the population of one of the Fe^{2+} sites grows at the expense of the other. For the above behaviour, a clear explanation has not been found. In [82A1, 84A1] similar spectral features were reported for a natural Ca- and Fe^{2+} -containing aegirine. The authors interpreted the temperature variations of the two doublet areas as being the result of a thermally activated electron exchange between Fe^{2+} and Fe^{3+} on adjacent M1 sites. The slightly broadening of their Fe^{3+} doublet indicates the appearance of relaxation effects. The onset of the magnetic ordering was observed below 10 K. At 5 K, it is not yet complete, but still strongly influenced by relaxation effects [84A1]. For a composition $0.5\text{NaFe}^{3+}\text{Si}_2\text{O}_6 - 0.5\text{CaFe}^{2+}\text{Si}_2\text{O}_6$, the ^{57}Fe NGR spectrum at 85 K was analyzed considering one Fe^{3+} doublet which was assigned to the M1-positions and three Fe^{2+} doublets which result from slightly different electric field gradients at Fe^{2+} in M1, due to the interaction with next nearest cation neighbours with different size and charge, e.g. Na^+ or Ca^{2+} [98A1]. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is close to the theoretical value. At RT, there is also an additional doublet with average isomer shift and quadrupole splitting which indicates the beginning of the electron hopping. In the temperature range 400...650 K, the number of doublets, due to mixed valent iron, and their areas have increased. This shows that the portion of Fe^{3+} and Fe^{2+} in M1 which participate in the electron exchange process, distinctly increase with temperature. Even at temperatures above 600 K not all Fe in the M1-chains takes part in the thermally activated intersite electron hopping which seems to be more or less restricted to localized Fe^{2+} , Fe^{3+} pairs. There is no formation of a narrow d-band or polaron band filled with delocalized electrons and therefore a discrete subpattern due to the narrow band cannot be observed (as for example in ilvaite). The reason for this are larger Fe-Fe distances of 3.17 Å in the M1-chains of the pyroxene (compared to 2.813...3.023 Å in the 8d chains of ilvaite) which diminish the d-orbital overlap through common edges and thus prevent the formation of a narrow band and extended electron delocalization. The ^{57}Fe NGR spectrum of natural silicate $(\text{Na}_{0.65}\text{Ca}_{0.34})(\text{Fe}^{3+}_{0.64}\text{Fe}^{2+}_{0.11}\text{Mg}_{0.19}\text{Al}_{0.04}\text{Ti}_{0.01})(\text{Si}_{1.98}\text{Al}_{0.01})\text{O}_6$ at 77 K was analyzed considering the presence of three doublets [97B1]. The largest doublet (87 % of the entire intensity) was assigned to Fe^{3+} in the octahedral site. Two additional doublets with much lower intensity were assigned to Fe^{2+} also in the octahedral M1 sites – Table 10. They have slightly different isomer shifts and quadrupole splittings and were observed in all comparable silicates [73E1, 82D1, 84A1]. The presence of the two Fe^{2+} doublets in the same crystal site may be due to different nearest-neighbours Na and Ca on M2 sites. The different field gradients generated by them lead to different quadrupole splittings on M1.

Aegirine – diopside

The ^{57}Fe NGR spectra for $\text{Ae}_{0.81}\text{Di}_{0.19}$ at RT and 80 K, show a single symmetric quadrupole doublet – Table 10 – characteristic for iron ions in octahedral coordination. At 2 K, the spectrum consists of three well defined magnetic patterns [88D1]. The patterns were analyzed considering different local environments of Fe^{3+} ions. The probabilities for the presence of one, two and three ferric ions around another ferric ion in a M1 site are 9:37:53. This describes well the spectrum, where the fitted ratios of areas are 11:36:52 – Table 10.

Omphacites

The natural omphacites were studied by the ^{57}Fe NGR method [60M1, 69B1, 71B1, 71W2, 73D1, 78A1, 79B1, 82D1, 84A1, 85D2, 97B1, 05L1]. For example, in [78A1] spectra at 295 K were analyzed for both C2/c and P2/n omphacites annealed at 300 to 1000°C and 1.5 to 1.8 GPa. The spectra were analyzed considering three ferrous doublets due to Fe^{2+} in M1 position. The three M1 doublets arise from next-nearest-neighbour effects caused by different combinations of Ca^{2+} , Na^+ cations in the M2, M21 positions. The doublets are characterized by ΔQ values of $\cong 2.8$, $\cong 2.2$ and $\cong 1.8$ mm/s, and arise respectively from the Ca^{2+} , Na^+ combinations: 1Ca2Na; 2Ca1Na; and 3Ca. The trend in the relative ferrous peak areas with Ca/(Na+Ca) ratios was in agreement with theoretical predictions, and the observed and theoretical relative ferrous peak areas are in good agreement, particularly for C2/c samples. The ^{57}Fe NGR spectra of P2/n omphacites annealed below and above the P2/n \leftrightarrow

C2/c transition temperature are similar. Thus, the nearest-neighbour environment of Fe^{2+} in omphacite seems to be independent of $(\text{Mg}, \text{Fe}^{2+})$, Al^{3+} and Ca^{2+} , Na^+ long-range order. In $\text{Na}_{0.48}\text{Ca}_{0.47}\text{Mg}_{0.42}\text{Fe}^{2+}_{0.05}\text{Fe}^{3+}_{0.03}\text{Al}_{0.52}\text{Si}_2\text{O}_6$, the ^{57}Fe NGR spectra were analyzed starting also from various possible M2 nearest neighbour configurations (3Na; 2Na1Ca; 1Na2Ca; 3Ca). In particular, the C2/c sample with only one position for Fe^{2+} to enter, shows a broad complex spectrum. One type of Fe^{2+} gives rise to more than one doublet due to a different M2 site composition [73D3]. In both the C2/c and P2/n samples the three doublets were attributed to different (Ca,Na) nearest neighbour configurations. The calculated relative intensities are in semiquantitative agreement with the observed values [79B1].

Li-aegirine, $\text{LiFeSi}_2\text{O}_6$

The ^{57}Fe NGR spectra of $\text{LiFeSi}_2\text{O}_6$ below T_N were studied by [88B1, 98A1, 98L1]. The reported parameters are quite normal for Fe^{3+} in an octahedral environment (M1) except the disappearance of the quadrupole splitting below T_N . This feature was interpreted as a possible geometrical change of the local Fe^{3+} environment. Later on, the studies were extended on single crystals [98A1, 98L1]. The spectrum at 10 K is shown in Fig. 79a and the parameters obtained by fitting the experimental data are listed in Table 10, together with those reported by [88B1]. The spectra were fitted by one hyperfine field pattern. The high value of the effective field, $B_{\text{eff}}(0)$, of 49.8 T, and the isomer shift of 0.47 mm/s at 10 K show that iron is exclusively as Fe^{3+} in the sixfold-coordinated M1-position. In the antiferromagnetic region, strong relaxation effects were observed which diminish with decreasing temperature down to $T = 5$ K [88B1]. In contrast to a 1D Heisenberg chain with direct exchange, the Fe^{3+} -O chains are “diluted” by separating diamagnetic ions that may lead to delayed ordering and thus to the observed relaxation features. The ^{57}Fe NGR spectra could be satisfactorily refined yielding a slightly dependent angle $\varphi \cong 42^\circ$ between the main component of the electric field gradient, V_{zz} , and the crystallographic *b*-axis. The EFG is almost axially symmetric. The angle between V_{zz} and $B_{\text{hf}}(0)$ is $\theta = 125^\circ$. From the above value and the orientation of V_{zz} , it can be concluded that the *c*-axis is the most probable direction of the internal field, $B_{\text{hf}}(0)$, in agreement with the results of magnetic measurements [88B1]. A small residual angle of $\cong 10^\circ$ let us expect a small canting [98A1]. In contradiction with data obtained on powder, ΔQ does not disappear below T_N .

In the paramagnetic range, the ^{57}Fe NGR spectrum of $\text{LiFe}^{3+}\text{Si}_2\text{O}_6$ consists of two symmetric and narrow-split resonance absorption lines corresponding to one Lorentzian-shaped doublet for Fe^{3+} on the M1 site. Within the temperature variation of the ferric quadrupole splitting, ΔQ , a discontinuity in the temperature range $200 \leq T \leq 250$ K was shown – Fig. 79b [01R1]. The observed decrease in ferric quadrupole splitting in the 180...260 K range can be directly ascribed to altered geometrical environments of the ^{57}Fe nucleus due to the C2/c \rightarrow P2₁/c phase transition. The data suggest a decrease in polyhedral distortion for the Fe^{3+}O_6 octahedron in the P2₁/c phase [01R1].

Other pyroxenes

Iron bearing clinopyroxenes were synthesized under hydrothermal controlled oxygen fugacity in the binary joins: $\text{CaMgSi}_2\text{O}_6 - \text{CaFeSi}_2\text{O}_6$, $\text{CaMgSi}_2\text{O}_6 - \text{NaFeSi}_2\text{O}_6$, $\text{CaFeSi}_2\text{O}_6 - \text{NaFeSi}_2\text{O}_6$, $\text{CaFeSi}_2\text{O}_6 - \text{NaCrSi}_2\text{O}_6$, $\text{NaFeSi}_2\text{O}_6 - \text{NaCrSi}_2\text{O}_6$, and $\text{NaFeSi}_2\text{O}_6 - \text{LiFeSi}_2\text{O}_6$ [82D3]. Several types of spectral changes as function of composition were observed. According to [82D3], in isovalent solid solutions, only small to moderate changes in ΔQ of narrow-line for ferrous and ferric doublets were observed. In solid solutions, where atoms with different valences are mixed on the same sites, substitution results in marked changes involving line broadening and strong changes in quadrupole splitting. The spectra were fitted with multiple doublets having large quadrupole splitting – Table 10. The doublets were interpreted as either to be due to different NN configurations or to a combination of temperature and less specifically localized compositional effects.

In [97L1] a correlation was analysed between quadrupole splitting ΔQ of Fe^{2+} ions and the distortion of their octahedral coordination in chain silicates. The temperature variation of δ and ΔQ in hedenbergite was also discussed [99D1].

8.1.4.1.5 Nuclear magnetic resonance (NMR) data

(CaMgSi₂O₆)_x(CaAl₂SiO₆)_{1-x}

²⁹Si MAS NMR studies were performed on crystals and glasses along the join Di – CaTs in order to obtain information on the Si-Al distribution [73K1, 80L1, 83S1, 85C3, 85K4, 86K3, 00K1, 01W2, 02F1]. The X-ray analyses of the crystal structures were not all in agreement. In [74O1] was revealed that CaTs has space group C2/c, consistent with complete disorder at the tetrahedral sites. The activity-composition relations emphasized short-range ordering of tetrahedral Si-Al [76W1]. It was also suggested that the above ordering could be coupled to octahedral Al distribution. In [66H1] and [81G1] two different positions in *p-T* space for the equilibrium reaction $3\text{CaAl}_2\text{SiO}_6 = \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 2\text{Al}_2\text{O}_3$ were determined. Then it was suggested [84W1] that the inconsistencies between various studies could be reconciled if the two sets of pyroxenes have different degrees of Si-Al cation ordering. Thus, pyroxenes reported by [66H1] were disordered and those analysed by [81G1] contained short-range order. Compositions across the Di – CaTs solid solutions follow the general formula $\text{Ca}^{[6]}[\text{Mg}_{1-x}\text{Al}_x]^{[4]}(\text{Si}_{1-x/2}\text{Al}_{x/2})\text{O}_6$. Cation substitution is governed by Tschermak's substitution $^{[4]}\text{Si}^{4+} + ^{[6]}\text{Mg}^{2+} = ^{[4]}\text{Al}^{3+} + ^{[6]}\text{Al}^{3+}$. Clinopyroxene structures of intermediate compositions are complicated by cation-order-disorder occurring simultaneously on both the tetrahedral and octahedral sites.

The ²⁹Si MAS NMR spectrum of diopside crystal consists of a single narrow peak at –84.7 ppm [80L1, 86K3], –84.4 ppm [02F1] or –84 ppm [83S1], resulting from the single ordered environment around Si, which is in the range of silicon Q² site – Fig. 80. As already mentioned, the Qⁿ notation represents the number of bridging oxygens per Si tetrahedron. The spectrum of CaTs end member exhibits three broad peaks [02F1] – Fig. 80 and Table 11. Multiple peaks are the result of Si-Al disorder over the tetrahedral sites (as octahedral sites in CaTs contain only Al). We note that in [86K3] a peak at –88.1 ppm and weak shoulder at –79 ppm was initially reported. Peak positions in ²⁹Si MAS NMR spectra are sensitive to Al substitution, both in the corner-sharing NN tetrahedral sites on the single chain and in one of the three NN octahedral M1 sites – Fig. 80 [02F1]. The substitution of Al for Mg on the M1 causes the ²⁹Si chemical shift to be shielded by about the same magnitude as the deshielding caused by substitution of Al for Si in NN tetrahedra, causing severe overlap among central peaks. Four peaks were resolved in the ²⁹Si MAS NMR spectra for samples with *x* = 0.25; 0.50 and 0.75. The same spectrum was obtained for a sample having *x* = 0.50, by [01W2]. The peak widths increase with increasing CaTs component as a result of increasing cation disorder due to addition of Al. These peaks are not true single peaks, but are the result of chemical shift dispersions resulting from cation substitution at the various M1 sites and/or distant tetrahedral sites such as on adjacent chains. The positions of each of the four-peak centroids change continuously by about –1 ppm to lower frequency with increasing tetrahedral Al/Si ratio. A similar behaviour has been reported for glasses along the Di – CaTs join [86K3]. Substitution of Al into corner-sharing NN tetrahedral sites cause chemical shift to change by +4 ppm [02F1]. In order to analyze the spectra, the presence or absence of Al in the NN octahedral M1 site bonded to Si by considering also Al in octahedral environment were considered – Table 11. The diopside peak of –84.4 ppm was assigned to Si(0Al)[0Al], while the CaTs peaks to Si(0Al)[1Al], Si(1Al)[1Al] and Si(2Al)[1Al] to indicate the presence of Al in the NN octahedral M1 sites bonded to Si. For intermediate compositions two pairs of the unique local environments have similar chemical shifts, leaving only four peaks resolved in the spectrum, from six site assignments. The ²⁹Si MAS NMR peak intensities for end member CaTs are consistent with 70 % of Si in the tetrahedral chain being locally ordered into alternating ^[4]Al-O-Si-O-^[4]Al linkages, although space group C2/c would suggest the Si and Al are long-range disordered over tetrahedral chain. Thus, CaTs violates the Löwenstein's Al-O-Al avoidance rule [54L1], having 0.175 Al-O-Al linkages per formula unit. For intermediate members of solid solution, site populations have been modeled using a random distribution model (RD), an Al-O-Al avoidance model (AA) and a modified AA model, which couples the cation distribution between the tetrahedral and octahedral sites (AAOC). The RD model fits the ²⁹Si MAS NMR peak intensity poorly. The AA and AAOC models fit the data well to at least 75 % CaTs, suggesting that Di-rich clinopyroxenes obey the Al-O-Al avoidance rule. For composition >75 % CaTs, observed cation distributions deviate considerably from that predicted by the Al-O-Al avoidance, indicating formation of Al-O-Al linkages. The AAOC model yields an improved fit for peak intensities, particularly near *x* = 0.5, implying the presence of ^[4]Si-O-^[6]Mg and ^[4]Al-O-^[6]Al couples. This suggests the presence of short-range ordering on both tetrahedral and octahedral sites in Di – CaTs join.

²⁹Si MAS NMR studies on Di – CaTs glasses were also performed [86K3].

The ²⁷Al MAS NMR spectra of CaMgSi₂O₆ – CaAl₂SiO₆ glasses and crystals show the presence of a center band resonance between 56 and 64 ppm indicative of tetrahedrally-coordinated site [81M2, 86K3] – Table 11.

The ^{27}Al resonances of the corresponding glasses do not change in linewidth when changing the composition. There is a systematic deshielding (more positive chemical shift) at ^{27}Al with increasing Al content, paralleling the variation observed for crystals. The above results were interpreted as indicative that the glasses become increasingly polymerized with increasing CaTs content and that CaTs glass is fully polymerized.

The ^{25}Mg MAS NMR spectra of crystalline and glassy diopside revealed that the chemical shift in the disordered phase corresponds to that of the mineral, suggesting that sixfold coordination is essentially retained upon vitrifications [00K1].

MSiO₃ (M = Ca, Sr, Ba, Cd), Cd₇[Ge₆Si]O₇

The ^{29}Si NMR spectra of wollastonite were analysed considering only one resonance line, at -89.2 ppm [80L1, 83S1]. In [90S2] the spectra were resolved considering the presence of three lines, corresponding to the three crystallographic sites with relative intensities 1:1:1 as expected on the basis of crystal structure – Table 11. In [91K3] the high-pressure phase of the CaSiO₃ system was studied by ^{29}Si NMR.

Two peaks were evidenced in the ^{29}Si NMR spectrum of CdSiO₃ but there is also a second phase [00C4]. In the case of the Cd-pyroxmangite (Cd₇[Ge₆Si]O₇) spectrum, three different peaks were evidenced – Table 11. These were attributed mainly to three different NNN configurations having 0, 1 and 2 Ge atoms. This interpretation assumes that the topologies of the different (four) tetrahedral sites are too similar for Si at different sites, for their ^{29}Si chemical shift to be resolved [00C4].

The ^{29}Si NMR spectra for SrSiO₃ and BaSiO₃ were analyzed admitting the presence of only one line – Table 11 [83S1].

Enstatite, spodumene

The ^{29}Si MAS NMR measurements of enstatite and spodumene (as well as on diopside and wollastonite) allowed the determination of the isotropic chemical shift, δ_i , the principal values of the chemical shielding tensor, δ_{11} , δ_{22} and δ_{33} , the shielding anisotropy $\Delta\delta = \delta_{33} - (1/2)(\delta_{11} + \delta_{22})$ and the asymmetry parameter $\eta = (\delta_{22} - \delta_{11})(\delta_{33} - \delta_i)^{-1}$ [83S1] – Table 11.

For nuclear quadrupole resonance of Li⁺ and Al³⁺ in spodumene see [52V1, 53P1].

Na₂BaSi₂O₆, NaAlSi₂O₆

The ^{23}Na MAS NMR spectra of Na₂BaSi₂O₆ and NaAlSi₂O₆ consist of one or two patterns with well defined quadrupole line shapes – Fig. 81 [93X1].

LiAlSi₂O₆-II

The analysis of the β -LiAlSi₂O₆ structure suggests that there are essentially two different possible Li jump processes: long-range jumps from one pair of Li sites to the next, and a localized motion by hops between the sites of a pair. Some aspects of the former process was studied by NMR [92F2]. There, the spin-lattice relaxation rate, T_1^{-1} , of ^7Li was measured from 150 K up to 930 K in the glass (which is slightly below the glass transition temperature, $T_g \cong 960$ K) and up to 1300 K in the polycrystalline material. Pronounced $T_1^{-1}(T)$ maxima were found at various temperatures depending on the Larmor frequency, in the range from about 650 K to 850 K and were attributed to the long-range jumps in glassy and crystalline β -spodumene. The spin lattice relaxation rate of β emitter ^8Li was measured [05H1] down to temperatures of 12 K by using β -radiation detected NMR (β -NMR). The above study was focused on dynamical processes. Structural characterizations were also performed by ^{29}Si and ^{27}Al solid state NMR as well as via positron annihilation lifetime spectroscopy [95N2, 96J1]. Impedance measurements have been reported [92M3, 94B2, 96B2, 01R2]. A comparison of motional correlation times obtained from NMR and conductivity measurement [92M3, 93N2, 97W4] was made. A computer simulation study of Li ion migration in β -spodumene was also performed [97M3]. As example of the ion hopping NMR study in crystalline and glassy β -LiAlSi₂O₆ we present in Fig. 81A the ^7Li spin-lattice relaxation rate as function of reciprocal temperature [05Q1]. In crystalline material, the global maximum in T_1^{-1} occurs at higher temperature and is considerable larger than in the glass. In addition to a pronounced rate maximum at high temperatures, stemming from the long-range Li motion, a weak maximum was found in the crystalline sample

near 120 K. The latter result confirms the existence of a local double-well structure in which Li ions reside. The activation energy, E_a , obtained from the slope at the low-temperature side of the T_1^{-1} peak is 0.50(2) eV for the crystal and 0.34(3) eV for the glass. The reduced T_1^{-1} maximum in the glassy sample suggests that the distribution of ion hopping is broader.

LiGaSi₂O₆

The ^{69}Ga NMR on LiGaSi₂O₆ showed that although in clinopyroxene structure there is only one crystallographical Ga site, two different types of octahedral Ga atoms were evidenced [95O1]. The above data suggest the existence of two electronic states for the octahedral Ga³⁺ ions. There is also a phase transition when decreasing the temperature.

Na₂SiO₃, Li₂SiO₃

For the Na₂SiO₃ phase, the ^{23}Na MAS NMR spectrum has three recognizable peak maxima, suggesting that there are at least two Na sites [93X1]. However, the crystal structure determination [67M1] shows the presence of only one Na site. It was suggested that either Na positions, in this phase, are partially disordered or that more one crystallographically Na site is present. The ^{23}Na isotropical chemical shift correlates with both the Na coordination and the degree of polymerization.

The ^{29}Si MAS NMR spectra on Li₂SiO₃ show a chemical shift ($\cong -73.5$ ppm), which suggests that the main silica species are Q² [84S2].

The ^{29}Si MAS NMR spectra of Li₂O – SiO₂ glasses (15 < Li₂O < 40 mol %) have been interpreted in terms of Qⁿ distribution, which emphasizes the characterization of the structure of silicate glasses in terms of their local silicon environments [84S2]. The predominant local silicon environments consist of Q², Q³ and Q⁴. Metastable liquid immiscibility in the composition region between 17 and 30 mol % Li₂O may be due to the presence of Q², at low Li₂O concentration, but can also be ascribed to a cooperative arrangement of Q³ [84S2]. The devitrification experiments indicate that nucleation rates in the Li₂O – SiO₂ system depend on similarities between Q species in glasses and their crystalline analogues.

8.1.4.1.6 Electron paramagnetic resonance (EPR) data

CaMgSi₂O₆: Mn²⁺

Several EPR studies were performed on Mn²⁺ in CaMgSi₂O₆ [64V1, 69G1, 75G1]. In order to locate the Mn²⁺ ion in diopside, in [64V1] the orientation of EPR axes was compared with respect to the positions of the immediate surroundings of the ions that may be substituted by Mn²⁺. They concluded that Mn²⁺ cations were distributed on M1 and M2 sites, and that Mn²⁺ in the Ca²⁺ site was responsible for the spectrum with the larger hyperfine structure. Later on, [69G1] confirmed the spin Hamiltonian constants determined by [64V1], but they reversed the site assignment previously assumed. According to [69G1], three types of Mn²⁺ sites have been found in natural diopsides: (1) most Mn²⁺ in the Ca-site; (2) most Mn²⁺ in the Mg-site and (3) all Mn²⁺ in the Mg-site. Natural and synthetic diopsides, known to have been crystallized above 900°C and containing $\cong 0.001$ % Mn or less, invariably show all Mn²⁺ in the Mg-site. A natural diopside with a Mn concentration of 0.005 % and 76 % of Mn²⁺ located in Ca-site has been heat-treated to induce a redistribution of Mn²⁺ in the Ca and Mg-sites. The exchange begins at 900°C and is essentially complete at 1050°C, at which point the Mn²⁺ distribution is reversed, with 85 % of the Mn²⁺ in the Mg-site. Two possible exchange reactions were suggested: (1) $\text{Mn}^{2+}_{\text{Ca}} + \text{Mg}^{2+}_{\text{Mg}} \rightleftharpoons \text{Mn}^{2+}_{\text{Mg}} + \text{Mg}^{2+}_{\text{Ca}}$; (2) $\text{Mn}^{2+}_{\text{Ca}} + \square_{\text{Mg}} \rightleftharpoons \square_{\text{Ca}} + \text{Mn}^{2+}_{\text{Mg}}$, the subscripts denoting Ca- and Mg-sites and by \square a vacancy. Because relative concentrations of Mn²⁺ in the Ca²⁺ and Mg²⁺ sites depend on the growing conditions of crystals, in [75G1] the EPR method was used to locate Mn²⁺ in a natural single crystal. Two different spectra of Mn²⁺ were observed and were attributed to Mn²⁺ in both possible substitutional sites M1 and M2. The pseudo-symmetry of the fourth-order term of the spin Hamiltonian has been studied and has been compared to the crystal field calculated on the basis of a point-charge model. It was shown that the environment of Mn²⁺ in M1 has a good pseudo-cubic symmetry, while the M2 site, when occupied by Mn²⁺, is highly distorted.

LiAlSi₂O₆: Fe³⁺, Mn²⁺

The first EPR study of Fe³⁺ impurity ions in spodumene was performed by [65M1]. EPR measurements of Mn²⁺ centers in spodumene [68H2, 68H3] reveal 11 Mn²⁺ complexes which reduce to 6 distinct centers. Center I was assigned to an isolated Mn²⁺ ion on the octahedral Al³⁺ site. Centers II, III, IV and V were thought to be due to Mn²⁺ on the Al³⁺ site but modified by various arrangements of nearest neighbour alkali ions, which were necessary to achieve charge balance. The VI-th center was tentatively assigned to Mn²⁺ on a Si⁴⁺ site. On heating, centers II - V become equivalent to center I. The spectroscopic splitting factors g_z and g_y for above centers are: I (2.0013(3), 2.0011(3)); II (2.0009(5), 2.0012(5)); III (2.0004(3), 2.0012(3)); IV (2.0012(5), 2.0012(5)); V (2.0012(5); 2.0012(5)); VI (2.0012(10); 2.0024(10)).

Wollastonite: Mn²⁺

The EPR spectrum of natural wollastonite has a strong angular dependence that was interpreted as originating from Mn²⁺ ions distributed among the six-coordinated Ca sites (Ca1, Ca2) and the seven-coordinated Ca site (Ca3) [90D1]. The spectrum shows superposition of spectra from Mn²⁺ ions in two magnetically nonequivalent kinds of sites described by the Hamiltonian $\mathbf{H} = g\mu_0 \mu_B HS + ASI + D [S_z^2 - (1/3) S(S+1)] + E [S_x^2 + S_y^2]$ with the parameters $g_1 = g_2 = 2.002$, $A_1 = A_2 = 85 \text{ cm}^{-1}$, $D_1 = D_2 = -357 \text{ cm}^{-1}$, $E_1 = E_2 = 90 \text{ cm}^{-1}$ and $g_3 = 1.998$, $A_3 = 87 \text{ cm}^{-1}$, $D_3 = -231 \text{ cm}^{-1}$ and $E_3 = 19 \text{ cm}^{-1}$. The subscripts refers to the sites Ca1, Ca2, and Ca3, respectively.

8.1.4.1.7 Heat capacity**Fe_xMg_{1-x}SiO₃**

The temperature dependences of the heat capacity for some Fe_xMg_{1-x}SiO₃ OPx were analysed [85K5, 85K6, 91R1]. For a synthetic MgSiO₃ – Fig. 82a – between 298 K and 1000 K, the heat capacity is described by $C_p = 350.7 - 0.1473 T + 1.679 \cdot 10^{-6} T^2 - 4296 T^{-0.5} + 5.826 \cdot 10^{-5} T^2$ [J/mol K] while for Mg_{0.85}Fe_{0.15}SiO₃, in the same temperature range, $C_p = 207.9 - 0.01489 T + 1.921 \cdot 10^{-5} T^2 - 2135 T^{-0.5}$ [J/mol K] – Fig. 82b [85K5]. The measured C_p values of the Mg_{0.85}Fe_{0.15}SiO₃ silicate are significantly greater at low temperatures than those for synthetic enstatite – Fig. 83 [85K5]. The larger C_p/T values arise from the anomalous heat capacity between 5 and 30 K, attributed to a Shottky anomaly. The Debye temperatures in the Fe_xMg_{1-x}SiO₃ system are composition dependent, decreasing linearly from 812 K ($x = 0$) to 561 K ($x = 1.0$). The Grüneisen parameter range from 0.85...0.89 and do not seem to vary with compositions.

The enthalpy of Mg-Fe ordering in En_{0.5}Fs_{0.5} orthopyroxenes was measured using the transposed temperature drop calorimetric method [00C1]. Heat effects associated with two consecutive drops were recorded. From the difference of the heat effects measured in the two experiments, the enthalpy of disordering associated with the temperature change from 823 K to 1173 K was calculated. The observed enthalpy corresponds to a change in the mole fraction of Fe at the M2 site of –0.096(1). The enthalpies of Fe-Mg ordering in orthopyroxenes, determined by various authors, are listed in Table 12b. There are significant differences between values given in literature.

The heat capacity of MgSiO₃ **perovskite** was also studied [86K4, 93A1, 98A2]. It was shown theoretically [98A2] that MgSiO₃ perovskite is a Debye-like solid because the heat capacity and entropy calculated up to high temperature (1800 K) from Debye theory agree with available data, especially those above 400 K.

The experimental heat capacities of MgSiO₃ **ilmenite** are smaller, by 4...10 % than those of orthopyroxene in the entire temperature range [88A3]. The heat capacity differences are consistent with lattice vibrational model [87M4] and suggest an entropy change of –18(3) JK^{–1} mol^{–1}, approximately independent of temperature for the pyroxene – ilmenite transition.

ZnSiO₃

The heat capacities of ZnSiO₃ ilmenite is 3...5 % smaller than that of ZnSiO₃ clinopyroxene [90A1] – Fig. 84a. The entropy of transition was calculated using the measured enthalpy and free energy determined from the phase equilibrium data. The enthalpy, entropy and volume changes of the pyroxene – ilmenite transition in ZnSiO₃ are similar in magnitude to those in MgSiO₃.

Rhodonite, pyroxmangite

In [87B1] the heat capacities were reported for natural pyroxmangite ($\text{Mn}_{0.93}\text{Ca}_{0.056}\text{Mg}_{0.01}\text{Fe}_{0.01}\text{SiO}_3$) and zincian rhodonite ($\text{Mn}_{0.632}\text{Ca}_{0.21}\text{Zn}_{0.09}\text{Mg}_{0.05}\text{Fe}_{0.02}\text{SiO}_3$). They show a λ -like transition in C_p values of pyroxmangite at 272.1 K and Schottky anomalies in heat capacities of pyroxmangite and zincian rhodonite at 11 K and 8 K, respectively. The anomaly at 272.1 K was attributed to the melting of ice in fluid inclusions in pyroxmangite [95R1]. In MnSiO_3 rhodonite, the absence of a pronounced λ -transition was shown at $T \geq 6$ K – Fig. 84b [95R1]. It was suggested that the irregularity in the coordination polyhedra may be the reason that MnSiO_3 does not exhibit a sharp λ -transition above 6 K. There is an anomalous behaviour below 20 K and the heat capacity is higher than in a natural sample where a fraction of Mn^{2+} has been replaced by diamagnetic ions [87B1]. According to [95R1], the observed behaviour of C_p could arise from the persistence of short-range magnetic order above a cooperative magnetic transition, at temperatures below 6 K.

CaSiO_3

The temperature dependence of the molar heat capacity for CaSiO_3 (wollastonite) at $T \leq 300$ K is plotted in Fig. 82b. The entropy change is $S_{298}^0 - S_0^0 = 81.69(12)$ J/mol K [85K5]. In [91R1, 94R1] the heat capacities of wollastonite, pseudowollastonite (PWo) and CaSiO_3 glass and liquid were studied. There is a small difference in C_p values for wollastonite and PWo. This can be correlated with the fact their structures are closely related. Wollastonite shows a first-order phase transition at 995 K with a small enthalpy of transition of 200 J/mol K – Fig. 82c [91R1]. In the temperature range 350...1000 K, the heat capacity can be described by the relation: $C_p = 200.8 - 0.02590 T - 1.579 \cdot 10^5 T^{-2} - 1826 T^{-0.5} + 7.435 \cdot 10^{-6} T^2$ [85K5].

$\text{CaMgSi}_2\text{O}_6$

The heat capacity of $\text{CaMgSi}_2\text{O}_6$ diopside was analysed by [32W1, 57K1, 85K5]. The temperature dependences of the heat capacity are given in Figs. 83 and 85 [85K5]. We note that the data of [57K1] and [85K5] are in agreement but differ from those of [32W1]. The entropy change is $S_{298}^0 - S_0^0 = 142.7(2)$ J/mol K. The low-temperature heat capacity of diopside glass was reported by [86R2]. In the temperature range 350...1000 K, the heat capacity can be described by the relation: $C_p = 470.25 - 0.09864 T - 2.453 \cdot 10^5 T^{-2} - 4823 T^{-0.5} + 2.813 \cdot 10^{-5} T^2$ [85K5].

$\text{CaAl}_2\text{SiO}_6$

The heat capacities of $\text{CaAl}_2\text{SiO}_6$ pyroxene and glasses were studied by [84H1] in the temperature range 5...380 K. The differences in the heat capacities $C_p(\text{glass}) - C_p(\text{crystals})$, at low temperatures – Fig. 86 – show the influence of structural state. The differences in C_p are quite large at very low temperatures, the glass having the higher heat capacity as expected from a density consideration. As temperature increases the relative difference diminishes, the pyroxene having a slightly greater heat capacity from 300 to 380 K. The data suggested that a small amount of short-range order is present in CaTs pyroxene [84H1].

$\text{CaAl}_2\text{SiO}_6 - \text{CaMgSi}_2\text{O}_6$

The enthalpies of the $\text{CaAl}_2\text{SiO}_6 - \text{CaMgSi}_2\text{O}_6$ join were studied by [77N1]. In [78T2] their heat capacities were measured in the temperature range 350...1000 K.

$\text{CaCoSi}_2\text{O}_6, \text{CaNiSi}_2\text{O}_6$

Low-temperature heat capacity measurements reveal, for both Co and Ni samples, the presence of a λ -type anomaly at 9.75(8) K and 20.2(4) K, respectively which corresponds to the maxima in the temperature dependence of magnetic susceptibilities – Fig. 87a, b [96D3]. The increase of the heat capacity at higher temperatures is mainly due to the phonon contribution. These anomalies confirm the stabilization of long-range magnetic ordering. The high-temperature data have been fitted to the relationship $C_p = AT^{-2} + BT^3$, where the first term was ascribed to magnetic correlations while the second one deals with lattice contribution. After subtracting the latter (full line), the heat capacity of magnetic origin was obtained. It also allows the determination of the magnetic entropy, S_{magn} . The experimental ΔS_{magn} values associated with the magnetic transition – Fig. 87b,d – agree with theoretical ones determined by $\Delta S_{\text{magn}} = R \ln(2S + 1)$ where S is the spin value.

NaTiSi₂O₆

The temperature dependence of the heat capacity of NaTiSi₂O₆ shows a broad peak at the temperature roughly corresponding to that of the spin-gap opening – Fig. 88 [02I1]. The entropy change was estimated to be $\Delta S = 2.8$ J/mol K and the Debye temperature $\Theta_D = 450$ K. The entropy change cannot be separated into lattice and magnetic contributions, but it is equal to about one half of the theoretical estimate for the magnetic entropy released at a purely magnetic phase transition $R \ln(2S+1) = 5.76$ J/mol K.

AVSi₂O₆ (A = Li, Na)

The temperature dependences of the heat capacity C_p are plotted in Fig. 89 [04I1, 04V1]. Pronounced peaks in $C_p(T)$ were seen at temperatures where $d\chi/dT$ curves are at maximum. In LiVSi₂O₆, an additional anomaly was seen at 204 K. According to [04V1] it corresponds to some structural change. To separate the magnetic contribution of the heat capacity of vanadium-based pyroxenes, the temperature dependences of the heat capacity of Sc-based nonmagnetic pyroxene was analysed – Fig. 89a, b. These curves show no anomalous behaviour indicating the absence of structural changes in the temperature range studied. The temperature dependences of the magnetic entropy in AVSi₂O₆ pyroxenes – Fig. 90 [04V1] – show that the large part of magnetic entropy is released well above T_N , which is the signature of a low-dimensional magnetic system. The ratios of magnetic entropies released below T_N , to total magnetic entropy $R \ln(2S + 1) = 9.13$ J/mol K released over the entire temperature range, is 0.10 for A = Li and 0.19 for A = Na. The Debye temperatures are listed in Table 12.

Li₂SiO₃, Na₂SiO₃

The heat capacities of lithium and sodium metasilicates were studied [92T1, 94R1, 96R3]. The differences between the data for Li₂SiO₃ and Na₂SiO₃ were attributed to an excess heat capacity related to sodium mobility in Na₂SiO₃.

NaAlSi₂O₆

The heat capacity of synthetic jadeite was measured between about 15 and 850 K [98H1]. At $T > 298.15$ K, the C_p values can be described by $C_p = 259.08 + 0.038032 T - 2518908 T^{-2} - 1332.57 T^{-1/2} - 8.8 \cdot 10^{-6} T^2$.

8.1.4.1.8 Electrical conductivity**Fe_xMg_{1-x}SiO₃**

The electrical conductivities of Fe_xMg_{1-x}SiO₃ enstatites, perovskites and ilmenites were studied [87C2, 90L1, 93S2, 98K1]. The data obtained in case of a sample with $x = 0.07$ are plotted in Fig. 91 [98K1]. In the first heating cycle, the conductivity gradually increased with temperature from 300 to 1000 K. From 1100 to 1300 K, the conductivity increased rapidly and then dropped off slightly. In the range 1500...2000 K, the conductivity increased again. The $\log \sigma$ vs T^{-1} shows a linear dependence. On quenching from 2000 to 310 K, the normal conductivity dropped by five orders of magnitude. In the second cycle, the conductivity increased gradually up to 400 K. The change on slope of the electrical conductivity in the first heating cycle was attributed to changes in the structure. Up to 1000 K, the enstatite starting material persisted, but it began to transform to ilmenite at 1100 K. The ilmenite then transformed to perovskite at temperatures from 1300 to 1500 K. This perovskite, subsequently quenched from 2000 K, persisted at temperatures from 310...900 K in the second heating cycle. In the perovskite stability field (1500...2000 K in the first cycle and 500...900 K in the second one) the electrical conductivity is described by $\sigma = \sigma_0 \exp(-E_a/k_B T)$ where σ_0 is the conductivity at infinitely high temperature and E_a is the activation energy. The activation energies for stable and quenched perovskites are 0.92 and 0.41 eV, respectively. A value of 0.42 eV at 23 GPa was reported for a quenched perovskite at similar temperature. [93S2].

For electrical conductivity see also: pyroxene [73D4, 74P1, 79D1, 79H1, 79V2, 79W1, 82P2]; enstatite [73D5, 78S1, 81H1].

Diopside

Impedance spectra for two natural diopside single crystals were obtained at 800 to 1300°C and 1 bar pressure over the frequency range 0.001 Hz to 1000 kHz in a system closed to all components but oxygens [88H1]. For the near end-member composition $\text{Ca}_{0.96}\text{Na}_{0.03}\text{Mg}_{0.96}\text{Fe}_{0.03}\text{Al}_{0.02}\text{Si}_2\text{O}_6$, over the $\log f_{\text{O}_2}$ (f_{O_2} in bars) range from -9 to -14 , at 1000°C and -8 to -12 at 1200°C, the conductivity [$\Omega^{-1}\text{m}^{-1}$] for three crystallographic orientations at 1 bar pressure is given by: [100]: $\log \sigma = 1.43 - 10850/T - 0.181 \log f_{\text{O}_2}$; [010]: $\log \sigma = 0.88 - 10170/T - 0.12 \log f_{\text{O}_2}$; [001]: $\log \sigma = 1.58 - 11080/T - 0.15 \log f_{\text{O}_2}$. The activation energy is 2.1 eV. At both higher and lower f_{O_2} values, no f_{O_2} dependence of conductivity was observed, indicating the presence of different conduction mechanisms. At $T < 1000^\circ\text{C}$, the activation energy is 1.3 eV, also suggesting a different conduction mechanism. Thus, at least four regimes were necessary to describe the behaviour of diopside in the T - f_{O_2} space. The approximately $\partial \log \sigma / \partial \log f_{\text{O}_2} = -1/(7(1))$ value, in the high-temperature region, suggests a reaction by which oxygen vacancies control the conductivity. A diopside with greater Fe content, $\text{Ca}_{0.96}\text{Na}_{0.02}\text{Mg}_{0.85}\text{Fe}_{0.12}\text{Si}_{1.99}\text{O}_6$, is more conducting and has a smaller activation energy, $E_a = 1.0$ eV, over the range 1050 to 1225°C and shows only a weak negative f_{O_2} dependence: [100]: $\log \sigma = -0.89 - 4640/T - 0.03 \log f_{\text{O}_2}$; [010]: $\log \sigma = -0.25 - 5270/T - 0.02 \log f_{\text{O}_2}$, suggesting that oxygen vacancies are present but are not the dominant defect in controlling the conductivity.

For electrical conductivity of diopside see also [81H1, 88H1, 00S2].

Aegirine

The electrical conductivity of aegirine is $\sigma(573 \text{ K}) \cong 10^{-4} \Omega^{-1}\text{cm}^{-1}$, at atmospheric pressure [74P1, 82P2]. This is 2...5 orders of magnitude higher than in Fe-poor natural pyroxenes. Later on, the dc and ac electrical conductivities were measured on two different aegirine crystals denoted LA²³⁾ and SM²⁴⁾ (footnotes see Table 10) [04S1]. The temperature dependences of the extrapolated dc conductivity σ_{dc} and of ac conductivity $\sigma'(\omega)$ (with $\omega = 1\text{ MHz}, 100 \text{ kHz}, 10 \text{ kHz}$) recorded parallel and perpendicular to [001] direction are plotted in Fig. 92a. The interpretation of $\log \sigma$ vs T^{-1} in terms of two straight lines with a break seems not to be adequate. However, in [04S1] each curve was approximated by straight lines in the limit of high and low temperatures, which allows different activation energies. By applying the model of a hopping charge transport by small polarons between localized states of nearest neighbours [69A1, 82L1], the activation energies in the low and high-temperature limit were determined. For measurements || [001] in the high-temperature range, $E_a = 0.42$ eV (SM) and 0.47 eV (LA) was obtained, while for those performed at low temperatures, $E_a = 0.33$ (SM) and 0.37 eV (LA). The same values were shown for measurements \perp to [001]. The value for the SM sample of σ_{dc} || [001], at 300 K, $\sigma_{\text{dc}} = 2 \cdot 10^{-6} \Omega^{-1}\text{cm}^{-1}$, is depending on temperature and by a factor of 2-10 above that measured \perp [001]. This means anisotropic charge transport. Below $\cong 350$ K, the ac conductivity $\sigma'(\omega)$ is enhanced relative to σ_{dc} for both directions, with an increasing difference for rising frequencies on lowering the temperature. The ac conductivity curves merge into the σ_{dc} curve, at different temperatures – Fig. 92b. An approximate power law for $\sigma'(\omega)$ was shown, at higher frequencies and low temperatures, with $\sigma'(\omega) \propto \omega^s$, a relation frequently observed for amorphous and disordered semiconductors. Scaling the $\sigma'(\omega)$ data was possible with reference to σ_{dc} , which results in a quasiuniversal curve for different temperatures. The experimental data were discussed in light of theoretical models of hopping charge transport and of a possible $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ electron hopping mechanism [04S1]. In terms of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ electron hopping, transport paths along zig-zag chains || [001] are evident in pyroxene structure, while \perp [001] such paths are only possible via intervening M2 and/or T sites as well as via impurities and vacancies. The thermopower S (Seebeck effect) in the temperature range $\cong 300 \text{ K} < T \leq 770 \text{ K}$ is negative, for both directions and both crystals – Fig. 92c. There is a linear $S = f(T^{-1})$ relationship above $\cong 400$ K with activation energies $E_s \cong 0.03$ eV (|| [001]) and 0.07 eV (\perp [001]).

For electrical resistivity of pyroxenes see also [79H1].

8.1.4.1.9 Dielectric properties

Diopside, spodumene

The dielectric constants and dissipation factors for $\text{LiAlSi}_2\text{O}_6$ and $\text{CaMgSi}_2\text{O}_6$ in both the crystalline and amorphous forms are listed in Table 13 [92S1]. The dielectric properties of spodumene glass, progressively crystallized at different conditions, was also determined. As the crystallization temperature was increased from 720 to 920°C, the dielectric constants, ϵ' , increased from 6.22 to 6.44. The dissipation factor, $\tan\delta$, remained constant at 0.020. Similarly, as the crystallization time increased from 0.5 h to 60 h at 750°C, ϵ' increased from 6.28 to 6.35. Diopside with Ca and Mg ions having normal bond valence sums, exhibits no abnormal deviation from the additivity rule. Larger positive deviations in amorphous $\text{LiAlSi}_2\text{O}_6$ and $\text{CaMgSi}_2\text{O}_6$ are postulated to arise from a combination of closely bonded cations and disordered O^{2-} ions, where the oxygen dielectric polarizability increased from its normal value of 0.2 \AA^3 in well behaved oxides, to $2.2\text{--}3.0 \text{ \AA}^3$ in the amorphous phase.

Aegirine

The dielectric permittivity, $\epsilon'(\omega)$, of aegirine LA^{22} (see Table 10 for composition) at higher temperatures shows a considerable dispersion, while it is weak at low temperatures – Fig. 93 [04S1]. The tendency towards similar values, at higher frequencies, is qualitatively seen – Fig. 93b. At 1 MHz, a weak variations with temperature can be recognized.

8.1.4.1.10 XANES and EXAFS data

$\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$

Silicon K-edge absorption near edge structure (XANES) spectra in enstatite shows in general, features A, C, D, E, F and G related to the SiO_4^{4-} cluster [95L1] – Fig. 94. Peak A is attributed to the transition of Si 1s electrons to the antibonding 3s-like state. This peak is very weak. Peak C was assigned to the transition of Si 1s electrons to the antibonding 3p-like state. The transition is allowed by the selection rules, so that peak C is very strong. This peak is located at 1846.7 eV in MgSiO_3 and 1846.3 eV in MnSiO_3 rhodonite showing a Q^2 -type polymerization. The peak is referred to as the Si K-edge. Peaks E and G were attributed to the transitions of Si 1s electrons to the e and t_2 states characterized by the empty Si 3d states, respectively, and called “symmetry-forbidden shape resonances” [72D1]. Peaks D and F were qualitatively attributable to the multiple scattering effects from more distant atoms.

The $\text{Mg}_2\text{Si}_2\text{O}_6(\text{En}) - \text{Fe}_2\text{Si}_2\text{O}_6(\text{Fs})$ orthopyroxenes have been studied by XANES spectroscopy with mainly the aim to interpret the variation found in the spectra due to the Mg-Fe substitution [90M2, 91M4, 94P1, 95F1, 95P1, 96C1, 96W3, 02G1]. The experimental XANES spectra, at the Fe K-edge, are shown in Fig. 95a [02G1]. Several variations occur in the spectra of the En – Fs join at increasing En content: (1) the relative intensity of peaks A and B changes. (2) peak C splits into two components with increasing En content, (3) peak D broadens and shifts to lower energies and additional peaks (E, F) become more evident with increasing En content. The peaks at higher energy C, D, E result from superposition of contributions from the first-shell oxygens and the next-nearest Mg, Fe, Si and O atoms. Thus, they are affected both by the local structure around the absorber in the M1 and M2 sites and, due to the strong difference in phase shift and backscattering power between Fe and Mg, to the local environment around Fe. Particularly, peaks C and D are single and less broad in the more Fe-rich spectra and progressively split at high En content (>30 %). The continuous intensity variation of peaks A and B can be related to both the variable chemistry along the En – Fs join, and also to the distribution of Fe (and Mg) in the two octahedral sites [94P1]. A linear relation between intensity ratios I_B/I_A versus En content was observed. The experimental XANES spectra at the Mg K-edge are shown in Fig. 95b. They are composed of pre-edge peak (P), three narrow peaks (A, B and C) in the edge region, and a broad D peak. As for the Fe K-edge spectra, the intensity ratio of the more intense peaks I_B/I_A are approximately linear dependent on the En content. Theoretical spectra have been calculated, both at the Fe and Mg K-edge, to interpret the experimental data. These spectra, obtained by locating Fe (or Mg) in M1 and M2 sites and weighing these contributions according to occupancy data obtained by the Rietveld structure refinement, reproduce well the experimental spectra.

For MgSiO_3 perovskites, by XANES studies, it was suggested that Fe is likely to be substituted by Mg within (8+4)-coordinated sites [94F1, 95F1].

Ca-Na pyroxenes

The XAS studies were performed on Ca-Na pyroxenes at the K edge of Al on jadeite [85M1] and omphacite [95L2], at the Mg K edge on diopside [94Y3, 95I1, 96L1] and diopside (augite) [98C1]. The data on Fe M1 atoms were also reported [85D1]. The spectra were broad and unresolved, as they contain contributions from both Fe^{2+} and Fe^{3+} . Theoretical studies on Ca-Na pyroxenes were performed for the Al K edge of jadeite [89M5] and for the Mg K edge of diopside [98C2]. In [99M1] the synthetic end member diopside (Di) and jadeite (Jd) and a series of natural clinopyroxenes compositionally straddling the Jd – Di join were studied by X-ray absorption spectra at the Mg and Al K edges. The spectra of C2/c end members and intermediate member solid solution series (C-omphacites) are different from those of the intermediate members having P2/n symmetry (P-omphacites). Atomic clusters with at least 89 atoms, extending to more than 0.60 nm away from Mg or Al absorbers, were necessary to reproduce the experimental spectra. This shows that in the clinopyroxene systems, XANES detects medium-rather than short-range order-disorder relationships. Certain near-edge features of C-omphacites reflect the octahedral arrangement of the back-scattering six O atoms being nearest neighbours of the probed atom (Mg or Al) located at site M1 of the crystal structure, thus being indicators of short-range order. Others arise again from medium-range order. P-omphacites show more complicated spectra than C-omphacites. Their additional features reflect the increased complexity of the structure and the greater local disorder around the probed atom induced by the two alternative M1, M11 configurations of the six O atoms forming the first coordination shells. Mg and Al were confirmed to be preferentially partitioned in the M1 and M11 sites of the P-omphacite crystal structure, however, with a certain degree of local disorder. The relative heights of certain prominent features were directly related to sample composition in terms of Di/Jd ratio in the Al K-edge spectra, whereas they show abrupt variations in the Mg K-edge spectra [99M1].

The pyroxene samples were studied by Ca K-edge XANES [87D2, 95P1]. The Ca-Na pyroxenes were also analyzed by Na, Mg and Al K-edges XANES method [96M1, 97M1].

CaFeSi₂O₆ glass

In [00R2] the environment of ferrous iron in CaFeSi₂O₆ glass was studied by EXAFS. Two average coordinations were found: fourfold and fivefold, associated with distorted tetrahedral and trigonal bipyramids, respectively. The medium-range order is characterized by the presence of cations Fe^{2+} and Ca^{2+} as NNN at short distances, characteristic of edge-sharing polyhedra. The iron polyhedra are apex connected to the silicate network, while edge-linked to each other and the calcium polyhedra. The occurrence frequency of these edge sharing polyhedra is that expected from a random distribution or a limited segregation of iron in the glass.

For EXAFS and XANES studies of amorphous silicates as jadeite glass, diopside see [87C1].

8.1.4.1.11 Raman and infrared spectroscopy data

Fe_xMg_{1-x}SiO₃

Raman spectroscopic studies were performed on pyroxene [88M1, 00H1], particularly on the end member compositions [75W1, 87M1, 89S2, 89S3, 92C2, 94G3, 94W1, 99C2, 01U1]. According to [98C3, 99C2] in pyroxenes having space group Pbc_a there are $30A_{1g}(R) + 30B_{1g}(R) + 30B_{2g}(R) + 30B_{3g}(R) + 30A_{1u} + 30B_{1u}(IR) + 30B_{2u}(IR) + 30B_{3u}(IR)$ modes, where R and IR denote Raman and IR active modes, respectively. In [00H1] less than 20 Raman active modes were observed – Fig. 96. Some modes are degenerate, others are too weak to be observed. In general, these pyroxenes are characterized by: (1) the Si-O nonbridging and bridging modes at 1020(50) cm⁻¹ and 900(50) cm⁻¹, respectively. (2) the Si-O bending modes at 600(90) cm⁻¹ and (3) metal-oxygen bending and stretching modes below 600 cm⁻¹. Peaks in the 800...1100 cm⁻¹ region are generally assigned to Si-O stretching vibrations, normally related to the nonbridging Si-O bond. The wavenumbers of the Si-O stretching modes of the bridging O atoms (Si-O_{br}) were assigned to those in the range 650...750 cm⁻¹. The bending modes are those from the O-Si-O bends with a wavenumber between 500...590 cm⁻¹. Therefore, in the OPx series, there are four modes from the stretching bridging O atoms, three modes from the stretching nonbridging O atoms and four modes from the bending O-Si-O. In addition, two modes may result from the Mg-O octahedron (375...490 cm⁻¹) and two modes from the Fe-O octahedron (225...325 cm⁻¹). The variation of Raman peak positions with Fe^{2+} content is shown in Fig. 97 [00H1]. Most frequencies decrease with increasing Fe content. This phenomenon was attributed to an increase in both the bonding lengths and reduced mass, as Fe^{2+} is substituted for Mg. However, two modes at ≈ 900 cm⁻¹ increase in frequencies when the Fe content increases. A

possible explanation is the shortening in the Si-O-Si bridging bonding bonds when the M2 sites are preferentially occupied by iron cations.

Normal coordinated calculations, producing synthetic IR and Raman spectra were performed on pyroxenes [87D3].

The single crystal polarized Raman spectra of MgSiO_3 **orthoenstatite**, from various scattering geometries with their group-theoretical mode assignments are shown in Fig. 98 [98C3]. The long-wavelength phonon modes at the Γ point were mentioned above. The A_g , B_{1g} , B_{2g} and B_{3g} modes are Raman active. The B_{1u} , B_{2u} and B_{3u} modes are IR active, while the A_u modes are optically inactive. There are 120 Raman active modes in orthoenstatite. The calculated phonon frequencies are in overall fair agreement with experimental Raman data [98C3]. The most intense observed A_g Raman bands are at 82, 132, 343, 663, 687, 1014 and 1033 cm^{-1} . The 1014 and 1033 cm^{-1} modes are intense only in the $Z(XX)\bar{Z}$ geometry. There is a cell doubling in going from protoenstatite [94G3] to orthoenstatite and, correspondingly, more peaks are observed in the Raman spectra of orthoenstatite compared to protoenstatite. Consistent with lattice-dynamical calculations, the lowest Raman active A_g mode in protoenstatite, at 104 cm^{-1} , softens to 82 cm^{-1} in orthoenstatite. The peak corresponding to the A_g mode at 667 cm^{-1} in the Raman spectra of protoenstatite splits into two peaks in the orthoenstatite spectra at 663 and 687 cm^{-1} . The single peak in the protoenstatite spectra corresponds to the symmetric stretching vibrations of the bridging oxygen atom O3. In protoenstatite, there is only one kind of silicate tetrahedral chain resulting in only one mode frequency. In orthoenstatite, there are two kinds of tetrahedral chains A and B, with their kinking angle nearly 19° apart at RT, resulting in two closely spaced mode frequencies. The 663 (686) cm^{-1} modes correspond to the symmetric stretching vibrations of the bridging oxygens O3B [O3A] of the B(A) chains with two types of Si-O3 bond lengths: longer average, 1.676 Å, and shorter average 1.657 Å, respectively [98C3]. The corresponding calculated mode frequencies are at 734 and 758 cm^{-1} , respectively. The A_g modes at 1014 and 1033 cm^{-1} involve stretching of the Si-O nonbridging oxygens in the B(A) chains.

The high-pressure $C2/c \rightarrow P2_1/c$ transition in enstatite was studied by Raman spectroscopy of MgSiO_3 quenched from the stability field of the high- p $C2/c$ enstatite [01U1]. The pressure induced transition of orthoenstatite has been estimated by Raman spectroscopy to occur at ≈ 5 GPa [92C2] or ≈ 9 GPa at RT [97H3, 99C2]. In contrast to what was observed in ferrosilite, Raman spectroscopic data show that the phase transition of enstatite is reversible at RT [92C2, 99C2]. The recovered enstatites show different Raman spectra [92C2, 99C2]. In [03L1] the phase behaviour of synthetic orthoenstatite was analysed up to ≈ 22 GPa by using Raman spectroscopy. Below 10 GPa, neither the lattice modes nor the internal modes of SiO_4 have a discontinuous change in slope of the ν - p plots. The continuous and smooth frequency shifts in Raman modes do not confirm the argument that the SiO_4 tetrahedra are incompressible within 4 GPa. At 10 GPa, orthoenstatite begins to transform to a high-pressure phase. The forward phase transition finishes at 11...12 GPa. Above 10 GPa, all the frequencies of Raman bands increase with increasing pressure again, and a further transition was not observed up to ≈ 22 GPa. Upon decompression, the high-pressure phase remained stable down to ≈ 9.5 GPa and then gradually transformed back to orthoenstatite, only this phase being observed at $p < 7$ GPa. The transition type has been inferred to be of first order and the high-pressure polymorph may be the intermediate between orthoenstatite and the high-pressure clinoenstatite (i.e. high- p $C2/c$ phase). The high-pressure polymorph was suggested to be an intermediate between orthoenstatite and high- p $C2/c$ phase [03L1]. The pressure-temperature (p - T) boundary between orthoenstatite and high-pressure clinoenstatite has been determined [77Y1, 90P1, 91K1, 01U1]. Nevertheless, one cannot preclude the possibility of the presence of any stable and/or metastable phase between orthoenstatite and high- p $C2/c$ enstatite at low temperatures, because the above p - T boundaries were valid for $T > 600^\circ\text{C}$. The phase transitions of synthetic clinoenstatite have been further studied by using Raman spectroscopy at various pressures and at RT [04L1]. The Raman spectra of the high-pressure polymorphs of clinoenstatite and orthoenstatite at RT are plotted in Fig. 99a, b [04L1]. It is obvious that the two spectra are different although the frequencies of some bands in the two phases are close. In comparison with orthoenstatite, the transition pressure for the forward transition of clinoenstatite is 3.5 GPa lower than that of orthoenstatite, and the transition rate and mechanism in clinoenstatite are different from those in orthoenstatite. Thus, the two enstatites have different high-pressure polymorphs. According to [04L1] the high-pressure polymorph of orthoenstatite may be an intermediate phase between orthoenstatite and the high- p $C2/c$ enstatite. Contrary to what was observed in clinoenstatite, the high- p $C2/c$ enstatite displays a positive pressure dependence in the average pressure derivative of Raman frequencies – Fig. 99c. This behavior has been correlated with a

significant rotation in silicate chains and the formation of highly kinked SiO_4 chains in the high- p $C2/c$ enstatite during the compression [04L1].

The factor group analysis of MgSiO_3 **ilmenite** gives the number and symmetries of expected bands as follows: $5A_g(R) + 5E_g(R) + 4A_u(IR) + 4E_u(IR)$. Therefore, the Raman spectrum should contain 10 bands. For MgSiO_3 ilmenite 7 definite bands were observed – Fig. 100a [84R2]. The highest frequency modes occur near 800 cm^{-1} and are probably at least partly associated with silicon-oxygen stretching motions. The unpolarized IR reflectance spectra of MgSiO_3 ilmenite possessed all eight peaks, required by symmetry, between 337 and 850 cm^{-1} – Fig. 100b [92H2]. There are three distinct strong peaks near 377 , 448 and 619 cm^{-1} , an intense band from 665 to 951 cm^{-1} with subsidiary features, a medium-weak peak at 536 cm^{-1} and possible weak features at 380 , 600 and above 950 cm^{-1} . The sharpness and periodicity of the multitude of weak peaks below 300 cm^{-1} suggests that these are due to diffraction fringes arising from the small sample size. Weak features above 950 cm^{-1} are more likely overtones.

The polarized Fourier transform IR spectra of hydrous MgSiO_3 akimotoite, having ilmenite-type structure, containing 350 ppm (wt) H_2O as hydroxyl, were studied [02B1]. The presence of 3300 and 3320 cm^{-1} bands, due to hydroxyl groups oriented nearly perpendicular to the c -axis as well as a strong band at 3390 cm^{-1} caused by OH molecules aligned nearly parallel to c were shown. Unpolarized IR measurements performed up to 13.8 GPa show that the bands shift to lower frequencies with increasing pressure, which is consistent with hydrogen bonding. At $\approx 9\text{ GPa}$, the bands initially at 3300 and 3320 cm^{-1} merge, suggesting that these two bands represent the same type of hydroxyl group [02B1].

For MgSiO_3 **perovskite** the number and symmetry of expected modes and their Raman and infrared activity are: $7A_{1g}(R) + 7B_{1g}(R) + 5B_{2g}(R) + 5B_{3g}(R) + 8A_{1u}(\text{inactive}) + 7B_{1u}(IR) + 9B_{2u}(IR) + 9B_{3u}(IR)$ [87W1, 87W2]. A much smaller number of peaks were observed: four in the Raman spectrum between $250\ldots 500\text{ cm}^{-1}$ and four in the mid-infrared region between 500 and 800 cm^{-1} ; the positions of the peaks in the mid-IR region are shown in Fig. 101a [87W1]. These bands were divided into three separate groups: high-frequency ($\approx 800\text{ cm}^{-1}$) modes caused by asymmetric silicon-oxygen stretching motions; intermediate-frequency ($370\ldots 690\text{ cm}^{-1}$) modes predominantly due to octahedral stretching and bending vibrations and the low-frequency ($200\ldots 300\text{ cm}^{-1}$) modes involving Mg^{2+} motion. The pressure shift of the four mid-IR modes – Fig. 101b – yields an average Grüneisen parameter of $1.36(15)$. See also [86W1].

CaSiO_3

Pseudowollastonite Raman spectra were investigated by [98R3] and those of wollastonite, the stable form of CaSiO_3 below 1400 K , by [69G3, 71R3, 96S5, 98R3, 00H1]. The Raman spectra of wollastonite and pseudowollastonite are similar, although the former is somewhat simpler than the latter – Fig. 102 [98R3]. These similarities allowed general band assignments to be made for pseudowollastonite. The frequency of most of the bands of pseudowollastonite vary linearly with temperature. At high frequencies, the three bands observed should represent mainly Si-O stretching modes. The linewidths of the $\nu_{12} = 932\text{ cm}^{-1}$ and $\nu_{14} = 1075\text{ cm}^{-1}$ bands increase at a rate twice as that of the most intense $\nu_{13} = 989\text{ cm}^{-1}$ mode. At intermediate frequencies, the $\nu_{10} = 558\text{ cm}^{-1}$ band broadens markedly before being overwhelmed by the much more intense $\nu_{11} = 580\text{ cm}^{-1}$ mixed stretching bending of the Si-O-Si bridging band. At low frequencies, the seven bands distinguished at RT between 217 cm^{-1} and 428 cm^{-1} should represent deformation of the silicate network along with Ca-O stretching. They eventually form a broad feature, at the highest temperature, partly as a result of a large increase in width of the $\nu_8 = 373\text{ cm}^{-1}$ and $\nu_9 = 428\text{ cm}^{-1}$ bands.

The IR spectra of CaSiO_3 perovskite was also reported [88W1].

$\text{Li}_{0.3}\text{Sc}_{0.3}\text{Mg}_{1.4}\text{Si}_2\text{O}_6$

The analysis of the crystal structure of $\text{Li}_{0.3}\text{Sc}_{0.3}\text{Mg}_{1.4}\text{Si}_2\text{O}_6$ protoenstatite shows that the silicate is completely ordered with Li^+ in M1 and Sc^{3+} in M2 sites [77S4]. The long wavelength phonon modes at the Γ point can be classified as $14A_g + 16B_{1g} + 14B_{2g} + 16B_{3g} + 14A_{1u} + 16B_{1u} + 14B_{2u} + 16B_{3u}$ [94G3, 94G4]. The A_g , B_{1g} , B_{2g} and B_{3g} modes are Raman active; the B_{1u} , B_{2u} and B_{3u} modes are IR active, while the A_u modes are optically inactive. The recorded spectra are plotted in Fig. 103 [94G3]. An important consequence of doping is the broadening of the spectra as compared to pure $\text{Mg}_2\text{Si}_2\text{O}_6$. In situ measurements at 1320 K show that the Raman spectra of pure $\text{Mg}_2\text{Si}_2\text{O}_6$ [89S2] are similar to the observed spectra in the doped compound. Because the dopants are completely

ordered with Li^+ in the M1 and Sc^{3+} in the M2 site, the formal charges of these sites are 1.7 and 2.3, respectively. The experimental frequencies and mode assignments with the corresponding calculated values show good agreement. The most intense observed A_g bands are at 103, 300, 313, 369, 671 and 1030cm^{-1} . The eigenvector of the Raman active A_g mode at 103 cm^{-1} involves Mg translations, silicate translations, rotations and Si-O3 stretch. The 300 and 313 cm^{-1} modes involve significant displacements of all the atoms and a mixing of internal and external modes. The 671 cm^{-1} mode was attributed to the symmetric stretching of the bridging oxygen in the chain. The A_g mode at 1030 cm^{-1} involves symmetric stretching of the Si-O nonbridging oxygen.

For (Li,Sc) protoenstatite see [89S3].

ZnSiO₃

Raman scattering and IR powder absorption spectra were collected for ZnSiO₃ clinopyroxene and ilmenite [89L1]. The entropy change for the clinopyroxene – ilmenite transition was calculated from the spectra and estimated for the directionally-averaged acoustic velocities. The values $\Delta S = -12(5)\text{ J/mol K}$, calculated using a variety of plausible densities of states, agrees with the value from phase equilibria, $\Delta S = -12.7(6.0)\text{ J/mol K}$.

Diopside

The earlier works, who studied the vibrational properties of diopside, had carried out factor group analysis to obtain the number of vibrational modes and their symmetries [70E1, 71O1, 71R3, 72E1, 75W1, 76Z2, 80T1, 81F1, 81O1, 82O1, 96S4, 98R3]. In [97S2] the mode assignment was completed. An example of the Raman spectra is given in Fig. 104a. The temperature evolution of the modes display different temperature dependencies – Fig. 104b – with slopes from $-0.021\text{ cm}^{-1}/\text{K}$ to $-0.004\text{ cm}^{-1}/\text{K}$. The temperature shift of low-frequency modes is generally higher. The frequencies of normal modes of vibration, for a long chain $(\text{Si}_2\text{O}_6)_n$ module, in both IR and FIR absorption spectra were calculated. These were found in agreement with those measured [71O1].

Raman spectra of diopside were analyzed up to 71 GPa [02C2]. Changes in the pressure dependence of the modes occurred in spectra at three different pressures. First, at approximately 10 GPa, the two Raman modes at 356 and 875 cm^{-1} disappeared, while the mode at 324 cm^{-1} splits into two modes, diverging at this pressure with significantly different pressure shifts. Second, at approximately 15 GPa, a small (1 to 2 cm^{-1}) drop in several of the frequencies was observed accompanied by changes in the pressure dependence of some of the modes. Above 55 GPa, the modes characteristic of chains of tetrahedrally-coordinated silicon disappeared, while those for octahedrally-coordinated silicon appeared. The first change at 10 GPa appears to be a C2/c to C2/c transition involving a change in the Ca coordination. This transition is possible since pyroxene crystallizes in three C2/c structures [94H2] and the transition may be from the RT diopside structure to a high-pressure form in which the silicate chain is substantially kinked with an O3-O3-O3 angle below 135° and an octahedrally coordinated M2 site. The third change, above 55 GPa, appears to be a change in the silicon coordination. At 15 GPa, it was suggested that a change in compressional mechanism takes place.

Diopside – hedenbergite

Raman spectroscopic patterns for some $(\text{Mg,Fe,Ca})\text{SiO}_3$ pyroxenes are plotted in Fig. 96 [00H1]. The discussion concerning the spectra is on the same line as for the $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ system. The Raman active modes in CPx are $14A_g + 16B_{1g}$ [71R3]. For a constant calcium content, frequencies of Raman modes in the diopside – hedenbergite (CPx) series decrease with an increase in the Fe content – Fig. 105. The effect of Fe substituting for Mg on the frequency shift in CPx is less important than in OPx because the larger M2 site was occupied by Ca and substitution of Fe and Mg in the M1 site results in a less significant change in the bond length.

The Raman spectral features were used to characterize the structural and compositional pyroxenes $(\text{Mg,Fe,Ca})_2\text{Si}_2\text{O}_6$ [01W1]. Values of $\text{Mg}/(\text{Mg} + \text{Fe} + \text{Ca})$ ratios were determined with accuracy ± 0.1 .

CaScAlSiO₆ – CaAl₂SiO₆

The Raman studies show that the T-O-T stretching band of CaScAlSiO₆ pyroxene can be deconvoluted in three bands – Fig. 106 – corresponding to Al-O-Al, Al-O-Si and Si-O-Si stretching vibrations, although in the case of CaAl₂SiO₆, the spectrum can be convoluted into two bands (Al-O-Al + Al-O-Si) and Si-O-Si [88S3]. The Al-O-Si Raman shifts of CaScAlSiO₆ and CaAl₂SiO₆ pyroxenes were found to fall on the linear plot of the relationship

with T-T distances suggesting that Al-O-Si chains are relatively long. The experimental data suggest that there is more disorder in the tetrahedral sites in $\text{CaAl}_2\text{SiO}_6(100)$ than in $\text{CaScAlSiO}_6(100)$. This disorder coincides with covalent character of $\text{AlAl}(100)$.

$\text{CaScAlSiO}_6 - \text{CaTiAl}_2\text{O}_6$

Deconvolution of Raman spectra of the above clinopyroxenes indicates that the chains in the CaScAlSiO_6 pyroxene are composed, as above, of Si-O-Si, Si-O-Al and Al-O-Al bonds and aluminium, “avoidance” rule is violated [83O3]. The weakness of the Si-O-Si stretching vibration band in $0.7\text{CaScAlSiO}_6 - 0.3\text{CaTiAl}_2\text{O}_6$ indicated that Al and Si are not randomly distributed throughout the tetrahedral sites but there is a Si/Al ordering to some extent.

Augite – jadeite

Infrared spectra of ordered P2/n and disordered C2/c pyroxenes belonging to the join augite – jadeite were investigated at RT in the range $70 \dots 1400 \text{ cm}^{-1}$ [98B2]. Some IR spectra for natural ordered and experimentally disordered samples are shown in Fig. 107. The phase transition $\text{P2/n} \rightarrow \text{C2/c}$ produces an increase in band widths and the number of resolved peaks decreases. The autocorrelation function quantified changes in linewidths due to these effects. Phonons are at low frequencies very sensitive to both changes in composition and degree of order and are indicative of a non-ideal mixing behaviour for the C2/c solid solution. At high frequencies, phonons depend on the average composition of the sample and not on local configuration changes related to the order-disorder transition. High degrees of local heterogeneity were suggested by Δ_{corr} values of the C2/c omphacites at intermediate compositions. We note that Δ_{corr} is a function proportional to the average of the linewidth of the spectral range considered [98B2]. This effect is most evident in the low-frequency region of the spectra, corresponding to modes involving, primarily, the M cations. The changes in frequency due to ordering, $\Delta\omega$, and the change in linewidths, $\delta(\Delta_{\text{corr}})_{100-200}$, for the spectral region $100 \dots 200 \text{ cm}^{-1}$ and $\delta(\Delta_{\text{corr}})_{210-800}$ for the range $210 \dots 800 \text{ cm}^{-1}$ have been used to characterize the state of local order at different compositions.

Hydrous components in anhydrous minerals have been studied by IR [96R4]. It was concluded that in natural enstatite, diopside and augite, the contents of H_2O are 650, 515 and 529 ppm wt. These data proved the suggestion [72M3] that hydroxyl resides as point defects in the structure of pyroxenes.

$\text{LiFeSi}_2\text{O}_6, \text{NaFeSi}_2\text{O}_6$

Synthetic aegirines, $\text{LiFeSi}_2\text{O}_6$ and $\text{NaFeSi}_2\text{O}_6$, were studied by IR and Raman spectroscopy in the $20 \dots 300 \text{ K}$ temperature range [02Z1]. For the C2/c phase of $\text{LiFeSi}_2\text{O}_6$, 25 of the 27 predicted IR bands and 26 of 30 predicted Raman bands were recorded at RT. $\text{NaFeSi}_2\text{O}_6$ (C2/c type) shows 25 IR and 26 Raman bands. On cooling, the C2/c – $\text{P2}_1/\text{c}$ structural phase transition of $\text{LiFeSi}_2\text{O}_6$ (see section 8.1.4.1.1) is characterized by the appearance of 13 additional recorded peaks. This indicates the enlargement of the unit cell at the transition point. The appearance of an extra band near 688 cm^{-1} in the monoclinic $\text{P2}_1/\text{c}$ phase, which is due to the Si-O-Si vibration in the Si_2O_6 chains, indicates that there are two nonequivalent Si sites with different Si-O bond lengths. Most significant spectral changes appear in the far-infrared region, where Li-O and Fe-O vibrations are mainly located. Infrared bands between 300 and 330 cm^{-1} show unusually dramatic changes at temperatures far below the transition. Compared with the IR data of $\text{NaFeSi}_2\text{O}_6$, measured at low temperatures, the change in $\text{LiFeSi}_2\text{O}_6$ spectra is interpreted as the consequence of mode crossing in the frequency region.

$\text{NaTiSi}_2\text{O}_6$

The infrared reflectivity and Raman scattering spectra of $\text{NaTiSi}_2\text{O}_6$ were measured both below and above T_C [05P2]. From modes predicted by factor group analysis for the monoclinic symmetry (27 IR and 30 Raman), at RT 20 IR and 21 Raman were observed. By lowering temperature, changes (new modes or mode splitting) appear at the positions where modes of different symmetry have nearly the same energy. At the transition temperature, the antisymmetric (B) modes become symmetric (A) and the modes closed in energy start to couple. As example of changes we analyse the temperature dependences of modes in the $500 \dots 575 \text{ cm}^{-1}$ and $930 \dots 990 \text{ cm}^{-1}$ frequency range – Figs. 108a, b [05P2]. The mode at 553 cm^{-1} , B_g^{10} , due to O1-T1-O2 and O1-Si-O2 bending, first hardens by temperature lowering, and at about 200 K starts to soften due to the coupling with a

neighbouring mode. By further temperature decrease the coupling becomes stronger resulting in a mode repulsion and intensity exchange (inset Fig. 108a). The mode at $\approx 946\text{ cm}^{-1}$ softens for about 10 cm^{-1} while the mode at 966 cm^{-1} splits and hardens by 25 cm^{-1} – Fig. 108b. The linewidth of the 965 cm^{-1} phonon line increases up to a maximum located at $\approx 210\text{ K}$ and then decreases to saturation value – Fig. 108c. This means that the bond fluctuations are considerably larger in the high-temperature than in the low-temperature phase. The normalized frequencies for several Raman active modes together with normalized magnetic susceptibility are plotted in Fig. 108c [05P2]. Analysing the phonon frequencies and damping as function of temperature as shown in Fig. 108c, it can be shown that the phase transition leaves a finger print in the phonon dynamics of $\text{NaTiSi}_2\text{O}_6$ [05P2].

Li_2SiO_3 , Na_2SiO_3

The Raman spectra of Li_2SiO_3 [77D1, 96R3] and Na_2SiO_3 [75B1, 76K1, 96R3] are similar, but vibrational frequencies are lower for Na_2SiO_3 than for Li_2SiO_3 . These shifts are of the order of $10\text{--}15\text{ cm}^{-1}$ for modes involving essentially Si-O bending and stretching. They are higher for the low-frequency modes involving alkali-oxygen stretching whose wavenumbers range between 520 and 210 cm^{-1} for Li_2SiO_3 and between 510 and 170 cm^{-1} for Na_2SiO_3 [96R3]. The Raman frequencies of Li_2SiO_3 vary regularly with temperature up to the melting point, which is consistent with the lack of premelting effects in calorimetric measurements. In contrast, Na_2SiO_3 undergoes a transition at about 850 K ($\text{Cmc}2_1 - \text{Pmc}2_1$) and shows changes in the Raman spectra near 1200 K that correlate well with the premelting effects, as determined from calorimetry observations. Premelting in Na_2SiO_3 was associated with extensive deformation of the silicate chains as evidenced near the melting point by similarities in the Raman spectra of the crystalline and liquid phases.

8.1.4.1.12 Other optical properties

$\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$

The optical properties of $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ OPx with $x = 0.15$ and $x = 0.395$ were studied by observing bands around 11000 , 5400 and 3100 cm^{-1} in the α , β and γ spectra along the b , a and c axes of the crystal, respectively [66W1, 67B1, 67W1, 73R1, 77G1]. These bands were assigned to different transitions between the energy levels arising from the ground term ^5D of the $3d^6$ configuration of the Fe^{2+} ion, placed at the noncentrosymmetric distorted M2 site, which is subject to different perturbations like spin-orbit coupling and considerable distortion from the regular octahedral symmetry. The spectra from Fe^{2+} at the M1 site was not observed as it was much weaker and may have overlapped by the stronger absorption lines due to the former. In [77G1] the spectra of $\text{Fe}_{0.15}\text{Mg}_{0.85}\text{SiO}_3$ enstatite were studied and a band was found at 2350 cm^{-1} instead of 3100 cm^{-1} , as reported earlier [66W1, 67B1]. They also analysed the spectra of Fe^{2+} at the M2 site considering 2mm (C_{2v}) symmetry, using the crystal field theory based on a point charge model, appropriate for an ionic system and neglected the spin-orbit interaction as well the covalency effect. According to [65G1], the higher degree of covalency of Fe^{2+} at the M2 site, as evidenced by two short M-O bonds between Fe^{2+} and two underbonded oxygens, is the driving force for the strong site preference. In [70B1] the higher value of the crystal field stabilization energy at the M2 site was suggested to account for the site preference. In [01V1] was shown that the strong site preference of Fe^{2+} for the M2 site originates from the fact that all the degeneracies of the energy levels of the Fe^{2+} ions at the M2 site are lifted by ligand field effect, resulting in greater stabilization arising from the combination of the site distortion and the relatively greater degree of the covalency of the bonds between Fe^{2+} at the M2 site and underbonded oxygens in the orthopyroxene crystal structure. The electronic absorption spectra of ferrous ions in orthopyroxenes was a subject of debate. There is fair agreement on the transition between energy levels of the Fe^{2+} in the distorted M2 octahedra of site symmetry 1. In [77G1] a review of the previous literature was given and symmetry allowed $\text{Fe}^{2+}(\text{M2})$ transition in OPx was assigned on the basis of the pseudosymmetry 2mm (C_{2v}): $^5\text{A}_1 \rightarrow ^5\text{A}_1$ α -polarized 11000 cm^{-1} ; $^5\text{A}_1 \rightarrow ^5\text{B}_1$ β -polarized 5400 cm^{-1} ; $^5\text{A}_1 \rightarrow ^5\text{B}_2$ γ -polarized 2350 cm^{-1} . Some divergencies concerning the bands caused by Fe^{2+} in M1 octahedra were reported. In [70B1] the band at 8500 cm^{-1} as well as a band lying beneath the main absorption near 11000 cm^{-1} were attributed to ferrous ions in M1, whereas in [79G2], on the basis of heating experiments, a band near 13000 cm^{-1} and the band at 8500 cm^{-1} were assigned to this origin. Also, the position of a $\text{Fe}^{2+}\text{-Fe}^{3+}$ charge transfer (CT) band is controversial. In [70B1] the following ranges of wavelengths for the $\text{Fe}^{2+}\text{-Fe}^{3+}$ CT band were mentioned: $16666\text{--}14286\text{ cm}^{-1}$ and $18182\text{--}14286\text{ cm}^{-1}$. Based on this assignment, [79G2] interpreted a band at 17000 cm^{-1} as $\text{Fe}^{2+}\text{-Fe}^{3+}$ CT. In

[75L4, 81B2] a $\text{Fe}^{2+}\text{-Fe}^{3+}$ CT band was localized at 14500 cm^{-1} . We note that the $\text{Fe}^{2+}\text{-Fe}^{3+}$ and $\text{Fe}^{2+}\text{-Ti}^{4+}$ charge transfer in earlier papers was correlated with nuclear distances in orthopyroxenes [70B1] and aegirine [80A1]. Later on, the criteria used to identify $\text{Fe}^{2+}\text{-Fe}^{3+}$ and $\text{Fe}^{2+}\text{-Ti}^{4+}$ intervalence charge transfer absorption bands in electronic spectra were reviewed [87M3]. No correlation between energy and distance was reported. In [88S5] such a correlation was evidenced.

The polarized spectra of synthetic ferrosilite were reported by [77L1, 88S5]. Some data given by [88S5] are shown in Fig. 109. Similar spectra were evidenced in $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{Si}_2\text{O}_6$ enstatite and $(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{Si}_2\text{O}_6$ hypersthene [88S5]. The 11000 cm^{-1} band was considered to be caused by Fe^{2+} in M1 (${}^5\text{B}_{2g} \rightarrow {}^5\text{A}_{1g}$) and Fe^{2+} in M2 (${}^5\text{A}_1 \rightarrow {}^5\text{A}_1$), the 8500 cm^{-1} band by Fe^{2+} in M1 (${}^5\text{B}_{2g} \rightarrow {}^5\text{B}_{1g}$) and the 5000 cm^{-1} band by Fe^{2+} in M2 octahedra (${}^5\text{A}_1 \rightarrow {}^5\text{B}_1$). The $\text{Fe}^{2+}\text{-Fe}^{3+}$ charge transfer band was identified at 12500 cm^{-1} in the spectra of synthetic $\text{Fe}^{3+}\text{-Al}$ bearing ferrosilite. This band shows a strong γ -polarization and therefore was considered as caused by $\text{Fe}^{2+}\text{-Fe}^{3+}$ -ions in edge-sharing octahedra. The energy of the spin-allowed Fe^{2+} -transition in pure ferrosilite near 8500 cm^{-1} does not change significantly on a $(\text{Fe}^{3+}\text{Al})$ for $(\text{Fe}^{2+}\text{Si})$ substitution, whereas the Fe^{2+} transition near 11000 cm^{-1} might be slightly reduced in energy by incorporation of $(\text{Fe}^{3+}\text{Al})$. The third band near 5000 cm^{-1} was measured in enstatite and Fe^{3+} -bearing ferrosilite. The introduction of Fe^{3+} drastically changes the shape of the γ -spectra of ferrosilite by creating a strong band with large half width and maximum at 12500 cm^{-1} . This band is missing in the α -spectrum.

The spin-forbidden absorption bands of Fe^{2+} in M2 site in orthopyroxenes were calculated [86Z1, 87Z1, 87Z2]. By means of only one parameter, most of the spin-forbidden bands of Fe^{2+} have been determined. When a similar treatment was made for the M1 site, the entire spin-forbidden spectrum of Fe^{2+} in OPx could be semiquantitatively explained. The spin forbidden transitions are ${}^5\text{A}_1 \rightarrow {}^3\text{A}_1$, ${}^3\text{A}_2$, ${}^3\text{B}_1$ and ${}^3\text{B}_2$. In the above papers the transition from the ground state ${}^5\text{A}_1$ to the triplet ${}^3\text{A}_2$ was neglected on the basis of its being doubly forbidden, both by orbital symmetry and because $\Delta S \neq 0$. In [87R3] was shown that neglecting the ${}^5\text{A}_1 - {}^3\text{A}_2$ transition is without justification.

The electronic absorption spectra of **clinoferrosilite** at ambient conditions and at high pressures were reported [96S2]. Four absorption bands were shown at ambient conditions: around 11000 cm^{-1} attributed to Fe^{2+} in the M2 site (${}^5\text{A}_1 \rightarrow {}^5\text{A}_1$), around 10000 cm^{-1} attributed to Fe^{2+} in the M1 site (${}^5\text{B}_{2g} \rightarrow {}^5\text{A}_{1g}$), around 8100 cm^{-1} attributed to Fe^{2+} in the M1 site (${}^5\text{B}_{2g} \rightarrow {}^5\text{B}_{1g}$), and a weaker band at 5100 cm^{-1} due to Fe^{2+} in the M2 site (${}^5\text{A}_1 \rightarrow {}^5\text{B}_1$). The crystal field stabilization energy for Fe^{2+} in M1 and M2 sites are 3924 cm^{-1} and 3863 cm^{-1} , respectively. The bands at 11000 cm^{-1} and 10000 cm^{-1} do not shift linearly with pressure, but display discontinuity between 1.61 and 1.9 GPa, corresponding to the $\text{P2}_1/\text{c} \rightarrow \text{C2}/\text{c}$ transition [96S2].

Crystal field spectra of Mn^{3+} -bearing **clinopyroxene** have been reported [86G1]. They assigned absorption bands at 19000, 17300, 16800 and $\approx 8000\text{ cm}^{-1}$ to spin-allowed electronic dd transitions in trivalent manganese at the six-coordinated M1 site. From these energies they calculated a value $10 Dq = 13650\text{ cm}^{-1}$ for Mn^{3+} at this site.

The optical absorption spectra of synthetic **perovskites** $\text{Mg}_{0.94}\text{Fe}_{0.06}\text{SiO}_3$ [94K2], $\text{Mg}_{0.95}\text{Fe}_{0.05}\text{SiO}_3$ and $\text{Mg}_{0.90}\text{Fe}_{0.10}\text{SiO}_3$ [94S2] were analysed. The spectrum – Fig. 110 – shows three main features: (1) A system of crystal field bands centered at 7000 cm^{-1} , which is caused by the transition ${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$ of Fe^{2+} in the dodecahedral site. (2) A broad band due to $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ intervalence charge transfer occurs at 14900 cm^{-1} . (3) A sharp increase in absorption above 20000 cm^{-1} probably results from O-Fe^{3+} charge transfer. The crystal field splitting of Fe^{2+} was reported as $\Delta = 6835\text{ cm}^{-1}$ and crystal field stabilization energy (CFSE) as 4350 cm^{-1} [94K2]. In [94S2] a value of 3332 cm^{-1} was reported for CFSE.

For optical spectra of pyroxenes see also [75L4].

$\text{Mg}_{1-x}\text{Co}_x\text{SiO}_3$, $\text{Mg}_{1-x}\text{Ni}_x\text{SiO}_3$

The clinoenstatites $\text{Mg}_{1-x}\text{M}_x\text{SiO}_3$ ($\text{M} = \text{Co}, \text{Ni}$) exhibit spectra characteristic for transition metal ions in octahedral site. For cobalt compounds, the spectra show additional splittings from site distortion [71W1]. The crystal field parameter for Ni^{2+} in clinoenstatite is 690 cm^{-1} and much smaller than in diopside. This suggests that Ni^{2+} in clinoenstatite orders on the larger M2 site. The Dq value for Co^{2+} in clinoenstatite is similar to the value determined for diopside. This provides circumstantial evidence that Co^{2+} is mainly located on the M1 site [71W1].

Diopside

The room temperature α -, β - and γ -polarized spectra of Cr^{3+} doped diopside – Fig. 111 – show in the near UV to near IR spectral regions two broad and strong band systems [94T1]. These resemble close to those of Cr^{3+} in clinopyroxenes [85A1, 85K3]. The bands are typical of spin-allowed Cr^{3+} dd-transitions derived from $^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}$, the U-band ($\sim 15400\text{ cm}^{-1}$), or from $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}$, the Y-band ($\cong 23000\text{ cm}^{-1}$), in octahedral fields [94T1]. The data were interpreted similar as in [85A1, 85K3], that the three sharp component maxima of the low-energy band system originate from spin-forbidden dd-transitions of Cr^{3+} . Thus, the U-band is superimposed by these spin forbidden bands. The same is true for the Y-band because of the strong influence of the absorption edge – Fig. 111. The integral intensity of both U and Y bands do not significantly change with increasing temperature because of opposite effects of band broadening and maxima lowering. A broad band, showing up near 12500 cm^{-1} strongly gains intensity on cooling. All these properties would be consistent with Fe^{2+} - Fe^{3+} charge transfer, which is possible on the basis of sample composition: (wt %) 58.07 SiO_2 , 0.03 TiO_2 , 0.32 Al_2O_3 , 0.76 Cr_2O_3 , 1.69 FeO , 0.05 MnO , 15.40 MgO , 23.10 CaO , 0.52 Na_2O . The crystal field strength of Cr^{3+} is $Dq = 1553\text{ cm}^{-1}$ and the Racah parameter $B = 702\text{ cm}^{-1}$ [94T1].

The Mn^{3+} dd-absorption band in Fe-free synthetic diopside single crystals were studied [96H1]. Some differences compared with those reported by [86G1] were shown. Curve resolved spectra show – Fig. 112 – that the band around 17400 cm^{-1} ($E \parallel b$) is not a true single absorption, but the sum of absorption bands at 16800 and 18600 cm^{-1} . An additional band exists at 20350 cm^{-1} , which is obscured by strong UV edge absorption in Fe-containing samples. The pleochroic behaviour of Mn^{3+} bands is not consistent with the scheme predicted by the oxygen ligand arrangement at the M1 site, (2 (C_2) symmetry); it was suggested that charge contributions from next-nearest ions and vibronic coupling effects have to be considered. A weak and sharp absorption peak at 24400 cm^{-1} , interpreted previously as an Fe^{3+} - Mn^{2+} pair transition [86G1], is present also in spectra of Fe-free synthetic samples and was assigned in [96H1] to a Mn^{2+} - Mn^{3+} pair transition.

The crystal field spectra of Mn^{3+} in aegirine – diopside clinopyroxene were analysed [86G1]. The Mn^{3+} ion occurs in octahedral M1 site, resulting in a considerable distortion of this site by the Jahn-Teller effect of the Mn^{3+} ion. A crystal field parameter $10Dq = 13650\text{ cm}^{-1}$ and crystal field stabilization energy of 146 kJ/g-atom were determined.

$\text{CaMg}_{1-x}\text{Co}_x\text{Si}_2\text{O}_6$, $\text{CaMg}_{1-x}\text{Ni}_x\text{Si}_2\text{O}_6$

The diffuse reflectance spectra of $\text{CaMg}_{1-x}\text{Ni}_x\text{Si}_2\text{O}_6$ are characteristic for transition metal ions in an octahedral field [71W1]. Only the cobalt compounds have spectra with the expected additional splittings from site distortion. Values $Dq = 840\text{ cm}^{-1}$ for Ni^{2+} and 802 cm^{-1} for Co^{2+} in the above diopsides were determined [71W1].

Rhodonite: Mn^{2+}

The optical absorption spectra of Mn^{2+} in rhodonite have been studied [68M1, 72L1, 73L1, 75M1, 81L2, 86Z2, 89G1]. The spectra were calculated assuming a high site symmetry $m3m(\text{O}_h)$ [68M1, 81L2], considering the splitting as result of the spin-orbit coupling [73L1] or based on the detailed strong-field matrix including the $4\text{mm}(\text{C}_{4v})$ crystal field, the electron-electron interaction and the spin-orbit coupling [89G1]. The calculated data from [68M1, 73L1, 81L2] were not in agreement with experimental results. It was suggested that there must be some tetragonal distortion in the crystal field surrounding the Mn^{2+} and the contribution to dd transitions should be considered [73L1]. According to [73L1], values of spin-orbit coupling $\xi = 320\text{ cm}^{-1}$ and $Dq = 750\text{ cm}^{-1}$ were obtained. It was shown by [89G1] that the calculated dd transition energy levels are similar for the M1, M2 and M3 sites. Therefore the absorption spectrum of Mn^{2+} in rhodonite for the M1, M2, M3 sites cannot be distinguished by optical absorption experiments.

Kanoite, $\text{MnMg}(\text{Si}_2\text{O}_6)$

The temperature dependence of the birefringence is plotted in Fig. 113 [97A2]. Starting at RT, the retardation of the P_{21}/c phase (low kanoite) increases slightly up to the beginning of the $\text{P}_{21}/c - \text{C}2/c$ transition at $\cong 205^\circ\text{C}$. With continued heating, an abrupt change of interference colours is observable corresponding to an increase of retardation. At 215°C , the grain is divided into $\text{C}2/c$ and P_{21}/c phase fields. At $T \cong 240^\circ\text{C}$, kanoite grain changes completely to the high kanoite form. A $\text{P}_{21}/c - \text{C}2/c$ two-phase field extends over approximately 30°C .

Spodumene: Mn²⁺

The absorption and emission spectra of Mn²⁺ doped spodumene (kunzite) are shown in Fig. 114a [92C1]. In the absorption spectrum, two very weak bands are observed and assigned to the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (18870 cm⁻¹) and ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (23260 cm⁻¹) transitions, respectively. The emission spectrum of LiAlSi₂O₆ consists of a single broad band at roughly 16000 cm⁻¹ – Fig. 114b. Except for narrowing, there is little change in lineshape with decreasing temperature. The lineshape and emission wavelengths are about as expected for Mn²⁺ in the approximately octahedral M1 site.

CaSiO₃: Pb²⁺, Mn²⁺

CaSiO₃: Pb²⁺ gives violet-blue emissions and is useful as black light phosphorus [49S1]. The luminescence of CaSiO₃: Pb²⁺, Mn²⁺ has been found to vary with crystal structure of the matrix [48F1, 48F2, 52F1]. The luminescence properties are given in Table 14. Among them, δ-CaSiO₃: Pb²⁺ was found to give a strong violet blue emission (\approx 341 nm) as well as β-CaSiO₃: Pb²⁺ [82M2]. In β-Ca_{1-x}Pb_xSiO₃ the emission band of samples shifted to longer wavelength and broadened with increasing content of Pb²⁺ ions [82M2]. For samples with $x \geq 0.07$, the emission spectra were found to consist of two bands. A concentration quenching effect on luminescence was observed.

SrSiO₃: Pb²⁺, Eu³⁺, Bi³⁺

The emission intensity of SrSiO₃: Pb²⁺ drastically increased when the host lattice transformed into the high-pressure phases (δ- and δ'-forms). In SrSiO₃: Eu³⁺, Bi³⁺, the effect of high pressure obviously makes the intensity and quantum luminescence efficiency to decrease, the half-width increase and the red shift of the emission peak increase to 756 cm⁻¹ – Fig. 115 [93L2]. The variation in luminescence characteristics was attributed to the pressure induced change in crystal structure during synthesis. For luminescence properties of SrSiO₃: Eu³⁺, Bi³⁺ [93L2] as well as of CaSiO₃: Eu²⁺ see Table 14. For Eu³⁺ doped metasilicate see [82M3].

CdSiO₃: Sm³⁺

Cd_{1-x}Sm_xSiO₃ synthesized by conventional solid state reaction exhibits a pink light emitting long-lasting afterglow, when excited by a 254 nm light for 1 min [04L2]. The long-lasting phosphorescence seems to result from the recombination of holes and electrons trapped in the CdSiO₃ matrix that can be thermally released at RT.

NaCrSi₂O₆

The reflectance spectrum of NaCrSi₂O₆ (kosmochlor) shows two strong absorption bands at 15600 and 22000 cm⁻¹ characteristic of Cr³⁺ in sixfold coordination [71W1]. The crystal field and Racah parameters for Cr³⁺ are $Dq = 1560$ cm⁻¹ and $B = 646$ cm⁻¹, respectively.

NaCrSi₂O₆ – NaScSi₂O₆

The optical transition of octahedral Cr³⁺, ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (ν_2 band), shows two separate trends in the wavenumber-composition diagram, reflecting the conditions under which the pyroxenes were formed [87O4]. The lower-energy band splits into three minor bands. These bands represent transitions from the resolved d orbitals of the t_{2g} groups to the low-energy orbital of the resolved e_g groups (${}^4A_{2g} \rightarrow {}^4T_{2g}$).

CaMgSi₂O₆ – NaCrSi₂O₆

The absorption spectra of the diopside – kosmochlor system show that these are due to octahedrally-coordinated Cr³⁺ ions with triplet-splitting at the lower-energy major band and broadened splitting at the higher-energy major band, owing to the distortion of the M1 site from cubic symmetry [74I1]. Crystal field splitting parameter 10 Dq and Racah parameter are nearly constant through this series, as expected from their structural data.

CaMgSi₂O₆ – NaCrSi₂O₆ – NaScSi₂O₆

The crystal field spectra were analysed [83O1].

Cs₅CoSiO₆

The absorption spectrum of Cs₅CoSiO₆ gives some support for the presence of a high-spin [CoO₄]⁵⁻ complex. The IR spectrum shows characteristic stretching modes for orthosilicates [01H1].

Some refractive indices of pyroxenes, pyroxenoids and related silicates are listed in Table 15.