

### 8.1.4.8 Fenaksite, deerite, haradaite and related silicates

The silicates from the above groups are listed in Table 1 as well their compositions [91N1]. The physical properties of alamosite,  $\text{PbSiO}_3$ , were already presented (see Chap. 8.1.4.1). Synthetic silicates having related compositions are included. In addition to data from Chap. 8.1.2.2 (subvolume 2712), some physical properties of  $\text{BaCu}_2\text{Si}_2\text{O}_7$  are included.

#### 8.1.4.8.1 Crystal structures. Lattice parameters

The atomic sites for some representative silicates are listed in Table 2. In Table 3 we give the lattice parameters as well as the space groups of silicates from the groups listed in Table 1.

#### Fenaksite, litidionite

The crystal structure of **litidionite**,  $\text{KNaCuSi}_4\text{O}_{10}$  [75P1] is similar to that of fenaksite,  $\text{KNaFeSi}_4\text{O}_{10}$  [71G1]. The silicates crystallize in a triclinic lattice having space group  $P\bar{1}$ . The basic structural feature of both silicates is a tubular silicate radical  $[\text{Si}_8\text{O}_{20}]^{8-}$  – Figs. 1a, b [75P1]. This radical is made up by condensation of two vlasovite-type chains [62V1] which are formed by rings of four tetrahedra. The tubular chains are parallel to  $c$  and are interconnected by Cu(Fe) and Na atoms. Potassium occurs in the large cavities existing in the pipe-like tetrahedral chains. The coordination polyhedron of Cu in litidionite is a fairly regular square pyramid whose base is formed by four oxygen atoms at distances ranging, in litidionite, from 1.96 Å to 1.99 Å. An oxygen atom, 2.55 Å from copper, is the vertex of the pyramid. The distances to the next closest oxygen is 3.24 Å. In **fenaksite**, the oxygen atoms of the base have Fe-O distances, ranging from 1.98 to 2.16 Å, while the apical oxygen is 2.37 Å from Fe. In litidionite the coordination polyhedron around Na atoms is similar to that around copper but is more distorted. Each coordination pyramid around copper is connected by edge sharing to another copper pyramid and to one sodium pyramid in such a way that pairs of pyramids around copper alternate with pairs of pyramids around sodium forming serrate chains parallel to  $c$ . A similar arrangement can be seen in fenaksite. The atomic sites for litidionite are given in Table 2.

#### $\text{Na}_2\text{MSi}_4\text{O}_{10}$ , (M = Co, Ni, Cu)

The  $\text{Na}_2\text{CoSi}_4\text{O}_{10}$ ,  $\text{Na}_2\text{NiSi}_4\text{O}_{10}$  [97D1] and  $\text{Na}_2\text{CuSi}_4\text{O}_{10}$  [77K1] silicates are isostructural. The compounds crystallize in a triclinic lattice having space group  $P1$ . The structure is made up of silicate pipes, exhibiting  $[\text{Si}_8\text{O}_{20}]^{8-}$  radicals as shown in Fig. 2a, drawn using the same unit cell transformation as [77K1] to get a structure similar to litidionite. Such radicals are connected to each other in the  $c$ -axis direction (pipe axis) by oxygen atoms. In the  $b'$  axis direction, the  $\text{SiO}_4$  tetrahedra from two adjacent radicals, do not share oxygen atoms and the cohesion of the structure is realized by means of Na1 polyhedra with four intraradical and two interradsilical Na-O bonds, Na1 atoms being inside the  $[\text{Si}_8\text{O}_{20}]^{8-}$  units, whereas M and Na2 are outside. In the  $a'$ -axis direction, the silicate pipes are linked by M and Na2 polyhedra. Both Na atoms have an irregular environment with seven oxygen neighbours. The main difference of M = Co, Ni samples to samples with M = Cu concerns the M environment. Whereas copper has four nearest neighbours in the form of a square and one additional oxygen atom at much longer distance, the environment around Co and Ni looks like a more regular square pyramid. As shown in Fig. 2b, two edge-sharing square pyramids around M atoms define isolated  $(\text{M}_2\text{O}_8)^{4-}$  dimers with M-M distances around 3.17 Å. The lattice sites are given in Table 2.

#### Vlasovite, $\text{Na}_2\text{ZrSi}_4\text{O}_{11}$

The X-ray analysis of vlasovite [62V1, 67F1] showed that the structure was characterized by a silicon-oxygen radical: a  $[\text{Si}_4\text{O}_{11}]_\infty^{6-}$  strip. The structure was refined later [74V1]. Two layers cut out parallel to the (001) plane from the heterogeneous Si-Zr framework. Each of these pseudotetragonal layers is, in general features, similar to the analogous layers of narsarsukite,  $\text{Na}_2\text{TiSi}_4\text{O}_{11}$ . In addition to this, Fig. 3 demonstrates the basic scheme of the geometrical transition from the structure of vlasovite to the crystal structure of narsarsukite. For this compound the layers neighbouring one another in the  $z$ -direction should be mutually displaced by  $b/2$ . The subsequent "vertical" conjunction of the octahedra into an infinite chain and the fourfold Si rings into a "tubular" strip accompanied by the necessary rotation of the polyhedra, constitutes the final stage in the creation of the other heterogeneous framework, namely, the Si-Ti framework of narsarsukite.

### Agrellite, $\text{NaCa}_2\text{Si}_4\text{O}_{10}\text{F}$

The agrellite crystallizes in a triclinic structure having space group  $P\bar{1}$  [76G1, 78G1, 79G1]. The crystal structure consists of: (a) silicate tubes cross linked by sodium atoms into sodium silicate layers; (b) calcium polyhedral layers both parallel to the (010) plane, alternating along the *b*-axis to form a three-dimensional framework [79G1]. The silicate tube consists of two centrosymmetrically-related single silicate chains. Each single chain is formed by corner-sharing four-membered tetrahedral rings (Si1- Si2- Si3- Si4 in Fig. 4) and is the same as the  $[\text{Si}_4\text{O}_{11}]$  chain found in vlasovite [62V1, 67F1]. Within each chain two tetrahedra and the four-membered ring point up and two down along the *b*-axis. Two centrosymmetrically related chains are connected by sharing opposing tetrahedral corners, giving rise to silicate tubes with the composition  $[\text{Si}_8\text{O}_{20}]$  whose diameter is defined by a basket-shaped six-membered ring [Si2- Si3- Si1- Si4- Si3'- Si1']. In addition, each tube contains two different boat-shaped eight-membered tetrahedral rings (Si1- Si4- Si2- Si1'- Si3- Si4'- Si2'- Si3' and Si3- Si4- Si2- Si3'- Si1- Si4'- Si2'- Si1') which have four tetrahedra in common. There are two crystallographically distinct silicate tubes (A and B), whose configurations are only slightly different from each other. These silicate tubes run parallel to the *c*-axis and are hexagonally close-packed in the (001) plane. The silicate tubes occur in layers parallel to the (010) plane. Within each layer they are packed in a staggered fashion, leaving cavities at the boat-shaped eight-membered rings. The sodium atoms occur within these cavities in eightfold coordination. The  $\text{Na(A)}\text{O}_8$  and  $\text{Na(B)}\text{O}_8$  polyhedra are distorted cubes with very similar configurations. Each Na polyhedron shares six corners with the silicate tube below and two with the silicate tube above. In addition, two Na polyhedra occurring on either side of a silicate tube share a polyhedral edge (O6-O6') thereby forming a dimer. Two crystallographically distinct sodium silicate layers (A and B), parallel to the (010) plane, with very similar stereochemical configurations are formed in this way [79G1]. Both Ca atoms (Ca1A, Ca2B) are coordinated to six oxygen and two fluorine atoms each. The irregular coordination polyhedron consists of two parts: (a) a square-pyramid formed by five oxygen atoms and (b) two fluorine atoms and an oxygen atom at the corners of a triangle occurring above the equatorial plane. Both Ca2A and Ca1B are surrounded by five oxygen and one fluorine atom each at the corners of distorted octahedra. The Ca1A site contains the most of rare-earth ions. If the calcium polyhedral layer is designated as C and its centrosymmetric equivalent as  $\bar{C}$  and the two different Na silicate layers as A and B, the stacking sequence of the layers along the *b*-axis is  $\text{ACB}\bar{C}\text{ACB}\bar{C}$  [79G1].

Silicate tubes with the composition  $[\text{Si}_8\text{O}_{20}]$  were shown in **agrellite**, **fenaksite**, [71G1], **litidionite** [75P1] and  $\text{Na}_2\text{CuSi}_4\text{O}_{10}$  [77K1]. In the last three isostructural compounds,  $[\text{Si}_8\text{O}_{20}]$  tubes are cross-linked by serrated chains of edge-sharing dimers of Fe(Cu)-square pyramids alternating with dimers of edge sharing Na-square pyramids. The potassium atoms (likewise one set of Na atoms in  $\text{Na}_2\text{CuSi}_4\text{O}_{10}$ ) occur in cavities created by the boat-shaped eight-membered tetrahedral rings and are closely comparable to the Na-coordination found in agrellite. However, in agrellite, there are two crystallographically distinct double chains, whereas in other mentioned compounds there is only one. This distinction is most likely created by the different coordination requirements of calcium and fluorine atoms in agrellite as opposed to the transition metals in fenaksite and litidionite [79G1]. In [78L1] the  $[\text{Si}_8\text{O}_{20}]$  tubes were termed as a "loop- branched dreier" (three tetrahedral repeat double chain). The group structures composed of silicate tubes are agrellite, narsarsukite [60P1, 62P1], canasite [69C1] and miserite [76S1]. The silicate tube in narsarsukite is defined by four-membered rings, whereas those in canasite and miserite are defined by two different types of eight-membered rings [79G1].

### $\text{Na}_2\text{Cu}_2\text{Si}_4\text{O}_{11}\cdot 2\text{H}_2\text{O}$ ; $\text{Na}_2\text{Cu}_2\text{Si}_4\text{O}_{11}$

The  $\text{Na}_2\text{Cu}_2\text{Si}_4\text{O}_{11}\cdot 2\text{H}_2\text{O}$  contains chains of edge-sharing  $\text{CuO}_6$  octahedra running along the [100] direction with a slight variation in Cu-Cu distances along the chains – Fig. 5a. The  $\text{Cu}^{2+}$  ions are coordinated by five  $\text{SiO}_4$  tetrahedra and one  $\text{H}_2\text{O}$  molecule. Adjacent  $\text{SiO}_4$  tetrahedra are linked along the chains by corner sharing [05M1]. The structure of the dehydrated copper silicate,  $\text{Na}_2\text{Cu}_2\text{Si}_4\text{O}_{11}$ , is similar to that of  $\text{Na}_2\text{Cu}_2\text{Si}_4\text{O}_{11}\cdot 2\text{H}_2\text{O}$ , the most significant difference being the change of the  $\text{Cu}^{2+}$  coordination, from octahedral to square pyramidal – Fig. 5b – due to the loss of coordinating water molecules with the corresponding slight rearrangement of the chain structure. In both structures the chains are separated from each other by  $\approx 5 \text{ \AA}$  and  $7 \text{ \AA}$  along the *b* and *c*-axes, respectively.

**Miserite,  $\text{KCa}_5\text{Si}_6\text{O}_{15}(\text{OH})\text{F}$** 

The crystal structure of miserite was studied by [60R1, 62K1, 67K1, 76S1]. The silicate crystallizes in a triclinic-type structure having space group  $P\bar{1}$  [76S1]. There are two crystallographically independent sub-chains in the cell, each extending parallel to  $c$ . These sub-chains are linked together into  $\text{Si}_6\text{O}_{16}$  double chains across a pseudo-mirror plane in  $ac$ . Operation of the  $\bar{1}$  symmetry of the space group produces a closed quadruple  $\text{Si}_{12}\text{O}_{30}$  composite chain, with the  $c$ -axis as its central axis, in which all tetrahedra share three corners. The pipe-like nature of the eight-membered ring of the composite chain is visible in  $c$ -axis projection at each corner of the cell. In  $b$ -axis projection pipes adjacent along  $a$  are seen to be displaced partially by  $c/2$ , producing the large  $\beta$  angle of the cell. Such a pair of pipes is cross-linked by 9-coordinated K atoms, each of which is bonded to six O atoms of the pipe in which it lies and to three O atoms in the pipe adjacent along  $a$  [76S1]. A feature of the miserite structure is the presence of a pair of independent  $\text{Si}_2\text{O}_7$  groups, isolated from the composite chains. Each group lies near the center of the cell and the two are related by the center of symmetry at  $1/2\ 1/2\ 1/2$ . The remainder of the cell is filled by columns of edge-sharing Ca polyhedra, linked both to the pipes and to the central  $\text{Si}_2\text{O}_7$  groups. As a result of the operation of the symmetry center at  $1/2\ 1/2\ 1/2$ , there are only three unique columns per cell. Within any column, each Ca polyhedron shares an edge with the ones above, below, before and behind it. In addition, polyhedra about the 7-coordinate calcium (Ca1 and Ca4) each share a different pair of edges with a single  $\text{Si}_2\text{O}_7$  group. The slab composed of Ca polyhedra and  $\text{Si}_2\text{O}_7$  groups form a stable structural unit, the anion matrix of which defines one 6-coordinate virtual cation site per asymmetric unit.

**Canasite,  $\text{K}_3\text{Na}_3\text{Ca}_5\text{Si}_{12}\text{O}_{30}(\text{O}, \text{OH}, \text{F})_4$** 

Canasite crystallizes in a monoclinic structure having space group Cm [59D2, 87R1]. The framework of silicate is represented by “tubes” of  $(\text{Si}_{12}\text{O}_{30})_\infty$ , that connect the “walls” of Ca-Na octahedra. It was found that one of the Ca positions is statistically occupied by Ca or Na. The general crystal chemical formula was suggested [87R1] to be  $\text{K}_3\text{Na}_{2+x}\text{Ca}_{6-x}\text{Si}_{12}\text{O}_{30}(\text{O}_{1-x}(\text{F}, \text{OH})_{3+x})_4$ . While the tube radius ( $\text{Si}_{12}\text{O}_{30}$ ) are quite identical for canasite and miserite [76S1], their structures differ in the construction of “walls” from Ca-Na polyhedra

**Lemoynite,  $(\text{Na}, \text{K})_2\text{CaZr}_2\text{Si}_{10}\text{O}_{26} \cdot (5-6)\text{H}_2\text{O}$** 

Lemoynite crystallizes in a monoclinic structure having space group C2/c [69P1, 74B1, 76L1]. The crystal structure consists of a  $\text{ZrSi}_5\text{O}_{13}$  framework with wide open tunnels where Na, K, Ca, atoms and the  $\text{H}_2\text{O}$  molecules are located. The  $\text{ZrSi}_5\text{O}_{13}$  frame comprises thick (7 Å) layers of hexagons of silicate groups. The sheets are bounded together by Zr atoms in sixfold coordination. These hexagons are tilted with respect to the layers plane (001). Silicon tetrahedra of the 7 Å sheets are bound to two, three or four other silicon tetrahedra. Lemoynite has four unit formulae  $(\text{Na}, \text{K})_2\text{CaZr}_2\text{Si}_{10}\text{O}_{26} \cdot (5-6)\text{H}_2\text{O}$  with a monoclinic C2/c cell, but shows a subcell with  $c' = c/2$  and a C2/m pseudo-symmetry. See also section on “altisite” below.

**Natrolemoynite**

Natrolemoynite, crystallizes in monoclinic structure having space group C2/m [01M1].

**Altisite,  $\text{Na}_3\text{K}_6\text{Ti}_2[\text{Al}_2\text{Si}_8\text{O}_{26}]\text{Cl}_3$** 

Altisite crystallizes in a monoclinic structure having space group C2/m [95F1]. The structure consists of (001) aluminosilicate tetrahedral slabs built up by pentamer  $[\text{AlSi}_4\text{O}_{16}]^{13-}$ , where an aluminium tetrahedron shares its corners with four silicon tetrahedra. Three slabs are connected by Ti octahedra and the resulting framework is crossed by three sets of infinite channels which contain the alkali atoms. Apart from the content of the channels, the same structural framework occurs in lemoynite, which has the space group C2/c and a double periodicity along [001]. The analysis of the temperature dependences of the cell parameters show a break at 400°C – Fig. 6. By keeping the crystal at 700°C, a slow continuous decrease of the cell parameters is observed. The break in the cell parameters dimensions, at 400°C, was attributed to minor modifications of the structure involving the occupancy factors of the two K sites and a slight shrinkage of the K1 coordination polyhedron.

Lemoynite [69P1] is structurally [74B1, 76L1] related to altisite, in spite of differences in their chemical and crystallographic characteristics [95F1]. Comparison of the two structures shows that altisite and lemoynite share

the same tetrahedral (001) slabs, without Al/Si substitution in the second silicate. The slabs are connected in the same way via octahedra which contain either Ti (altisite) or Zr (lemoynite). Consequently, the two structures display the same system of infinite channels. It is within these channels that the main differences are observed: ordered alkali cations in altisite and, apart from the ordered Ca atoms, disordered sites statistically occupied by Na, K and H<sub>2</sub>O in lemoynite. It follows that: (1) in lemoynite, Ca occupies the Na1 site of altisite; the higher charge of Ca causes some oxygens to have a lower coordination number; (2) the H<sub>2</sub>O present in lemoynite acts both as a donor and acceptor of hydrogen bonds and can play the role of Na<sup>+</sup> and Cl<sup>-</sup> in altisite; (3) the presence of Al and Cl in altisite makes available relative to lemoynite- a further five negative charges pfu, which are saturated by alkali cations. In spite of the fact that altisite and lemoynite are topologically identical, the substitution of (1/5)Si by Al in altisite provides a chemically new high-charge complex anion, [AlSi<sub>4</sub>O<sub>13</sub>]<sup>7-</sup>, which is particularly effective in building cages with high contents of alkalis. The additional presence of Cl<sup>-</sup> instead of H<sub>2</sub>O, as in lemoynite, makes the structure of altisite very stable and effective in incorporating alkalis [95F1].

#### **Penkvilksite, Na<sub>4</sub>Ti<sub>2</sub>Si<sub>8</sub>O<sub>22</sub>·4H<sub>2</sub>O**

The structure of the orthorhombic phase (penkvilksite 2O) has been considered in an earlier study to have space group Pmmn [77K2]. Later on, it has been reported to have space group Pnca [94M1]. The monoclinic phase (penkvilksite 1M) was reported to crystallize in space group P2<sub>1</sub>/c [94M1, 99L1]. Despite the different space group symmetries, the two polytypes have the same atoms, labeled in the same way, in the asymmetric unit. Actually they merely differ in the stacking of the same building blocks. Thus the same description is valuable for both polymorphs. The two independent tetrahedra play different roles in the structure. Si1-centered tetrahedra share two corners with other tetrahedra and two corners with TiO<sub>6</sub> octahedra – Fig. 7a. Si2-centered tetrahedra share three corners with tetrahedra and one corner with a TiO<sub>6</sub> octahedron. Spirals of corner-sharing tetrahedra develop along [010]. The periodicity of the spirals corresponds to six tetrahedral units. Si2-centered tetrahedra are shared between adjacent spirals, which are oriented in an alternate clockwise and counter-clockwise fashion. The stacking of the spirals along [001] gives rise to tetrahedral layers parallel to (100). The connection of neighbouring layers of tetrahedra is due to Ti<sup>4+</sup> cations in octahedral coordination [94M1]. An alternate way of describing the structure of penkvilksite is based on the fundamental blocks by TiO<sub>6</sub> octahedra and Si1-centered tetrahedra. The connection between octahedra and tetrahedra is made through the sharing of corners. Neighbouring blocks along (100) are linked by Si<sub>2</sub>O<sub>7</sub> groups [94M1].

The structure of penkvilksite bears some resemblance with that of lemoynite [76L1]. In the structure of lemoynite, layers of ZrO<sub>6</sub> octahedra occur, which are similar to the layers of TiO<sub>6</sub> octahedra in penkvilksite. However, the layers in lemoynite are connected to each other by means of layers formed by six-membered rings of SiO<sub>4</sub> tetrahedra instead of spirals of tetrahedra parallel to [010] as in penkvilksite. Moreover, the way the octahedra are connected by corner-sharing SiO<sub>4</sub> tetrahedra is different in the two structures [94M1].

The 2O and 1M polytypes of penkvilksite can be also described according to the OD theory [86D1], as two out of the four possible maximum degree of order (MDO) polytypes within a family of OD structures formed by two layers.

#### **Tumchaite, Na<sub>2</sub>(Zr, Sn)Si<sub>4</sub>O<sub>11</sub>·2H<sub>2</sub>O**

Tumchaite is isotypic with penkvilksite 1M and is chemically related to vlasovite [00S1]. The silicate crystallizes in space group P2<sub>1</sub>/c. As in both 1M and 2O polytypes of penkvilksite, the dominant structure feature is the silicate sheet [Si<sub>4</sub>O<sub>11</sub>] parallel to (100), which can be considered as a result of condensation of the tetrahedral spiral chains running along [010] with six tetrahedra in the repeat unit – Fig. 7b [00S1]. Adjacent spirals are oriented in alternate clockwise and counter-clockwise way. The silicate sheets revealed in penkvilksite and in tumchaite extend the ideas about polymorphism of tetrahedral complexes [Si<sub>4</sub>O<sub>11</sub>] which were reported before as bands (amphiboles, vlasovite) or as framework (neptunite, Chap. 8.1.4.9). Tumchaite contains two symmetrically independent SiO<sub>4</sub> tetrahedra: Si1 and Si2 have two and three bridging O atoms, respectively. The tetrahedral silicate sheets are connected by cationic octahedra with a disordered distribution of Zr and Sn (at 0, 1/2, 0). The Zr/Sn ratio in these octahedra is 4. In the framework of the Liebau terminology [85L1] tumchaite has an unbranched single sheet with the fundamental vierer chains running parallel to [001]. The three-dimensional heteropolyhedral framework of tumchaite belongs to the series of typical mixed frameworks with general formula M<sub>m</sub>T<sub>n</sub>O<sub>3m+2n</sub>, where M and T are octahedrally and tetrahedrally coordinated

cations, respectively [00S1]. In these frameworks, tetrahedra and octahedra are connected only through vertices, each vertex being shared only by two polyhedra. The mixed frameworks of zirconsilicates which belong to this category have the formula  $[\text{Zr}_m\text{Si}_n\text{O}_{3m+2n}]^{2m-}$ . If the negative charge of the mixed framework is compensated only by alkaline cations, one obtains the general formula  $A_{2m}^+\text{Zr}_m\text{Si}_n\text{O}_{3m+2n}$  [00S1]. This series comprises synthetic silicates and minerals, namely Na-containing vlasovite, tumchaite, gaidonnayite, hilairite (see subvolume 2713), elpidite (see Chap. 8.1.4.6) etc. The mixed framework in their structures are characterized by the formation of the almost equivalent bonds Si-O-Si or Si-O-Zr which determine the stability of such polyhedral configurations. Similarly with penkvilksite, the  $\text{H}_2\text{O}$  molecule is linked only to  $\text{Na}^+$  and form H bonds with O1 and O5. Water molecules and  $\text{Na}^+$  cations are located in the wide cavities and tunnels of the mixed heteropolyhedral framework. The topology of the mixed framework allows tumchaite to be considered as a microporous zirconosilicate.

#### **Charoite, $(\text{K}, \text{Na})_5(\text{Ca}, \text{Ba}, \text{Sr})_8\text{Si}_{18}\text{O}_{46}(\text{OH}, \text{F})\cdot n\text{H}_2\text{O}$**

Charoite crystallizes in a monoclinic-type structure [78R1].

#### **Narsarsukite, $\text{Na}_2(\text{Ti}, \text{Fe})\text{Si}_4(\text{O}, \text{F})_{11}$**

The narsarsukite crystallizes in space group  $I4/m$  [62P1]. The structure is based of an arrangement of silicon tetrahedra. It can be described as made up of tubes having composition  $\text{Si}_4\text{O}_{10}$  parallel to the  $c$ -axis. Chains of titanium octahedra run parallel to the  $c$ -axis and bond together the  $\text{Si}_4\text{O}_{10}$  tubes. Sodium atoms occupy voids between the tubes and chains and have an irregular coordination of oxygen atoms.

#### **Caysichite, $(\text{Ca}, \text{Yb}, \text{Er})_4\text{Y}_4\text{Si}_8\text{O}_{20}(\text{CO}_3)_6(\text{OH})\cdot 7\text{H}_2\text{O}$**

Caysichite crystallizes in an orthorhombic-type structure having space group  $\text{Ccm}2_1$  [74H1, 78M1]. The structure can be described as built up by double columns of alternating CaR (calcium and rare-earth) and Y polyhedra, parallel to [001]. In each column CaR and Y polyhedra alternately share an edge and a corner with the carbonate groups wedged between two succeeding corner-sharing polyhedra. Each double column is connected to four other double columns to build up a three-dimensional framework. The connections are assured by edge sharing in the [100] direction and by corner sharing in the [010] direction. Further tightening of the structure in the [010] direction is assured by wedging carbonate groups between symmetry equivalent corner-sharing Y polyhedra. The double-column connection defines a checkered pattern of channels – Fig. 8a – in which run four-repeat double chains of silicon-oxygen tetrahedra [78M1]. We note the presence of so-called double crankshaft chains – Fig. 8b. The repeat distance down a chain is 9.73 Å, where the chains are isolated. They run in the large channels and are connected to the four double columns of CaR and Y polyhedra delimiting the channels. In the conventional classification of silicates, caysichite belongs to the chain silicates, in the subgroup characterized by four-repeat double chains of silicon-oxygen tetrahedra together with narsarsukite [60P1, 62P1]. The Y cation is coordinated with two oxygen atoms of silicate chain, five oxygen atoms of carbonate groups and a water molecule. The cations in the CaR site are coordinated with two oxygen atoms of the silicate chain, three oxygen atoms of the carbonate groups, a water molecule and an oxygen atom which corresponds either to a water molecule or a hydroxyl anion with equal occupancies. CaR and Y polyhedra in caysichite correspond well to Ca and Y polyhedra in kainosite [67R1] – Chap. 8.1.3.2 (subvolume 2713). The two kinds of substitutions, Ca-R and  $\text{H}_2\text{O}$ -OH which take place in the structure, are related. If a water molecule is located in the O14 site, both cations linked to it are likely to be Ca cations, whereas if a hydroxyl anion is located in that site then one of two cations is a  $\text{R}^{3+}$ . With such a coupled substitution a satisfactory local balance of charges is obtained.

#### **Leucosphenite, $\text{Na}_4\text{BaTi}_2\text{B}_2\text{Si}_{10}\text{O}_{30}$**

Leucosphenite crystallizes in a monoclinic structure having space group  $\text{C}2/m$  [71S1, 72C1, 72P1].

#### **Howieite, $\text{Na}(\text{Fe}, \text{Mg}, \text{Al})_{12}(\text{Si}_6\text{O}_{17})_2(\text{O}, \text{OH})_{10}$**

Howieite shows a triclinic structure having space group  $\text{P}1$  [73W1, 74W2]. This is a chain silicate, a hybrid between a single and a double chain. In effect, a four octahedra wide ribbon of the octahedral layer of mica is

sandwiched between two hybrid  $[\text{Si}_6\text{O}_{17}]$  chains. As for the tetrahedral sheets in mica, the apical oxygens of these chains face (and are shaped by) this ribbon. The resultant structural units run parallel to  $z$ , their flat sides being parallel to  $(1\bar{2}0)$  in howieite which is thus analogous to (001) in the sheet silicates. Where the flat sides of two such structural units are adjacent, the basal oxygens of their  $[\text{Si}_6\text{O}_{17}]$  chains form the interstice that accommodates the large Na-atom. Those basal oxygen, more distant from the Na atom, and thus at the edges of the structural units, are shared by the octahedral ribbons of neighbouring structural units [74W2]. – See also section on "deerite" below.

#### **Deerite, $(\text{Fe}, \text{Mn})_6(\text{Fe}, \text{Al})_3(\text{Si}_6\text{O}_{17})\text{O}_3(\text{OH})_5$**

The ideal structural formula of deerite is  $\text{Fe}^{2+}_6\text{Fe}^{3+}_3\text{O}_3[\text{Si}_6\text{O}_{17}](\text{OH})_5$ . The silicate crystallizes in a monoclinic structure of space group  $\text{P}2_1/\text{a}$  [65A1, 67A1, 77F1]. The deerite structure – Fig. 9a – has three sets of three virtually equivalent M atom positions and six Si positions per asymmetric unit. All the M atoms are octahedrally-coordinated with oxygen. The M octahedra are organized through shared coordination edges into a strip (or band) oriented parallel to  $\{110\}$ , six octahedra in width and continuous along the  $c$ -axis direction – Fig. 9b. The Si tetrahedra form a  $[\text{Si}_6\text{O}_{17}]$  silicate chain – Fig. 9c – also continuous along the  $c$ -axis direction. This is the hybrid single-double silicate chain, first reported for howieite [74W2]. Thus, the deerite structure can be represented in terms of two structural units, an M octahedral strip and a  $[\text{Si}_6\text{O}_{17}]$  silicate chain. Apical and lateral (non-bridging) tetrahedral oxygen are shared with M octahedra. However, the familiar sandwich of tetrahedral-octahedral coordination polyhedra, found in many chain and sheet silicate structures is not well developed in deerite (Figs. 9a, b). Also, the interstice enclosed by the basal tetrahedral oxygens is a structural void. The octahedral strips are interconnected by three oxygens (O7, O8, O9) which are coordinated only to M atoms [77F1]. The  $\text{Fe}^{3+} \leftrightarrow \text{Al}^{3+}$  substitution was studied in synthetic deerite [77L1].

**Howieite**, which is a hydrous sodium ferrous-ferric silicate, as already mentioned, has a crystal structure with analogous structural units to those in deerite. There are strips of M octahedra, four octahedra in width, enclosed by  $[\text{Si}_6\text{O}_{17}]$  silicate chains [74W2]. However, all the octahedral oxygen atoms are shared with Si tetrahedra. Thus, the octahedral strips and silicate chains form a definite tetrahedral-octahedral-tetrahedral sandwich, and the sandwich units are arranged to give a pseudo-layer structure. Also, the interstitial site is occupied by Na, although the back-to-back displacement of the silicate chains (which results in the eightfold-coordinated site for Na) is similar to that deduced for deerite. The silicate chains in deerite and howieite have quite a different orientation with respect to the M octahedra than in amphibole and pyroxene – Fig. 9d [77F1]. Within an octahedral strip the oxygen atoms are arranged in two layers of hexagonal close-packed array. Adjacent apical oxygen of the associated silicate chains have to be nearest neighbours in the same close-packed layer, and chain orientation is constrained by this requirement. Thus, in deerite and howieite, the silicate chains are parallel to one of the octahedral edges in the plane of the octahedral strip – Fig. 9d1 – whereas in amphibole and pyroxene the chains are transverse to one of three edges – Fig. 9d2 [77F1]. According to [77F1] it appears likely that  $\text{Fe}^{2+}$  occupies M4 to M9 and  $\text{Fe}^{3+}$  occupies M1 to M3 sites.

#### **Haradaite, $\text{SrVSi}_2\text{O}_7$ ; suzukiite, $\text{BaVSi}_2\text{O}_7$**

**Haradaite** crystallizes in an orthorhombic-type structure having space group  $\text{Amam}$  [67T1] or  $\text{Ama}2$  [67T1, 74W1]. **Suzukiite** is the barium analog of haradaite. For this silicate, space group  $\text{Amam}$  or  $\text{Ama}2$  was reported [82M1]. The salient feature of the haradaite structure are the  $\text{Si}_4\text{O}_{12}$  chains running along the  $a$ -axis – Fig. 10. The configuration of the chain is similar to the component chains of the  $\text{Si}_4\text{O}_{12}$  tubes found in narsarsukite [60P1, 62P1]. Such a chain has also been found in an isolated configuration in the structure of batisite [62N1]. In the structure of haradaite, these chains are joined together by vanadium to form a sheet which is closely related to that of lamprophyllite (Chap. 8.1.2.5 (subvolume 27I2)). If Ti, in the sheet of lamprophyllite, is replaced by V and two sheets as such are combined so that the  $\text{Si}_2\text{O}_7$  groups may form an infinite  $\text{Si}_4\text{O}_{12}$  chain, the sheet of haradaite will be derived. V atoms have a slightly distorted square pyramidal coordination. Among five bonds, the apical bond has a very short length suggesting that the bond is highly polarized. Sr atoms have eleven oxygen neighbours and are located between the sheets.

**BaCu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>**

The crystal structure is orthorhombic having space group Pnma [02H1]. This is made of almost isolated CuO<sub>3</sub> corner-sharing chains running along the *c*-axis. The magnetic ions occupy the 8d positions forming four zigzag chains along the *c*-axis. The Cu-O-Cu bond angle is 124°.

**Ohmilite, Sr<sub>3</sub>(Ti, Fe<sup>3+</sup>)(O, OH)(Si<sub>2</sub>O<sub>6</sub>)<sub>2</sub>·2-3H<sub>2</sub>O**

**Ohmilite** crystallizes in a monoclinic-type structure having space group P2<sub>1</sub>/m [73M1, 83M1]. The *b*-axis projection of the structure is shown in Fig. 11 [83M1]. The TiO<sub>6</sub> octahedra are joined by sharing vertex oxygen atoms to form a chain parallel to *b*, the shared oxygen atoms being in the mirror planes perpendicular to the chain extension. Each octahedral chain thus formed is flanked by a pair of silicate chains, each having the chemical composition [Si<sub>4</sub>O<sub>12</sub>]. The resulting composite chain has a shape of a rod and has the composition [Si<sub>4</sub>O<sub>12</sub>(Ti<sub>2</sub>O<sub>2</sub>)Si<sub>4</sub>O<sub>12</sub>]<sup>12-</sup>. Three symmetrically independent Sr<sup>2+</sup> ions and three water molecules are located in the mirror planes and both play roles in joining together the above mentioned rods to form the composite crystal structure [83M1]. Each Sr ion is located approximately at the center of a distorted trigonal prism formed by oxygen atoms associated with the rods. The Sr ions are also coordinated by two or three additional oxygen atoms or water molecules – Fig. 11.

**Cu<sub>3</sub>Na<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>**

The synthetic Cu<sub>3</sub>Na<sub>2</sub>Si<sub>4</sub>O<sub>12</sub> silicate crystallizes in space group Pnma [76K1]. The structure consists of bent Si-O chains linked by three kinds of Cu and two kinds of Na atoms. The Cu atoms have four nearest neighbours of O atoms. The coordination polyhedra of Na atoms are irregular in shape with six nearest neighbours of O atoms.

Similar Si<sub>4</sub>O<sub>12</sub> chains occur as parts of the structure of **ohmilite**, **batisite** (Chap. 8.1.4.7), **haradaite** and Cu<sub>3</sub>Na<sub>2</sub>(Si<sub>4</sub>O<sub>12</sub>) – Fig. 12. In batisite, the Si<sub>4</sub>O<sub>12</sub> chains and Ti-octahedral chains share apical oxygens to form a three-dimensional structure [62N1]. Haradaite [67T1] and Cu<sub>3</sub>Na<sub>2</sub>(Si<sub>4</sub>O<sub>12</sub>) [76K1] are “quasi-layer silicates” as defined by [67T1] in which Si-O chains are joined together by V- and Cu-polyhedra, respectively, to make sheet structures extending infinitely in two dimensions and ohmilite forms the rod structure. The Si<sub>4</sub>O<sub>12</sub> and Ti octahedral chains constitute a one-dimensionally elongated structure.

**8.1.4.8.2 Magnetic properties****Na<sub>2</sub>MSi<sub>4</sub>O<sub>10</sub> (M = Co, Ni)**

The temperature dependence of the magnetic susceptibility for Na<sub>2</sub>NiSi<sub>4</sub>O<sub>10</sub> follows a Curie-Weiss law  $\chi = C(T - \Theta)^{-1}$  in the temperature range 100 K < *T* < 300 K where *C* is the Curie constant – Fig. 13a [97D1]. The slight increase of the  $\chi T$  product upon cooling down to 35 K – Fig. 13b – confirms the presence of predominant ferromagnetic interactions, while at low temperatures, the  $\chi T$  variation indicates that the ordering between Ni<sup>2+</sup> ions is antiferromagnetic [97D1]. Similar behaviour was observed for Na<sub>2</sub>CoSi<sub>4</sub>O<sub>10</sub>, showing Curie-Weiss behaviour in the temperature range 150 K < *T* < 300 K, in agreement with dominant ferromagnetic interactions – Fig. 13a. In fact, the temperature dependence of  $\chi T$  – Fig. 13b – slightly differs due to the spin-orbit coupling effect for the Co<sup>2+</sup> ion. A minimum of  $\chi T$  is observed around 30 K, then a slight increase up to 10.8 K and a drop below 10 K, related to antiferromagnetic couplings between Co<sup>2+</sup> pairs. Some magnetic properties are listed in Table 4. A fitting of the  $\chi T = f(T)$  curve for Na<sub>2</sub>NiSi<sub>4</sub>O<sub>10</sub> silicate has been performed. The expression of the magnetic susceptibility has been deduced from the spin Hamiltonian [97D1]:

$$\mathbf{H} = -2JS_1S_2 - D(S_{1z}^2 + S_{2z}^2) - g\mu_B B(S_{1z} + S_{2z}) - 2zjS_z\langle S \rangle$$

By *J* and *j* are denoted the intra- and inter-dimer interactions, respectively and by *D* the anisotropy parameter. The best fit was obtained for  $J/k_B = 10.9$  K,  $j/k_B = -1.9$  K,  $D/k_B = -16$  K and  $g = 2.09$ . These data are in agreement with a model which considers ferromagnetic intradimer interactions and antiferromagnetic interdimer interactions. The fact that no  $\lambda$ -type anomaly was observed in the specific heat, means that no long-range order is established at the lowest measured temperature. Order could therefore take place at lower temperatures. Thus, the magnetic behaviour agrees with a model considering ferromagnetic interactions within the (M<sub>2</sub>O<sub>8</sub>)<sup>4+</sup> units, while antiferromagnetic interdimer interactions dominate at lower temperatures.

### Deerite

The magnetic susceptibility data [66C1] were interpreted to indicate the presence of low spin  $\text{Fe}^{2+}$ , which is most probably related to the antiferromagnetic ordering [74F1]. The temperature dependence of the magnetic susceptibility is shown in Fig. 14 [66C1]. There is a deviation from the Curie-Weiss law. According to [81P1] the paramagnetic Curie temperature is  $\Theta = 36$  K. In [66C1] was proposed that some of the ferrous ions stay in the low spin state, coordinated with oxygen perhaps due to their distribution over octahedral and tetrahedral sites. In [81P1] was shown that if it is assumed the spin contribution of the hopping electrons (see section 8.1.4.8.3) is assumed to be zero, it follows that at high temperatures the susceptibility should be modified as part of the electrons are involved in the hopping process. The evaluated susceptibility at room temperature, in this model, is in good agreement with the experimental value [81P1].

### $\text{Na}_2\text{Cu}_2\text{Si}_4\text{O}_{11} \cdot 2\text{H}_2\text{O}$ ; $\text{Na}_2\text{Cu}_2\text{Si}_4\text{O}_{11}$

As mentioned in section 8.1.4.8.1, in both structures, the chains are separated along the *b* and *c*-axes and thus a negligible interchain interaction is expected. The thermal variations of magnetic susceptibilities are shown in Fig. 15. These are typical for low dimensional spin systems and show broad maxima at 61 K and 49 K for the hydrated and dehydrated form, respectively. The decrease of magnetic susceptibilities at low temperatures is an evidence for a singlet ground state. The slight upturn at even lower temperatures was ascribed to the magnetic chain terminations [05M1]. The presence of magnetic impurities may determine the same type of behaviour. In [05M1] was assumed that the singlet ground state in  $\text{Na}_2\text{Cu}_2\text{Si}_4\text{O}_{11} \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{Cu}_2\text{Si}_4\text{O}_{11}$  is a consequence of alternating exchange interactions within the  $\text{CuO}_6$  (or  $\text{CuO}_5$ ) chains. The distances Cu-O-Cu(1) and Cu-O-Cu(2) are 3.011 and 3.141 Å, respectively for the hydrated form and 2.992 Å and 3.103 Å, respectively for the dehydrated silicate. Hence the superexchange is strong for Cu-O-Cu(1), but insignificant for Cu-O-Cu(2). Although in the dehydrated form these distances are shorter, the Cu-O-Cu(1) superexchange angle is larger in  $\text{Na}_2\text{Cu}_2\text{Si}_4\text{O}_{11} \cdot 2\text{H}_2\text{O}$ , increasing the antiferromagnetic component of the exchange interaction relative to the ferromagnetic component. The Cu-O-Cu angles in  $\text{CuO}_6$  (or  $\text{CuO}_5$ ) chains are rather close to the critical angle of compensation of ferromagnetic and antiferromagnetic components in the superexchange interactions. Thus, the topology of the edge sharing  $\text{CuO}_6$  ( $\text{CuO}_5$ ) chains suggest that the magnetic subsystems in both compounds can be viewed as weakly interacting dimers, or alternatively, strongly alternating isolated chains [00J1]. For one-dimensional  $S = 1/2$  spin system with a spin gap  $\Delta$ , the magnetic susceptibility  $\chi^* = N_A g^2 \mu_B^2 / J_{\max}$  was described by the relation  $\chi^* = \frac{\exp(-1/t)}{t} \cdot \frac{1}{1 + 3 \exp(-1/t)} \cdot (1 - n)$ , where  $t = k_B T / J_{\max}$ ,  $J_{\max}$  is the largest exchange

interaction parameter, and *n* is the number of terminations of spin chains. By fitting the experimental  $\chi^*$  values as a sum of the above terms (a temperature independent term  $\chi_0$  and a Curie-Weiss term attributed to the *n* terminations of spin chains) values  $\Delta = 96$  K, *n* = 2.5 % and  $\Delta = 85$  K, *n* = 7.2 % were obtained for hydrated and nonhydrated silicates, respectively. The gap value depends on the presence of water molecules in the microporous framework being higher in hydrated system. The spin gap behaviour, as above mentioned, was ascribed to a strong dimerization within  $\text{CuO}_6$  ( $\text{CuO}_5$ ) chains, conditioned by their trans-cis edge-sharing topology. The modeling of the data with the numerical solution for an alternating exchange parameter chain [93K1], was also carried out. Alternating exchange parameters  $\alpha = J_1/J_2$  of  $\alpha = 0.22$  and 0.28 were obtained for the hydrated and dehydrated forms, respectively.

### $\text{BaCu}_2\text{Si}_2\text{O}_7$

The magnetic measurements [01T1] reveal that the *c*-axis is the easy axis of the spin ordering. Unusual spin-reorientations transitions were observed. When the magnetic field was applied along the easy anisotropy axis, two spin-reorientations were observed [01T1] at the fields  $\mu_0 H_{c1} = 2.0$  T and  $\mu_0 H_{c2} = 4.9$  T. Later, another phase transition at  $\mu_0 H_{c3} = 7.8$  T was reported for  $\mathbf{H} \parallel \mathbf{b}$  [02P1], i.e. when the field is perpendicular to the easy axis.

In a theoretical model [04G1], the two phase transitions at  $H_{c2}$  and  $H_{c3}$ , observed in  $\text{BaCu}_2\text{Si}_2\text{O}_7$ , were explained by a relatively strong dependence of the transverse susceptibility on the direction of the order parameter. The resulting anisotropic part of the Zeeman energy exceeds the change in energy of magnetic anisotropy above the corresponding critical fields.



Magnetic ordering in the quasi-one dimensional  $\text{BaCu}_2\text{Si}_2\text{O}_7$  was also investigated with ultrasonic waves propagating along the chain axis. Transverse waves are found to couple most strongly with the magnetic properties [02P1]. This is observed through an important velocity softening below 140 K and sharp stiffening in the ordered state at 9.2 K.

### 8.1.4.8.3 Neutron diffraction data

#### $\text{BaCu}_2\text{Si}_2\text{O}_7$

The magnetic unit cell of  $\text{BaCu}_2\text{Si}_2\text{O}_7$  coincides with the crystallographic one. Long-range magnetic ordering occurs at  $T_N = 9.2$  K [99T1]. The ordered magnetic moment is rather small,  $p_{\text{Cu}} = 0.15 \mu_B/\text{atom}$  [00Z1, 01K1]. At  $H = 0$ , the spins are parallel to the *c*-axis, with nearest-neighbour spins along *c* and *b*-axes antiparallel to each other and a parallel alignment of nearest-neighbour spins along *a*-axis as shown in Fig. 16a [01K1, 02Z1]. This type of spin arrangement minimizes all interchain interaction energies that were measured as example by inelastic neutron scattering [01K1]. The magnetic structure at  $\mu_0 H = 4$  T (phase II) is a slight distortion of a collinear one, with all spins parallel to the *b*-axis and the same relative alignment of spins in adjacent chains as at  $H = 0$  – Fig. 16b. The canting angle and the ordered moment yield  $\phi = 78(3)^\circ$  and  $p_{\text{Cu}} = 0.18(2) \mu_B/\text{atom}$  [01K1]. In [01K1] was also noted that the previously proposed structure [99T1] was inconsistent with the experimental data. The suggested structure at  $\mu_0 H = 5$  T (phase III) is a collinear one with all spins pointing along the *a*-axis and the same relative alignment of spin in adjacent chains as at  $H = 0$  – Fig. 16c. The field dependence of the ordered moments tilting angles,  $\alpha$ , (phase I) and canting angles,  $\phi$ , (phase II) are shown in Figs. 16d, e. In a field  $\mu_0 H = 2$  T applied along the *c*-axis (phase I) the spins are largely confined to the (*b*,*c*) crystallographic plane – Fig. 16f. In [04G1] a symmetry analysis of the magnetic phase was performed. The unusual spin reorientation transitions were explained to result from relativistic interactions, which are decisive due to the fact that the interchain Heisenberg-exchange interaction is very weak.

### 8.1.4.8.4 Nuclear gamma resonance (NGR) data

#### Deerite

The earlier  $^{57}\text{Fe}$  NGR studies on deerite [68B1, 74F1] showed the presence of three quadrupole doublets, but give a different interpretation of the data. Both works agree in the assignment of the two most intensive doublets to ferrous iron and ferric iron in distorted octahedral sites. The third doublet was attributed to tetrahedral  $\text{Fe}^{2+}$  [68B1] or octahedral  $\text{Fe}^{2+}$  [74F1], respectively. The discrepancy in the interpretation of  $^{57}\text{Fe}$  NGR spectra was then discussed [77F1, 79B1, 79P1, 80A1, 81P1] and it was concluded that the third doublet is due to electron exchange between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions.

In [80A1] the  $^{57}\text{Fe}$  NGR spectra at 77 K were fitted with six doublets – Fig. 17a. At room temperature a different fitting to that at 77 K was used since: (1) the quadrupole splittings of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  doublets decrease resulting in a stronger overlap of individual doublets; (2) additional absorption features are observed especially in the range between the high velocity  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  peaks. These additional absorption features have to be fitted at least by two doublets ( $\text{Fe}^{n+}$ ). Only two  $\text{Fe}^{2+}$  doublets could be observed at room and higher temperatures and only one  $\text{Fe}^{3+}$  doublet. At RT two  $\text{Fe}^{n+}$  doublets and at higher temperatures only one was observed – Table 5.

At 77 K the doublets were assigned in correlation with structural characteristic [77F1]. Thus, it was suggested that  $\text{Fe}^{3+}$  has a preference for the M1 to M3 sites and  $\text{Fe}^{2+}$  for the M4 to M6 sites and to a smaller extent also for M7 to M9 sites. The most intensive  $\text{Fe}^{2+}$  and the less intensive  $\text{Fe}^{3+}$  doublet were assigned to the M4 to M6 sites, the most intensive  $\text{Fe}^{3+}$  and the less intensive  $\text{Fe}^{2+}$  doublet to the M1 to M3 sites. From the analysis of the doublets area, the small excess of  $\text{Fe}^{3+}$  experimentally determined and the shortage of  $\text{Fe}^{2+}$  was considered as partially due to replacement of  $\text{Fe}^{2+}$  by  $\text{Mn}^{2+}$  and  $\text{Mg}^{2+}$  that is not compensated by an equal amount of trivalent cations (e.g.  $\text{Al}^{3+}$ ).

The isomer shift,  $\delta$ , and quadrupole splitting,  $\Delta Q$ , for doublets  $\text{Fe}^{n+}$  at RT and above, have values intermediate to the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  parameters, and were assigned to mixed valence states of iron resulting from a thermally activated electron delocalization process. These intermediate absorption lines appear first at 295 K and their intensities increase simultaneously with a decrease of the  $\text{Fe}^{2+}$  intensities, indicating changing populations of electronic levels – Fig. 17b. Interactions between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in neighbouring cation sites occur in most

cases across shared edges. In deerite, the  $\text{FeO}_6$  polyhedra are connected by common edges, for example M1 and M2 or M5 and M8 with an M-M distances of 3.188 Å. Also, the  $\text{FeO}_6$  octahedra of neighbouring octahedra sets share common edges, for example M7 and M5 with an M-M distance of 3.106 Å or M7 to M4 with an M-M distance of 3.119 Å. All these distances are within the range where  $\text{Fe}^{2+}$  -  $\text{Fe}^{3+}$  electron transfer is known to appear and there are many possibilities of  $\text{Fe}^{2+}$  -  $\text{Fe}^{3+}$  interaction. As above mentioned, in [80A1] only two distinct mixed valence doublets were considered. The fit with a single or two lorentzian lines is only an approximation since the high velocity  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  peaks have the appearance of an almost continuous absorption. There is a sharpening of the continuous absorption and at  $T > 295$  K, only one doublet was observed. Thus, at low temperatures, deerite has mainly trapped or discrete valences of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , which become partly depopulated with increasing temperature because of thermally activated electron exchange. At the beginning of this process, there is only an interaction between isolated  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  pairs which have sufficient energy to exchange one electron. The number of these pairs increases with temperature and more electrons become delocalized and occupy a common energy level associated with mixed valences.

In [79P1, 81P1] the  $^{57}\text{Fe}$  NGR data of [74F1] were reinterpreted suggesting also the presence of thermally activated electron delocalization associated with  $\text{Fe}^{2+}$  -  $\text{Fe}^{3+}$  charge transfer. The activation energies,  $E_a$ , of the charge transfer process were also evaluated [81P1]. The  $E_a$  values decrease when increasing the temperature from 0.043(3) eV at 233 K to 0.020(3) eV (311 K) and 0.006(3) eV at 386 K.

#### 8.1.4.8.5 Magnetic resonance

##### **BaCu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>**

The  $\text{BaCu}_2\text{Si}_2\text{O}_7$  silicate was also studied by magnetic resonance [02H1, 03O1, 05G1]. The resonance studies show that the low-field spectra are in good agreement with frequency-field dependences of a conventional two-sublattice antiferromagnet [55N1] which are represented by dashed lines in Fig. 18 [05G1]. When the magnetic field is applied parallel to the easy axis, a characteristic spin-flop transformation of the spectrum, with a vertical frequency drop, occurs at  $\mu_0 H_{c1} = 1.88(8)$  T. For the other directions, in the low-field range,  $\mu_0 H \leq 2.0$  T, there is one mode with a strong field dependence of the resonance frequency and one mode with an approximately constant frequency. At  $\mathbf{H} \parallel \mathbf{a}$ , the resonance mode with a strong field dependence starts from the larger zero-field gap, while at  $\mathbf{H} \parallel \mathbf{b}$  the larger gap corresponds to a mode with a weak field dependence of the resonance frequency. This low field behaviour allows the identification of the  $\mathbf{a}$ -axis as a hard axis of antiferromagnetic ordering and  $\mathbf{b}$ -axis as a middle axis of spin ordering. Upon increasing the magnetic field, an additional softening of the one of the two modes occurs. An additional softening occurs for the easy-axis orientation of the applied field ( $\mathbf{H} \parallel \mathbf{c}$ ) at the field  $\mu_0 H_{c2} = 4.78(10)$  T for the  $\mathbf{H} \parallel \mathbf{b}$  at the field  $\mu_0 H_{c3} = 7.74(8)$  T and for the  $\mathbf{H} \parallel \mathbf{a}$  orientation at the field  $\mu_0 H_{c4} = 11.0(5)$  T [05G1]. A model based on the macroscopic approach to the spin dynamics of an antiferromagnet, which describes quantitatively the observed AFMR spectra and the field induced phase transitions was developed. The model includes the anisotropy of the transverse susceptibility with respect to the order parameter orientation. The anisotropy of the transverse susceptibility and the strong reduction of the anisotropy energy due to the quantum spin fluctuations were proposed to be the reason for the observed spin reorientations [05G1].

#### 8.1.4.8.6 Heat capacity

##### **Na<sub>2</sub>MSi<sub>4</sub>O<sub>10</sub> (M = Co, Ni)**

The temperature dependences of the heat capacity for  $\text{Na}_2\text{MSi}_4\text{O}_{10}$  (M = Co, Ni) show the presence of a Schottky-type anomaly with a maximum in the range 3...5 K [97D1]. This anomaly is important for the  $\text{Co}^{2+}$  silicate – Fig. 19 – and less pronounced for the  $\text{Ni}^{2+}$  derivative. From the relation  $C_p = aT^{-2} + bT^3$ , where the first term is related to magnetic correlations and the second one to lattice contribution, the heat capacity of magnetic origin was determined. The observed variation of  $C_p$  confirms that short-range correlations dominate the magnetic behaviour in the temperature range of interest. The stabilization of magnetic ground state for dinuclear units does not promote ( $T > 1.5$  K) a long-range order.

**$\text{Na}_2\text{Cu}_2\text{Si}_4\text{O}_{11} \cdot 2\text{H}_2\text{O}$ ;  $\text{Na}_2\text{Cu}_2\text{Si}_4\text{O}_{11}$** 

The temperature dependence of the heat capacities are plotted in Fig. 20 [05M1]. By using the data obtained from magnetic study, the magnetic heat capacity of both compounds was calculated according to the relation

$$[00J1]: C^* = \frac{\exp(-T)}{T} \cdot \frac{1}{(1 + 3 \exp(-T))^2} \quad \text{where } C^* = C/3R \text{ and } R \text{ is the universal gas constant. The results of}$$

these calculations are shown in Fig. 20.

**8.1.4.8.7 Optical properties****Caysichite**

The infrared (IR) spectra of caysichite were analyzed [74H1]. The strong broad band in the region  $3700 \dots 2600 \text{ cm}^{-1}$  was attributed to hydrogen-bonded water. The strong bands in the region  $1700 \dots 1240 \text{ cm}^{-1}$  are due to vibrations of the  $\text{CO}_3$  group. The strong bands in the region  $1200 \dots 900 \text{ cm}^{-1}$  were attributed to Si-O stretching. The assignments of the minor bands in the spectra were:  $3020 \dots 2800 \text{ cm}^{-1}$  (overtone of  $\nu_3$  of  $\text{CO}_3$ );  $1720 \text{ cm}^{-1}$  (adsorbed water);  $830 \text{ cm}^{-1}$  ( $\nu_2$  of  $\text{CO}_3$ );  $790$  and  $740 \text{ cm}^{-1}$  (Si-Si stretching);  $690$ ,  $630$  and  $620 \text{ cm}^{-1}$  ( $\nu_4$  of  $\text{CO}_3$ ) [74H1].

**Ohmilite**

The infrared spectrum of **ohmilite** is plotted in Fig. 21 [83M1]. This is in accordance with the configuration of silicate chain. The spectrum shows four absorption bands at  $575$ ,  $636$ ,  $678$  and  $746 \text{ cm}^{-1}$ . Absorption bands in the range  $530 \dots 775 \text{ cm}^{-1}$  have been assigned [66R1] to correspond to the Si-O-Si symmetrical stretching of single chains of pyroxenes and pyroxenoids. In [66R1] was pointed out that the number of bands in this region corresponds to the number of tetrahedra in the repeat unit of the silicate chain. The structurally related silicate **batisite** (Chap. 8.1.4.7) also has four tetrahedra in the repeat unit and has four bands at  $573$ ,  $634$ ,  $713$  and  $768 \text{ cm}^{-1}$  [68L1]. The absorption bands of both silicates are similar in frequency.

Ohmilite has a small but sharp IR peak at  $1394 \text{ cm}^{-1}$  [83M1] which was attributed to an OH-bending mode. Broad bands at  $1571$  and  $1725 \text{ cm}^{-1}$  were considered to be due to OH-stretching vibration of a strong hydrogen bond. The strong broad peak around  $3000 \text{ cm}^{-1}$  was attributed to an OH-O bond and the small and sharp peak at  $1619 \text{ cm}^{-1}$  was assigned to adsorbed water.

For IR spectrum of **agrellite** see [76G1].

Some refractive indices are listed in Table 6.