

8.1.3.3 Cordierite- and beryl-type silicates

The cyclosilicates from group VIIIC06 are listed in Table 1 [91N1]. The atomic sites for indialite and beryl and the lattice parameters of cordierite and beryl-type silicates are listed in Table 2 and Table 3, respectively.

8.1.3.3.1 Crystal structures. Lattice parameters

Cordierite, indialite, sekaninaite

Cordierites are silicates with a tetrahedral framework structure having a simplified formula $^{[6]}(\text{Mg,Fe})_2^{[4]}(\text{Al}_4\text{Si}_5)\text{O}_{18}$ [30B1]. Two crystallographic forms were reported. The α -cordierite is hexagonal (high-cordierite) with space group P6/mcc. This is known as **indialite** when found as naturally occurring mineral [54M1]. The β -cordierite (low-cordierite) crystallizes in an orthorhombic-type lattice [28G1, 30B1, 36T1, 42B1, 62D1, 66G1, 71P1, 77S1] having space group Cccm. Cordierite crystallization from glass proceeds through an intermediate metastable stuffed β -quartz phase [61S1, 61S2, 71G1]. The transition phase is a metastable quartz based structure, of variable composition, that incorporates tetrahedral Al^{3+} and interstitial Mg^{2+} cations and is known to form with cordierite composition [61S1, 83C1]. It is structurally related to β -spodumene. Various terms were used to call this phase as μ -cordierite [53K1], silica-O [59R1], stuffed high-quartz [71G1] and β -quartz [85B1]. The transition from hexagonal to orthorhombic cordierite is made through a modulated hexagonal cordierite. **Sekaninaite** [75S1] is the Fe-analog of low cordierite and crystallizes in space group-Cccm.

The structure of α -cordierite is essentially a framework of Al, Si tetrahedra with M^{2+} octahedral coordination. Two types of topologically different tetrahedra can be distinguished in hexagonal cordierite structure: T_1 tetrahedra share two opposite edges with octahedra that coordinate the M cation. These edge sharing tetrahedra and octahedra form infinite, honeycomb-structural layers normal to the crystallographic c -axis (M layers). Distorted hexagonal rings of corner-sharing T_2 tetrahedra (T layers) are found between the M layers, inscribed into their large openings. Each T_2 tetrahedron shares two corners with T_1 tetrahedra in M layers above and below it. In this way, each T_1 tetrahedron connects two T_2 rings beneath and M layer to two others above it. The T_2 rings are contra rotated by $\cong 30^\circ$ in adjacent T layers, giving rise to two different types of T layers and to a c -repeat comprising two M layers and both T layers. Thus, an infinite stack of T_1 tetrahedra is formed parallel to the c -axis [01M1]. In the hexagonal form there are three tetrahedral T_1 sites and six tetrahedral T_2 sites – Table 2. Each O_2 atom is bonded only to two T_2 atoms and each O_1 is bonded to one T_1 , one T_2 and M atom – Fig. 1a. We note that the M-layer building block is not only found in the structure of cordierite and beryl. In the milarite structure (Chap. 8.1.3.7), the M layers combine with contra-rotated layers of tetrahedral double rings thus increasing the c lattice dimension relative to beryl structure.

Transformation of hexagonal to orthorhombic cordierite results in O_1 and O_2 splitting into two sets, each consisting of three non-equivalent oxygen atoms labeled O_{11} , O_{16} and O_{13} , and O_{21} , O_{26} and O_{23} , respectively [77C1, 77M1]. The third symbol of each atom label denotes the symmetry operation (1 = identity map, 6 = sixth-turn, 3-third-turn) that relates the atoms in equivalent sets. In addition, the T_1 atoms split into a set of two non-equivalent tetrahedral atoms labeled T_{11} , T_{16} and the T_2 atoms split into a set of three non-equivalent tetrahedral atoms labeled T_{21} , T_{26} and T_{23} . In terms of this nomenclature, the labels given by [66G1] for the T and O atoms of low cordierite correspond as follows: $\text{T}_{11} = \text{T}_1$; $\text{T}_{16} = \text{T}_2$; $\text{T}_{21} = \text{T}_3$; $\text{T}_{26} = \text{T}_5$; $\text{T}_{23} = \text{T}_4$; $\text{O}_{11} = \text{O}_1$; $\text{O}_{16} = \text{O}_2$; $\text{O}_{13} = \text{O}_3$; $\text{O}_{21} = \text{O}_5$; $\text{O}_{26} = \text{O}_4$; $\text{O}_{23} = \text{O}_6$ – Fig. 2. The structure may be viewed as a tetrahedral framework consisting of chains of 4-membered rings of alternating AlO_4 and SiO_4 tetrahedra cross-linked into 6-membered rings of $\text{Al}_2\text{Si}_4\text{O}_{18}$ composition – Fig. 1b. The M (M = Mg, Fe, Mn) atoms are located in the framework in slightly flattened octahedra that share three edges, two with a AlO_4 tetrahedron and one with a SiO_4 tetrahedron.

As above mentioned, the structure of anhydrous cordierite [66G1] is characterized by rings formed by six corner-linked tetrahedra, stacked together in such a way to form channels parallel to the crystallographic c -axis. The channel position at (0,0,0) in the center of the six membered ring is denoted Ch0. The position at (0,0,1/4) in the middle of a larger cavity situated between two six-membered rings, is designated Ch1/4. Charge deficiency in the framework structure can be balanced by incorporation of additional atoms in either channel position [66G1, 77C1, 79H1, 80W1]. The structure of beryl (see beryl) is very similar [68G1]. The channels do not have a uniform diameter, but instead consist of cavities with a diameter of $\cong 5.1 \text{ \AA}$, separated by “bottlenecks” with a diameter of about 2.8 \AA . Into these cavities, small molecules such as H_2O , CO_2 , N_2 etc. can be incorporated, while alkali cations may occupy the centers of the six rings. In natural samples very complex substitutions may

occur both in cordierite [77G1, 82A1, 85S1] as well as in beryl [91S1, 91S3]. Since of the similar behaviour of cordierite and beryl concerning the location of the cavities, a common discussion will be given on this matter [96W1]. There are about twice as many H₂O molecules than alkali ions. It has therefore been deduced that each alkali-ion is coordinated by two H₂O, one in each cavity below and above the center of six rings where the cation is located.

The incorporation and orientation of molecular CO₂ and H₂O in the channel cavities of cordierite, (Mg,Fe)Al₄Si₅O₁₈ × (H₂O, CO₂) were investigated by X-ray and neutron diffraction studies [77C1, 85A1], IR spectroscopy [67F1, 71S2, 77G1, 83M2, 84A1, 90V1, 00K2], proton NMR spectroscopy [82C1], quasi-elastic neutron scattering [94W2] and quantum mechanical calculations [94W3]. These studies showed that CO₂ is aligned parallel to the *x*-axis in cordierite [82A1, 82A2, 84A1, 85A1]. The behaviour of H₂O is more complicated. In [67F1] was found that the H₂O molecules lie in the *xz* crystal plane (010), with the H–H direction parallel to the channel axis [001]. In [77G1], following the work of [67W1] for beryl, was concluded that two types of H₂O molecules can be identified which they labeled as type I and II. The molecular plane of both type I and II H₂O is located in the *yz* crystal plane (100) but they differ in the orientation of their H–H vector which are either parallel (type I) or perpendicular (type II) to [001]. The apparent discrepancy over the orientation of the H₂O molecular plane proposed by [67F1], as compared to [77G1], can be explained by the different crystal settings used by the two groups. From neutron diffraction study [77C1], was proposed that the H₂O molecules are statistically disordered over four different orientations with their molecular plane nearly parallel to the *xy* crystal plane (001). In [79H1], by using X-ray method, a reinterpretation of neutron diffraction data was proposed that molecular plane of H₂O is tilted about 29° from (100). As a result of an X-ray diffraction study, [80W1] came to the conclusion that the H₂O molecule was in fact oriented. In [82A1] H₂O was reintroduced into previously evacuated natural samples and the refractive indices were determined. From the relative change of these indices it was concluded that H₂O was incorporated as “type I H₂O”. In [94W2] was considered that “type I H₂O” in synthetic Mg-cordierite is rotationally disordered about [001] and that a pure static description is inappropriate to describe its behaviour in the channel cavity. They proposed a two-orientation jump model (see later). In [00K2], two classes of H₂O molecules were considered (see section 8.1.3.3.9). In contrast to the static models, in [62S1] was pointed out that there may be dynamical disorder of the H₂O molecule in cordierite. ¹H NMR experiments on beryl [64P1, 66S1] were interpreted [64P1] as showing a dynamic disorder down to 4 K. An anisotropic motion was also deduced and the H–H vector was considered to be parallel to the channel axis only on a time average [64P1]. In addition, it was concluded that there was no hydrogen bonding present in the structure. In [66S2] the idea of fast moving H₂O molecules was rejected and it was stated that no dynamical disorder was present and instead the NMR data were interpreted on the basis of isolated OH groups. The fast intracage motion in beryl was confirmed by [74R1] and it was concluded that indeed there is a dynamic disorder of “type I H₂O” down to 4 K, while “type II H₂O” is immobile. It was also thought that the motion of the H₂O molecule was anisotropic. The first indication of the dynamic disorder in cordierite was obtained at room temperature from ¹H NMR [72T1]. Later on, [82C1], even at 100 K, reported a motional narrowing at the Pake doublets and proposed a hopping between type I and type II orientations. In [92S1] was concluded that channel H₂O in cordierite undergoes a fast isotropic reorientational motion similar to molecules in water.

The dynamics of H₂O in cordierite and beryl have also been described with models intermediate between the static models with H₂O of type I and II and the dynamic models which were based on a fast isotropic or anisotropic reorientational motion [96W1]. In [84A1] was concluded, from high-temperature IR spectroscopic study of beryl and cordierite, that when increasing the temperature, the dynamics of H₂O change qualitatively. The appearance of a broad band at *T* > 470 K was ascribed to dynamically disordered “unbound” H₂O. The thermogravimetric data obtained during investigation of the dehydration energetics and kinetics were interpreted in terms of two dehydration processes with distinct activation energies [89G1]. The process with smaller activation energy was ascribed to “unbound” H₂O leaving the structure, while the dehydration process with the larger activation energy was explained as being due to the “bound” H₂O leaving cordierite. We note that it already was shown that the presence of “structurally bound” H₂O molecules in either beryl or cordierite is very unlikely [76L1] as suggested by [75S2].

Neutron scattering experiments, at large energy transfers, on synthetic, alkali free cordierite [94W1, 94W2, 96W1] showed that there is only a weak temperature dependence in the external dynamics of the H₂O molecules. There are either two or three distinct hindered translational motions, but only one very broad excitation due to libration motion. This is consistent with a molecule confined to a cage, but being free to rotate about an axis.

Quasielastic neutron scattering experiments [94W2] showed that H₂O undergoes a fast hopping motion, with a radius of gyration of about 0.4 Å. This motion has been assigned to a revolution around the center of mass of the molecule which coincides with the center of the channel. During this motion, the hydrogen–hydrogen vector is always parallel to the channel axis. Hence, this motion is the same as that suggested for H₂O in beryl [74R1, 96W1]. Taking the results of the IR spectroscopic studies into account, it is most likely that this motion is not continuous, but rather consists of discrete jumps, where the H₂O flips by 180°. The time the molecule rests in one orientation is a few picoseconds only. It was shown, by quasi-elastic neutron scattering, that this dynamic disorder is present at 50 K and inferred that it will be present even at lower temperatures [94W1]. From the ¹H NMR, dielectric spectroscopy and quasielastic neutron scattering experiments can be concluded [96W1] that “type I H₂O” is dynamically disordered in cordierite and beryl, and revolves around the center of mass while the hydrogen–hydrogen vector stays parallel to the *c*-axis. The motion is most probably a fast jump between two orientations, and the correlation time of a few ps is long enough as to give the impression of a static molecule in IR studies. Both the dielectric [74R1] and neutron spectroscopic [94W2] studies indicate that it is not a flipping between the type I and type II orientation. Based on these findings, the interpretation of diffraction and thermodynamic data with a static model is questionable [96W1]. For “type II H₂O” no firm conclusions can be drawn yet, but it is likely that is immobile [96W1].

Other studies were also performed in analyzing the matter of H₂O in cordierite [60S1, 60S2, 70S1, 72N1, 77H1, 77M2, 79M1, 81J1, 81L1, 85A1].

In addition to adsorbed molecular H₂O and CO₂ [67W1, 77C1, 77H3, 80A1, 82A1, 81Z1, 82A1], other volatile species such as He, Ar, CO, N₂, O₂, Ne, H₂S and hydrocarbons [58D1, 76B1, 83M1] occur in the channels of natural cordierites. Space considerations indicate that maximum 1 mol of gas per formula unit (2.99 wt % H₂O or 6.99 wt % CO₂) in pure Mg-cordierite, can be accommodated in the channels [81J1]. The volatile molecules can be reversibly removed from the cavities via heating [82A1, 85A1, 90V1].

The site occupied by alkali ions in cordierites were also analyzed [65S1, 79H1, 80E1, 80W1, 84K1, 86A2, 90S1]. According to [79H1] in Na-rich cordierite, assigned Na to the Ch0 position. When a Na- and H₂O-rich crystal was degassed [86A2], the subsequent single crystal structure refinement proved that the Ch1/4 position became empty while a strong difference – Fourier peak remained at Ch0 which supports the assignment of Na to Ch0 and H₂O to Ch1/4. The role of Na in low cordierite-type structure having complex composition: Na_{0.23-0.32}Li_{0.02-0.04}Mg_{1.40-1.49}Fe_{0.50-0.60}Mn_{0.01-0.02}Al_{3.76-3.91}Be_{0.15-0.21}Si_{4.94-4.97}O₁₈ was analysed [86A2]. About 60 % of the structural cavities were occupied by water, and CO₂ is only a minor constituent. The electron microprobe Li and Be analyses and structure refinements indicate the substitutions: Na⁺ + Be²⁺ → Al³⁺ and Na⁺ + Li⁺ → Mg²⁺ or Fe²⁺. All crystals exhibit a high degree of (Si,Al) ordering. Partial incorporation of Na in the center of the six membered ring of oxygen atoms (O₂3-O₂6-O₂1-O₂3-O₂6-O₂1) causes the rings to predominantly compress along the *b*-axis, whereas the larger six-membered rings of cations (T₂3-T₂6-T₂1-T₂3-T₂6-T₂1) slightly expand along the same direction – Fig. 3. These opposing motions lead to an increasing in the *b*-axis and are responsible for a nearly hexagonal lattice geometry in Na-rich cordierites [86A2]. Thus, the distortion index $\Delta = 1.094(a - b\sqrt{3})$ [80P2, 80S1] decreases in Na-rich cordierites. The tetrahedral angles (O–T–O) and individual T–O bonds are thus affected by the Na content. The Al tetrahedron T₁1, interconnecting six-membered rings of tetrahedra, is the preferred site for Be substitution in cordierite [66N1, 86A2]. The smaller ionic radius of Be significantly decreases the mean T₁1–O bond length. Li partially occupies octahedral sites and substitutes for Mg or Fe. It was emphasized [86A2] that the Na-rich cordierites are also H₂O rich because each Na attracts two water molecules into the adjacent structural cavities to complete its coordination polyhedron of eight oxygen atoms. In anhydrous cordierites, the water molecules, in the channel cavities, are absent and the Na cations therefore show increased thermal motion along the channel axis [86A2].

The crystal structures analysis of K-substituted synthetic hexagonal cordierite, K_{0.17}Mg₂Al_{4.17}Si_{4.83}O₁₈ shows that K atoms have been located inside the channels of the cordierite framework [84K1]. According to [84K1] they are neither on the 2a (0,0,0) sites nor on the 2b (0,0,1/4) sites suggested for alkaline ions [80E1, 80W1], but they are statistically distributed at the center of channels on the four positions of a 4e (0,0,*z*) site with *z* ≈ 0.15.

In the high-temperature polymorph, Si and Al are distributed more or less statistically over the tetrahedral sites T1 and T2 leading to an overall hexagonal symmetry [77M1, 85A2, 92D1]. Annealing leads to an ordering of aluminium and silicon in the low-temperature form (orthorhombic) [66G1]. In this phase each six-membered ring contains two aluminium and four silicon atoms with a ratio Al/Si of 1/2 for the T2 tetrahedra. The respective ratio for the ring-connecting T1 tetrahedra is 2/1. Perfect ordering is only possible when the overall Al/Si ratio is

exactly 4/5 as in the magnesium end-member of cordierite, $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$. In its completely ordered structure every Si atom in a ring-tetrahedron T2 is connected to three Al-bearing tetrahedra (two T1 and one T2) and to one Si-containing T2 tetrahedron. Every ring connecting T1 tetrahedron occupied by Si is connected to four $[\text{AlO}_4]$ -ring tetrahedra. On the other hand, any Al-bearing tetrahedron (T1 and T2) is connected to four $[\text{SiO}_4]$ tetrahedra, thus, obeying the aluminium avoidance rule [54L1]. The nature of the Al,Si-ordering in pure Mg-cordierite during the high-low transformation has been subjected of various studies involving IR and NMR spectroscopy [85P1, 85P2, 86F1, 87P2, 87S1, 89G2, 89R1, 92D1]. It was concluded [87P2] that the temperature-time evolution of the cordierite structure is defined by two parameters. The first is the degree of Al,Si order and is described by the parameter $Q_{\text{od}} = (1 - N/3.3)^{1/2}$ where N is the number of Al–O–Al bonds per formula unit, normalized to 1 for complete order and 0 for complete disorder. The second parameter, Q , shows the tendency for the cordierite structure to distort to orthorhombic symmetry. In the hexagonal-orthorhombic transformation, the (211) peak in the hexagonal structure splits into the (131), (421) and (511) peaks of the orthorhombic structure and the distortion index, Δ , was defined as $\Delta = 2\theta_{131} - (2\theta_{511} + 2\theta_{421})/2$ [57M1]. The Δ index, normalized to 1 for $\Delta = 0.25$ (the maximum distortion) was used as the order parameter, Q [87P2].

As above mentioned, pure Mg-cordierite, $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, is orthorhombic under equilibrium conditions below about 1450°C; a hexagonal polymorph is stable above this temperature [55S1, 61S2, 80P2]. The transition between these two structures was associated with changes in (Al, Si) order. The hexagonal form cannot accommodate any long-range order of the Al and Si atoms, whereas the orthorhombic form can attain complete order of atoms on the Al and Si sites. The polymorphic transformations of $\text{M}_2\text{Al}_4\text{Si}_5\text{O}_{18} \cdot n\text{H}_2\text{O}$, where $\text{M} = \text{Mg}, \text{Fe}, \text{Mn}$ has been assumed to be related to disorder-order of (Al, Si) [55M1]. The silicate minerals can exist in all structurally intermediate states ranging from high cordierite to low cordierite [57M1, 60I1, 64S1, 66G1].

In [87P2] the hexagonal to orthorhombic phase transition was studied in synthetic Mg-cordierite. The samples were prepared from glass and were devitrified by annealing in air at temperatures of 1180°C, 1290°C and 1400°C for different periods of time. The first crystallization product was hexagonal cordierite which on annealing ultimately transforms in orthorhombic cordierite – Fig. 4. The formation of modulated hexagonal cordierite, within which a high degree of Al, Si order can be attained, results in a strongly nonlinear relationship between Q and Q_{od} . The transition from modulated to orthorhombic cordierite was reported to be strongly first-order under different temperature conditions and involves a large step in Q , while Q_{od} changes continuously throughout the ordering sequence with no marked discontinuity at the phase transition. Modulated cordierite has hexagonal symmetry and is characterized by the order parameter Q_{od} and the wave length of the modulation. It is however not characterized by the order parameter Q which is necessarily zero in this form. This means that the correlation between Q and Q_{od} is spontaneously broken at the point of transition between the modulated and the orthorhombic form. The Q disappears at the point of transformation to the modulated form and has to obey the correlation with Q_{od} in the orthorhombic form.

The first-order transition from α - to β -cordierite, mentioned above, is a complex process involving an intermediate modulated structure. Under non-equilibrium conditions, the transition occurs via the continuous development of metastable short range ordered modulated structure [80P1, 80P2, 83P1, 87P2]. The ordering of Al and Si on the tetrahedral framework is the rate-limiting process in this transformation, though the transition proceeds stepwise and Al,Si ordering only triggers the phase transition and is not directly involved [87S1, 89G2]. Near equilibrium, the transition takes place through a nucleation-growth process which results in different textures and microstructure [82K1].

As above mentioned, natural cordierites accommodate additional elements within the structure [85S1]. The addition of K directly affects the (Al,Si) ordering behaviour, since the substitution of $\text{K} + \text{Al}$ for $\square + \text{Si}$ alters the Al/Si ratio from that in pure Mg-cordierite. As in case of Mg-cordierite, the phase transition is triggered by a critical degree of (Al, Si) order, Q_{od} , which causes a sudden distortion of the structure that breaks the hexagonal symmetry. Additional effects may be introduced by local strains due to the incorporation of K. The local stress field associated with such point defect (K atom in a channel) may act as the conjugated field to Q and alter the phase-transition behaviour. In [89R1] the phase transition in K-bearing cordierite was studied. The structural states appear to be very similar to the pure Mg-cordierite with the following modifications: (1) the maximum distortion of the orthorhombic structure leads to a strain corresponding to a Δ index of $\Delta = 0.17$ as compared to $\Delta = 0.25$ in pure Mg-cordierite; (2) the kinetics of the transformation process are influenced by doping with K. The dependences between the potassium content and the state of order on one side and between annealing time and the state of order on the other side were analysed in $\text{K}_x\text{Mg}_2\text{Al}_{4+x}\text{Si}_{5-x}\text{O}_{18}$ cordierites [92D1]. The state of order

was a continuous function of annealing time for all compositions ($x \leq 0.25$) but the rate of ordering decreases with increasing the K content. Since the substitution $K^+ + Al^{3+} \rightarrow Si^{4+}$ leads to higher Al/Si ratios, the lower rate of ordering is discussed as a consequence of changed statistics for Al, Si site exchanges. The Al atoms replacing Si in the structure to balance the charge of potassium cations are not located close to the potassium ion but at a maximum distance from it. This was shown to be a consequence of an improvement in coordination of all oxygen atoms in the cordierite framework.

The structure, crystal chemistry and microstructure of the disordered and ordered Mg-cordierites synthesized in bismuth oxide were studied [94S1]. Bi-flux grown cordierites crystallize in both hexagonal and orthorhombic polymorphs – Table 3 – and contain 5 to 10 at % occupancy of bismuth on the channel sites. The microstructure of Bi-flux α -cordierite is characterized by the existence of local domains of disordered cordierite solid solutions with variable composition and significant vacancy concentrations of the octahedral site. The β -cordierites have a more homogeneous microstructure but are still Al-deficient, Si-rich solid solutions.

The structure of ferromagnesian cordierites has been studied [42B1, 66G1, 74D2, 77C1, 77G1, 79H1, 80S1, 80W1, 84V1, 85A3, 86A2, 00G1, 01M1]. The presence of Fe^{2+} complicates the crystal structures of cordierites. Most Fe^{2+} occupies the octahedral M-site [42B1]. However, several spectroscopic studies showed that some Fe^{2+} can occupy additional structural sites. Some investigations argued that this additional Fe^{2+} is located in channel cavities or in the six-membered rings that are parallel to the c -axis [74D2, 77G1]. Other investigations proposed that Fe^{2+} replaces Si^{4+} or Al^{3+} in one of the tetrahedral sites [84V1]. More recent studies analyzed this matter more carefully. In [80W1] six metamorphic low cordierites having $Fe/(Fe+Mg) = 0.07 \dots 0.42$ (atomic) were refined from X-ray data. No evidence of a suprastructure was found. It was also shown that the increase of Fe content causes: (1) the M site to enlarge, (2) the channels to move apart and (3) a and b lattice constants to increase. In addition, channel rings rotate, change their shape and move closer together within each channel, causing a decrease in c . Later on, the cation substitution and Al,Si ordering in the tetrahedral framework of (Fe,Mg)-cordierites were analyzed [01M1]. The mean bond distances in natural and heat-treated cordierites were shown to be consistent with a simple hard sphere model of the cordierite structures. This model requires the introduction of minor amounts of Fe^{2+} and Mg cations in the tetrahedral framework. Whereas direct spectroscopic evidence confirms the presence of Fe in tetrahedral coordination, the possibility of tetrahedrally coordinated Mg is inferred from chemical analyses (showing excess Mg content) and from the favourable size of Mg^{2+} compared to the Fe^{2+} ion in tetrahedral coordination. Almost complete (Al,Si) order is found in Mg-rich natural samples, whereas Fe-rich samples exhibit lesser (Al,Si) order due to an increased Al/Si ratio. The average size of the tetrahedrally coordinated T_1 cation increases systematically by $\approx 0.01 \text{ \AA}$ as the Fe content of the solid solution decreases toward the Mg end-member. For Fe-rich compositions, the mean tetrahedral bond length T_1-O is close to 1.749 \AA , a value expected for an AlO_4 tetrahedron in an aluminosilicate framework structure. It was suggested that the structural dilatation of the tetrahedral sites which is driven by the decreasing average size of the octahedral cation, is sustained by substitution of the large cations Mg and Fe^{2+} for Al. By ^{57}Fe NGR it was shown that up to 11 % of Fe^{2+} can be attributed to tetrahedral coordination in Mg-rich cordierite. Charge balance, involved by the substitutions, is either provided by introduction of Na^+ into a vacant Ch2(0,0,0) channel site or by substitution of an additional Al^{3+} by Si^{4+} . Almost complete Al,Si ordering among ring sites T_2 is encountered for most natural cordierites. Al,Si ordering among T_1 tetrahedra is less pronounced for Fe-rich compositions. Partial disorder was attributed to Al/Si ratio in excess of 4/5. Orthorhombic shear strain was shown to correlate with the derived average order parameter, if corrections for strain contributions from size effects of the octahedral cation and from channel constituents were considered.

According to [80S1], for $(Fe+Mn)/(Fe+Mn+Mg) = 0.046 \dots 0.989$, the a and b lattice parameters increase linearly with R_a , the average radius of ions on the octahedral sites. The c parameter decreases until R_a exceeds ca 0.765 \AA and then apparently increases.

The stabilities of Mn- and Co-cordierites have also been investigated [62E1, 74D1, 84W1, 99K1]. The synthesis of Mn-cordierite from oxides was reported [74D1]. The solid solutions between Mg-cordierite and Co-cordierite have also been studied [84W1]. These authors stated that attempts to synthesize Co-cordierite from oxide failed, and that instead gels had to be used as starting materials. The upper temperature limit for the stability of Co-cordierite was $T = 1423 \text{ K}$ [84W1]. Later on, the Mn and Co-cordierites were synthesized from oxides [99K1]. The homogeneous Co-glass, having cordierite composition, was crystallized at 1225 K in a few days. The pure Mn-cordierite was obtained for recrystallization temperatures above 1370 K . The Co-cordierite crystallizes in a hexagonal structure having space group P6/mcc (α -cordierite). There is a disordered Si/Al

distribution in the framework. The symmetry reduction from hexagonal to orthorhombic Cccm structure, in Mn-cordierite points to an ordering of the Si/Al atoms. The different structure were correlated with different synthesis conditions.

The temperature dependences of the lattice parameters of low cordierite were studied in samples with different compositions [79H1, 81M1, 86A1]. For example in [79H1, 81M1], a decrease of the *c*-axis with temperature is reported which is different from the data reported by [86A1] where *c* remains invariant. In addition, in [79N1, 81M1] an increase of the *b*-axis with temperature was described, whereas in the study of [86A1] was shown that *b* decreases. These discrepancies indicate that the temperature range and the chemical composition of the cordierite, especially the channel occupants have a strong bearing on the nature of thermal expansion.

High-pressure studies were performed on low cordierites [80M2, 82M1, 84M1, 86K1]. According to [84M1], low cordierite forms two high-pressure phases; one stable between 0.2 and 0.9 GPa and the other stable above 0.9 GPa. Both transitions were detected only as discontinuities of the compressibility which suggest that they are of second order. According to [86K1] the supposed discontinuity of lattice parameter *b* at nearly 0.3 GPa could not be established by the measurements taken, so that there is no evidence for a phase transition at this pressure. It was suggested that the observed tilting of two tetrahedra against each other in this structure could have led to the above misinterpretation. When water, but not fluorocarbon, is used as a pressure medium at 2.3 GPa, an additional electron density peak, presumably a water oxygen atom, appears in the channels. The water prevents the channels from shrinking and fixes their width at a value comparable to that of naturally hydrated cordierite. In one of the silica tetrahedra, the Si–O bond lengths are compressed almost by 1 % (2.3 GPa). This process may initiate a phase transition at higher pressures [86K1].

Mg₂Al_{4-x}Ga_xSi₅O₁₈

In [71L1] Ga-bearing cordierites were synthesized from glasses, at 1 atm as well as hydrothermally. The limit of stable solid solution is at about 12 mol % of the theoretical Ga- end member, at 750°C / 3 kbar, 900°C / 1 kbar or 1000°C / 1 kbar. The dry crystallization experiments performed at 1 atm on Ga-bearing cordierite glasses show that for appropriate conditions of annealing, single phases can be obtained up to 20 mol % of the theoretical gallium end member (*x* = 0.8). The most Ga-rich cordierite Mg₂Al_{3.2}Ga_{0.8}Si₅O₁₈ synthesized in the dry system at 1050°C/15 h was metastable. Ga-cordierites prepared at about 1000°C/1 atm are hexagonal. Lattice constants increase with increasing substitution of Ga for Al – Fig. 5 [71L1]. At 1350°C a hexagonal cordierite of composition Mg₂Al_{3.6}Ga_{0.4}Si₅O₁₈ could be transformed into a “low” cordierite. The structural distortion of hydrothermally synthesized samples increased with raising Ga-contents. A more complicated ordering scheme was suggested than in pure Al-cordierite [71L1].

Beryl, Be₃Al₂Si₆O₁₈; bazzite Be₃(Sc,Fe)₂Si₆O₁₈

The structure of the beryl was determined by [26B1, 51B1, 60Z1]. Then, the structural refinements of hydrous and anhydrous synthetic samples were reported [68G1]. The crystal structure of beryl is hexagonal with space group P6/mcc [68G1, 72M1]. The beryl structure has as a dominant feature hexagonal rings of Si-tetrahedra linked laterally and vertically to adjacent rings by mutual corners of Be-tetrahedra and Al-octahedra. The latter share a common edge with Be-tetrahedra. [Si₆O₁₈]¹²⁻ rings are arranged in layers parallel to (0001) and stacked to form a series of open channels along the *z*-axis – Fig. 6 [68G1]. Natural beryl crystals present a variety of impurities which may occupy either crystallographic sites of atoms of the host crystal or locations in the channels formed by silicate rings [68W1, 86B1, 88A1]. The chromium doped beryl is known as *emerald* and that doped with iron as *aquamarine*.

Beryl can accommodate additional constituents including Li, Na, K, Rb, Cs, H₂O, CO₂, He, Ar, etc. [87P1]. There have been discussions on the way in which these elements or molecules can be accommodated in the crystal structure. Elements and molecules such as K, Rb, Cs, H₂O and CO₂ occupy the large open channelways parallel to the *c*-axis. If K⁺, Rb⁺ and Cs⁺ were added to the channel ways, some type of charge-compensating substitution must take place [87P1]. The behaviour of H₂O and CO₂ in beryl was also analysed [84A1]. A discussion on this matter was presented in connection with cordierite (see cordierite section above).

The complex crystal chemistry of beryl has been evaluated on the basis of chemical analysis and X-ray structural refinements [88A1]. The main substitutions concern divalent and Li ions for Al in octahedral and Be in tetrahedral sites, respectively. Both substitutions need the entry of alkali in the 2a position in the channels

between the six-membered Si rings, whereas the 2b position at the center of each ring is occupied preferentially by water molecules. The extent of substitutions for Al and Be is limited by the imbalance arising from the bond-strength deficiency on O2. The effect of these substitutions on the lattice parameters allows the definition of three beryl series on the basis of the c/a ratio [88A1]: (1) the “octahedral” beryl, i.e. beryls where $\text{Al} \Leftrightarrow \text{M}^{2+}$, represent the main isomorphous replacement, are characterised by c/a values in the range 0.991...0.996; (2) the “tetrahedral” beryls where $\text{Be} \Leftrightarrow \text{Li}$ is the main substitution, with c/a values in the range 0.999...1.003; (3) the normal beryls with c/a ratios between 0.997 and 0.998 include those where the two substitutions occur together, though to a limited extent. A compositional gap exists between “octahedral” and “tetrahedral” beryls [88A1].

The iron substitution has been particularly analyzed. It was proposed that iron atoms can occupy all three crystallographic sites, but the replacement of Be^{2+} or Si^{4+} ($r = 0.35$ and 0.45 Å, respectively) by Fe^{2+} which has an ionic radius of 0.74 Å was considered to be unlikely. The existence of iron ions in the channels and the occurrence of an intervalence charge transfer between ferrous and ferric ions located either in the crystallographic sites or in the channels was proposed [68W1, 77P1, 78G1, 89I1]. The iron content in most natural beryls is less than 1 %, but some deep blue specimens may have up to 3 % [02V1]. According to [02V1], the Fe^{2+} is present replacing Al in the octahedral site and Be in the tetrahedral site, whereas Fe^{3+} is most probably replacing Al in the octahedral site.

In [89E2] was reported that in hydrothermal synthetic beryls Co occurs in both di- and trivalent forms. The authors believe that Co^{2+} enters the Al octahedron, whereas Co^{3+} occupies both Be tetrahedral and Al octahedral sites. In [01T1] was shown that in Co-bearing beryls $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, prepared by both flux and hydrothermal growth, the Co enters the structure mostly as Co^{2+} in the Al-site.

The composition of *bazzite* was determined by [64N1, 66C1] and the crystal structure was analysed by [56P1]. Bazzite has a beryl-type structure with two Si_6O_{18} rings at $z = 0$ and $1/2$ and with cations distributed at $z = 1/4$ and $3/4$ in three special positions (a), (c) and (f), respectively on 6-, 3- and 2- fold axis.

The deformation electron distribution, $\delta\rho$, in $\text{Na}_{0.04}\text{Fe}_{2.98}\text{Al}_2\text{Si}_6\text{O}_{18} \cdot 0.3\text{H}_2\text{O}$ natural beryl was analyzed [88E1, 90T1] – Fig. 7. The $\delta\rho$ characterises the redistribution of electrons in the ensemble at spherically symmetric atoms resulting from the chemical bond effects. The $\delta\rho$ peaks of $0.4 \text{ e}\text{\AA}^{-3}$ in height on Si–O bond are slightly displaced towards the oxygen atom and away from the bond line. The $\delta\rho$ peaks on the Be–O and Al–O bonds are about $0.1\text{...}0.2 \text{ e}\text{\AA}^{-3}$ and are strongly displaced toward oxygen atoms and also away from the bond line. Exploration of the deformation electron density (DED) in the Si–O ring established supplementary delocalization of electrons resulting in formation of $\delta\rho$ “bridges” between adjacent Si–O2 bond lines – Fig. 7a. The orientation of water molecules within channels was analysed. The oxygen atom in H_2O is on the 2a (0,0,1/4) site such that the H_2O symmetry axis L_2 (i.e. H–H vector and plane of molecule) is perpendicular to the L_6 axis of the beryl structure. The $\delta\rho$ maxima on the O–H bond line is about $0.3 \text{ e}\text{\AA}^{-3}$ – Fig. 7b. Six $\delta\rho$ peaks forming a ring-like circle have been observed around the O atom of the H_2O molecule in horizontal DED map at $z = 1/4$ – Fig. 7a. This DED topography has been interpreted as a partial statistic disorder of water molecules around the L_6 -axis. A similar distortion of the water molecule has been detected in cordierite [77C1], where the plane of the water molecule is also parallel to the $[\text{Si}_6\text{O}_{12}]^{12-}$ -ring plane. The Na^+ cation occupies the 2b (000) site within the channel.

Colored beryl varieties such as aquamarine, emerald as well as synthetic Co- and Cu-beryls have been studied [89E1, 90T1]. The main features of DED were found to be alike in all of the beryl samples. The Fe atoms in aquamarine were reported to occupy sites both in Be-tetrahedron and (predominantly) in the Al-octahedron. Co atoms are in the same positions. Cr^{3+} in emerald are only in the Al-octahedron and Cu^{2+} ions are only in the Be-tetrahedron.

The thermal expansion of beryl was studied [39E1, 72M1]. The temperature dependences of lattice parameters for two samples are given in Fig. 8 [72M1]. At room temperature the thermal expansion coefficients of beryl³⁶⁾ (for footnote see Table 3) are $2.6(1) \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $-2.9(4) \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ along the *a*- and *c*-axis, respectively while for emerald⁴¹⁾ the corresponding values are $1.7(1) \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $\sim 0.16(60) \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$. The linear expansion along the *c*-axis changes the sign. The *c*-values decrease up to 300°C or 100°C , for beryl and emerald, respectively, and then increase. The thermal expansivities are strongly dependent on impurity content.

The pressure dependences of the unit cell parameters are plotted in Fig. 9 [86H1]. The beryl linear compressibility is nearly isotropic with the *c*-axis approximately 20% more compressible than *a*. Beryl is composed of three symmetrically and chemically distinct polyhedra (tetrahedra of Si and Be and an octahedron of Al) all of which undergo significant compression up to 47 kbar. Polyhedral bulk moduli, calculated from

changes in volumes of enclosure defined by oxygen positions surrounding each cation are 1.4(4), 2.3(6) and 1.4(5) Mbar for Be, Si and Al, respectively. The bulk moduli of all three polyhedra are within one estimated standard deviation of the 1.7 Mbar crystal modulus, so the slight compression anisotropy cannot be ascribed unequivocally to any structural unit. The elastic constants of beryl are given in Table 4.

Microwave ultrasonic attenuation measurements have been made on beryl [73L1]. Values of the Debye temperature $\Theta_D = 792$ K, thermal conductivities 0.074 ($\parallel c$ -axis) and 0.057 ($\perp c$ -axis) W/cmK were determined. The measured attenuation at 9 GHz was ≤ 15 dB/cm and the calculated attenuation of longitudinal waves was 10 dB/cm, at RT. The room-temperature attenuation coefficients are consistent with the mechanism proposed by [39A1] which arises from interactions between the ultrasonic wave and the thermal phonon assembly.

8.1.3.3.2 Magnetic properties

Cordierite

The temperature dependences of the inverse magnetization for $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ and $\text{Co}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ cordierites are plotted in Fig. 10 [99K1]. In case of Co-cordierite, the paramagnetic Curie temperature is negative suggesting an antiferromagnetic coupling of Co^{2+} -ions – Table 5. Magnetic ordering might be expected below 1.5 K.

The effective moment of Mn in Mn-cordierite shows a slight deviation from the value characteristic of Mn^{2+} ion in a high-spin sp^3d^2 complex in octahedral field, namely $5.92 \mu_B$ [73W1]. The difference was suggested to be due to crystal field effects according to the sphenoidal distortion of the coordination polyhedron. For Mn-cordierite, short range antiferromagnetic correlations were observed at low temperatures – Fig. 10a. According to [99K1] the interaction between the magnetic ions is probably a super-exchange via TO_4 tetrahedra. The strongest interactions between Mn ions can be found along [001].

In analyzing the magnetic susceptibilities of natural cordierites having small iron content, corrections were made for ferromagnetic phase impurities and the paramagnetic contributions of minor constituents. There is a linear increase of the susceptibility with Fe^{2+} content – Fig. 11 [68P1].

For magnetic properties of Cr-doped beryl see section 8.1.3.3.6.

8.1.3.3.3 Neutron spectroscopy data

$\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, $\text{Co}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ cordierites

In the low-temperature range, no magnetic superstructure reflections were observed for both Mn- and Co-cordierites by neutron powder diffraction measurements [99K1]. Consequently, no antiferromagnetic long range order occurs down to 1.5 K. In Mn-cordierite, the difference plot of diffractograms measured at 2 and 100 K, respectively, shows a modulation – Fig. 12a. The diffuse scattering which may arise from static or dynamic spin disorder was analyzed by the Blech-Averbach formalism [64B1]. In this model the magnetic scattering intensity, normalized by the magnetic form factor j_o , I_Q/j_o^2 , is expressed by a sum over i shells of magnetic ions as a function of product between the scattering vector Q and the shell radius of magnetic ions d_i . The simplest model is an antiferromagnetic nearest-neighbour interaction of Mn^{2+} ions along [001] with the distance $d_i = 4.47$ Å. As seen in Fig. 12, this simple model describes reasonably the experimental data (solid line) [99K1].

The inelastic neutron scattering spectra of Co-cordierite show a magnetic excitation with an energy of 170 cm^{-1} (21 meV) – Fig. 12b. This was assigned to a spin allowed δ_1 transition which describes the lifting of the degeneracy of the t_{2g} triplet in the trigonally distorted octahedral ligand field [97W1]. – Fig. 12c. As discussed in section 8.1.3.3.9, for the assignment of the IR absorption bands at 170 cm^{-1} two models were considered. This can be due to a mode in which structural units (e.g. TO_4 tetrahedra) of the framework vibrate with respect to each other, or it is due to a “translational motion” of the 3d ions [99K1]. The inelastic neutron scattering was not observed at $\approx 170 \text{ cm}^{-1}$ in Mn-cordierite. Hence, it is in principle possible that the peak at 170 cm^{-1} in the neutron spectrum [97W1] was due to inelastic incoherent scattering, i.e., representative of the single particle dynamics of the Co ions [99K1]. This would imply that really the translational motion of the 3d-cation was observed. In [99K1] this matter was analyzed and it was shown that the peak at 170 cm^{-1} in cordierite is very likely not due to a translational motion of the 3d-ion. Thus, according to [99K1] the peak at 170 cm^{-1} was due to the motion of a structure unit such as TO_4 tetrahedra.

(Mg,Fe)₂Al₄Si₅O₁₈·nH₂O

Quasi-elastic neutron scattering experiments show that a static description of the orientation of the H₂O molecules is inappropriate [94W2]. A model was proposed in which the H₂O molecules in alkali-free cordierite, where ideally all the proton-proton vectors are aligned || [001] revolve around their center of gravity while maintaining their orientation. The model was based on the wave vector dependence of the elastic incoherent structure factor which leads to a very small radius of gyration ($\cong 0.4$ Å).

8.1.3.3.4 Nuclear gamma resonance (NGR) data

Beryl

The ⁵⁷Fe NGR method has been used to analyze the physical properties of beryls [76P1, 77P1, 78G1, 91S1, 02V1]. In [76P1] spectra were collected at different temperatures and for different samples. The main conclusions were that the ferrous ions are located in both octahedral and tetrahedral sites, whereas the ferric ions are probably in the octahedral sites. The low velocity line of one doublet which is symmetric at 4.2 K, broadens as the temperature increases, and at 77 K the shape of the doublet is very asymmetric. A relaxation effect was proposed as a possible cause for this behaviour, but no conclusive proof was offered. The RT ⁵⁷Fe NGR spectrum of blue beryl shows a quite broad central envelope near zero velocity and a relatively sharp peak close to 2.5 mm/s [77P1]. The presence of both Fe²⁺ and Fe³⁺ ions was a confirmation, according to these authors, for a charge transfer mechanism between Fe cations in the octahedral sites that have faces bridged by Si atoms. For the studied sample the spectrum suggests the predominance of Fe³⁺. The ⁵⁷Fe NGR spectrum of sodium-rich blue beryl [91S1] was similar to that reported by [77P1], but no asymmetry in the peak depths is apparent from the spectrum. In [78G1] another type of RT spectrum was reported for a deep blue beryl. The asymmetry of the doublet is visible and, according to these authors, the high-velocity peak was associated to a Fe²⁺ doublet whereas a very small absorption near 1.5 mms⁻¹ was associated with the presence of iron in the structural channels. The broad absorption near the center of the spectrum was attributed to the presence of Fe³⁺ in more than one crystallographic site. For a better understanding of the observed physical behaviour a carefully analysis of the spectra for deep-, light- and greenish blue- beryls was also performed [02V1]. In the following we give the result obtained by these authors which cover also the types of spectra previously reported.

The ⁵⁷Fe NGR spectrum of **deep blue beryl**, at 4.2 K, can be decomposed in three symmetric doublets, the most intense one having hyperfine parameters characteristic for octahedral Fe²⁺ – Fig. 13a [02V1]. The hyperfine parameters for the doublet accounting for about 10 % of spectral area are indicative for octahedral Fe³⁺ – Table 6. The hyperfine values for the third doublet are typical of ferrous ions in tetrahedral coordination [95M1]. The 14 K spectrum (not shown in Fig.) shows basically the same features, but the Fe²⁺ doublet is slightly asymmetric. At 30 K, an asymmetry in the line intensities of the main Fe²⁺ doublet is evident. In the 30 ≤ T ≤ 295 K temperature range, two independent widths and adjustable area ratios were used to characterize the major Fe²⁺ doublet. The asymmetry in the low velocity line increases with temperature, and at 295 K, a broad envelope is observed. The quadrupole splitting of the major Fe²⁺ doublet change from 2.74 mms⁻¹ at 4.2 K to 2.66 mms⁻¹ at 295 K indicating a relatively strong deformation of the axial symmetry of the involved crystallographic site [73B1]. We note that the spectrum at 295 K is close to that reported by [78G1]. At 500 K, the broad central envelope close to –0.3 mms⁻¹ has vanished and two relatively sharp doublets have emerged. The spectrum could be fitted with four doublets in which the two minor components, above mentioned, are still present but two Fe²⁺ doublets with almost the same isomer shifts were also identified – Fig. 13b and Table 6.

For **light blue beryl**, the ⁵⁷Fe NGR spectrum, at RT, is similar to that of deep blue beryl, but there are two differences – Fig. 13c. There is no evidence of Fe³⁺ and the middle doublet is present in higher proportion. The hyperfine parameters for the most intense doublet are representative for Fe²⁺, and the middle doublet has the same parameters as those obtained for deep blue beryl. At 80 K, the asymmetry in linewidth of the ferrous doublet is still present, but at 14 K it has almost vanished. At 500 K, the symmetric line is restored. The RT spectrum, recorded after cooling, as for deep blue beryl, is identical to that in the first run, evidencing the reversibility of phenomena determining the forms of the spectra. The RT spectrum is very close to that reported by [76P1].

The ⁵⁷Fe NGR spectra of **bluish green** and **greenish blue** beryls are similar and different from previous samples – Fig. 13d. The parameters for bluish-green beryl derived from the three-doublet fits are listed in

Table 6. The inner and outer doublets are due to ferric and ferrous ions, respectively whereas the doublet with $\Delta Q = 1.33 \text{ mms}^{-1}$ at RT seems to be similar to the weak ferrous doublet resolved for deep blue and light blue beryls. The relative areas for the ferric component are close to 30 %. The different shapes of these spectra compared to those discussed above are due to the presence of this component in higher proportion.

The ^{57}Fe NGR spectra of one **greenish blue** beryl are different from other spectra – Fig. 13e. The absorptions at RT, near zero velocity and 2 mms^{-1} have approximately the same intensity, and there is no apparent Fe^{3+} shoulder near the central peak. A two-doublet fit was considered acceptable – Table 6. No presence of Fe^{3+} was detected in this sample. At 80 K, the shape of the spectrum is similar, but at 14 K the lines are sharper and the two doublets have evolved to a more symmetrical pattern.

In order to analyse the physical reasons for the observed behaviour it was necessary to take into account the site preference of iron in the beryl structure and the origin of strong asymmetry in the RT spectrum. The doublet with the quadrupole splittings in the range $2.5 \dots 2.8 \text{ mms}^{-1}$ (14...500 K) is present for all samples, as reported by [76P1, 77P1, 78G1, 91S1, 02V1]. As above mentioned, two symmetrical doublets with similar hyperfine parameters were observed at 500 K. This implies that the Fe^{2+} ions must be located in two crystallographic sites with similar symmetry. Since there it is only one type of octahedral site, it was proposed [02V1] that some Fe^{2+} species are located in channel sites. The unusual temperature dependence of spectra was also analyzed. The diameter of the structural channels is approximately 2.8 \AA in the plane of the Si_6O_{18} rings and 5.1 \AA between two rings which is large enough to accommodate a variety of species [68W1]. A model structure was considered which admits two types of water molecules, one with the H–H vector parallel (type I) and the other with the H–H vector perpendicular (type II) to the c -axis [68W1]. According to [84A1] the channel cations are only coordinated by two type II water molecules, one below and one above in the channel. In addition, the channel ions are located in the center of the rings, i.e. at the most narrow spaces. Upon heating above 433 K, the water molecules become unbound and there is a partition of both types of water into a gas-like state. The cations have thus more freedom to move inside the channels. After cooling down, both types of water are again observed, indicating a reversible process. A hopping between types I and II occurs at $T < 300 \text{ K}$, whereas a random motion of the water molecules occurs at higher temperatures. At RT, the time scale of the bonded state (τ_b) is between that of NMR and IR spectroscopy [96C1]. Thus, the τ_b is of the order of the nuclear Larmor precession time ($\tau_L \approx 10^{-8} \text{ s}$). When $\tau_b \approx \tau_L$, the ^{57}Fe NGR spectrum is usually complicated, with broad lines, and therefore this kind of “relaxation” could explain the RT spectrum of deep blue beryl. It can be expected that at 500 K, $\tau_b \gg \tau_L$ so that a static average interaction will be experienced during the ^{57}Fe NGR event, and hence a well defined spectrum appears [02V1]. At 4.2 K, the water molecules are tightly bound to the iron species and a single sharp doublet is observed. The iron residing in channels are subject to different interactions, depending on the other constituents of the channels composition and this may cause a distribution of hyperfine parameters.

The Fe^{2+} ions are also present in octahedral sites. Only one ferrous doublet was included in the fits to account for the component with $\Delta Q \approx 2.5 \text{ mms}^{-1}$. It is reasonable to assume that in beryl the octahedral doublet would be symmetric, as found in deep blue beryl at 500 K. To refine the ^{57}Fe NGR spectra for deep blue beryl, at 4.2 and 295 K, four quadrupole doublets were introduced (second type of fit – Table 6). From the 500 K data it was found that the area ratio of the two major doublets is close to 1.1 and it is expected that this ratio does not vary significantly with temperature. Therefore, the 4.2 K spectrum was fitted with four symmetric components with fixed area ratio for the channel and octahedral Fe^{2+} doublets – Fig. 13b. The ΔQ and δ values for the channel and octahedral irons are nearly equal, in agreement with the data obtained at 500 K. The 295 K spectrum was fitted with three symmetric and one asymmetric doublet – Fig. 13b. The latter is to account for the “relaxed” component of the channel iron. The hyperfine parameters are in line with the 4.2 K and 500 K data, although a relatively broad doublet emerged for the octahedral Fe^{2+} – Table 6. The doublet with $\Delta Q \approx 1.5 \text{ mm/s}$ is present in higher proportions in light blue, blue green and one greenish blue beryls. The quadrupole splitting does not change drastically with temperature, indicating a strongly distorted coordination. In [02V1] was considered the above doublet to be due to Fe^{2+} in a tetrahedral site, as suggested by [76P1]. However, it was considered to be unlikely that Fe^{2+} ions would substitute on the Si or Be sites. The doublet seems to be present at all temperatures with more or less the same relative proportions. This was a reason for [02V1] to dismiss the assignment of the doublet to iron species involved in some kind of charge-transfer process as proposed by [77P1, 78G1]. However this process cannot be excluded. The hyperfine parameters of the doublet with $\Delta Q \approx 0.6 \text{ mms}^{-1}$ and $\delta \approx 0.35 \text{ mms}^{-1}$ at RT, are typical for Fe^{3+} in octahedral coordination. It was observed in samples of bluish green and deep blue beryls which have $\sim 30 \%$ of this component and most likely the doublet originates from Fe^{3+} ions replacing

Al in octahedral sites [02V1]. The color of the beryls seems to be determined by relative proportion of Fe^{3+} in the octahedral sites and of Fe^{2+} in the channels. Thus, deep blue samples have little Fe^{3+} , whereas greener samples have more Fe^{3+} or less channel Fe^{2+} .

Cordierite

The locations of iron in cordierites were also studied by the ^{57}Fe NGR method [74D2, 77G1, 77P1, 84V1, 00G1]. The ^{57}Fe spectrum shows the presence of one or two doublets corresponding to Fe^{2+} [84V1, 00G1] since of localization on different structural sites – Fig. 14 [00G1]. In some cordierites $\sim 10\%$ of the iron is not located on the octahedral site – Table 6. According to [74D2], this Fe^{2+} occupy a bipyramidal coordination along the inner wall of channel cavity. In [84V1] was suggested that Fe^{2+} substitutes for either Si^{4+} or Al^{3+} . According to [00G1] small amounts of Fe^{2+} replace tetrahedral Al_{11} site, where charge balance is achieved by placing Na in the center of six-membered rings. Little or no Fe^{3+} was observed by [00G1]. The presence of Fe^{3+} ions in tetrahedral coordination was reported at 77 K, but was not observed at 298 K [77P1]. According to [00G1], the amount of Fe^{3+} in nearly all natural cordierites is low, probably less than 2 % of the total iron.

8.1.3.3.5 Nuclear magnetic resonance (NMR) data

Cordierite

The ^1H NMR resonance study in low cordierite, $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18} \cdot n\text{H}_2\text{O}$ shows the presence of isolated water molecules in the channel formed of the $\text{AlSi}_5\text{O}_{18}$ rings with H–H directions along the crystallographic axes and with large vibration amplitudes [72T1].

The ^{27}Al NMR measurements in the above cordierite evidence the presence of two crystallographically nonequivalent Al sites. The Al1 and Al2 sites correspond to the distorted tetrahedral T_{11} site and T_6 site [72T1] – Table 7. The sharp satellite lines for ^{27}Al confirms the high degree of Al–Si ordering in low cordierite.

The ^{29}Si MAS NMR spectroscopy was used to analyze the degree of Al,Si order in cordierites [85P1, 85P2, 86F1, 87P2, 92D1]. For this reason cordierites were synthesized from glass of the same composition, by isothermal annealing at different temperatures (1185, 1290 and 1400°C) for periods from 2 min to 2000 hr [85P1, 87P2]. A sequence of ^{29}Si NMR spectra of synthetic cordierites isothermally annealed at 1185°C for increasing time is shown in Fig. 15 [87P2]. In the most disordered form, ^{29}Si MAS NMR spectra show eight distinct tetrahedral sites for silicon while there are only two distinguishable sites in the well annealed ordered form. For each group the ^{29}Si NMR lines can be seen for Si with 4Al, 3Al, 2Al and 1Al in their environment. Each type of environment gives rise to a separate peak in the NMR spectrum and the areas under those peaks are directly proportional to the populations of the respective structural units. These data may be used to calculate the number of Al–O–Al linkages per unit cell, $N(\text{Al–Al})$. The Al,Si ordering reduces $N(\text{Al–Al})$ to zero in the perfectly ordered orthorhombic form, and hence the progressive reduction in $N(\text{Al–Al})$ may be used as a measure of the degree of local Al,Si order – Fig. 16.

The entropy of Al,Si disorder in cordierite was calculated [96V1, 96V2] by using the data obtained from ^{29}Si NMR studies [85P1, 86F1, 87P2]. Also, a Monte Carlo method was developed [96D1] to determine the distribution of Al and Si cations from ^{29}Si MAS NMR spectra.

The ^{29}Si MAS NMR method was used also to analyse the Al,Si order in $\text{K}_x\text{Mg}_2\text{Al}_{4+x}\text{Si}_{5-x}\text{O}_{18}$ ($0 \leq x \leq 0.25$) cordierites synthesized by annealing glasses at 1290°C for different times [92D1]. As for Mg-cordierite, the increase of order is a continuous function of annealing time. The incorporation of potassium into the channel is balanced by the substitution $\text{K}^+ + \text{Al}^{3+} \rightarrow \text{Si}^{4+}$. These substitutions increase the Al/Si ratios. The rate of ordering is much lower for cordierites with higher K content. The incorporation of K and the increase of the Al/Si ratio reduces the rate of ordering as a consequence of the reduced probability for an Al,Si site exchange, to lower the number of Al–O–Al bonds or to take place at all – Fig. 17.

Beryl

In [51H1] beryl crystals were studied at $T \cong 20^\circ\text{C}$ by nuclear magnetic resonance absorption at ^9Be , ^{27}Al and ^{29}Si nuclei. Hyperfine structure due to nuclear quadrupole interactions were observed for ^9Be and ^{27}Al . No quadrupolar hyperfine structure was observed for ^{29}Si . Later on, in [54B1, 56B1], the quadrupolar hyperfine

structures of the ^9Be and ^{27}Al in beryl crystal at 300 K were examined. The nuclear quadrupole coupling constants and the asymmetry parameters were determined – Table 7.

NMR of the ^{27}Al nucleus in an emerald single crystal ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}:\text{Cr}^{3+}$) evidenced five resonance lines due to the quadrupole interaction of the ^{27}Al nucleus ($I = 5/2$) with the electric field gradient under a strong magnetic field [00K1]. The asymmetry parameter η is nearly zero [56B1, 00K1] – Table 7 – and implies that the ^{27}Al nucleus is in the local site with axial symmetry. The spin lattice relaxation time, T_1 , was measured by using a saturation recovery method. Only up to 30 % of the saturation value was inverted. This was probably caused by the fast relaxation mechanism due to the presence of paramagnetic Cr^{3+} impurity. The recovery curve of the saturation method shows the paramagnetic relaxation behaviour in the short delay time (t) region. The relaxation processes are shown in Fig. 18 for $T = 140$ K and 380 K [00K1]. The fast decreasing part in the relaxation process which is not covered by the straight line – Fig. 18a – and the linearly increasing part in recovery curve – Fig. 18b – represent the paramagnetic relaxation mechanism for the case of diffusion-limited relaxation [60B1]. The relation $M_0 - M(t) = A\exp(-t/T_1)$ was used as a fitting function. The relaxation time, T_1 , increases until about 200 K and then decreases. At temperatures above 200 K, the relaxation rate is proportional to T^2 , similar to the case when relaxation occurred by the two-phonon process (Raman process), via the emission or absorption of two phonons, or absorption of one phonon followed by an emission of another. There are also the direct process and the Orbach process [61A1]. Since $\ln T_1$ is nearly proportional to T^{-1} – Fig. 18c – the activation energy of the nucleus was estimated by using the Arrhenius equation $\tau = \tau_0 \exp(E_a/k_B T)$. Below 200 K, the paramagnetic contribution to the relaxation mechanism becomes dominant over the quadrupole relaxation induced by thermally activated phonons. Above 200 K, the quadrupolar interaction through Raman process is dominant. The activation energies, E_a , determined above and below 200 K are 0.053(5) and 0.038(7) eV, respectively.

For beryl a simple empirical relation, between the chemical shift, δ , of ^{29}Si and the positions of its second nearest neighbours (X) with a correction for the geometry of the Si-O-X triangle was also established [91S2, 91S3].

8.1.3.3.6 Electron paramagnetic resonance (EPR) data

Cordierite

In [66H1] the EPR spectra of Fe^{3+} ions located at one of the aluminium sites in low cordierite were analyzed, at RT and X- and K- band frequencies. The spectra exhibit large zero field splitting and have been fitted to a spin Hamiltonian of orthorhombic symmetry:

$$\mathbf{H} = g\mu_B \mathbf{B} \cdot \mathbf{S} + \frac{1}{3} B_2^0 [3S_z^2 - S(S+1)] + \frac{1}{3} B_2^2 (S_z^2 - S_y^2) \quad (1)$$

The g values and the crystal field parameters, B_2^0 and B_2^2 are given in Table 8. According to [66H1] the iron enters substitutionally into the lattice at the location of Al atoms.

The reactivity of cordierite precursor with CuO powder was also studied by EPR [92P1]. An ESR signal of Cu^{2+} was detected after heating the mixture of cordierite precursor with CuO at 500°C, showing that CuO begins to dissolve and the signal strongly increases between 700...800°C in relation to the transition amorphous – μ -cordierite. As already mentioned (see section 8.1.3.3.1), the metastable form μ -cordierite is isostructural with β - SiO_2 [53K1]. The crystallization of α -cordierite prevented dissolution. The dissolved Cu^{2+} is located within the amorphous phase and the EPR spectrum is characterized by $g_{\parallel} = 2.35$ and $g_{\perp} = 2.08$ – Table 8.

Beryl

The paramagnetic resonance studies were performed on Fe^{3+} and Cr^{3+} doped beryl. The determined parameters are listed in Table 8. There are EPR studies on emerald, i.e. antiferromagnetic exchange coupling [78E1], spin-lattice relaxation of Cr^{3+} EPR at 22.2 GHz in the temperature range of 1.5...45 K [80M1], a study of the ESR line widths of the inter-doublet [81A1] and Cr^{3+} and Fe^{3+} ESR studies [60D1, 82E1, 83M1, 87O1, 88M1].

In chromium doped beryl (emerald), Cr^{3+} ions substitute for Al^{3+} ions, so isolated Cr^{3+} ions are located at sites of D_3 (32) point group symmetry. Early spectroscopic studies were made on emerald in connection with possible application in a high frequency maser. In [59G1] was reported that the $^4\text{A}_2$ ground state of Cr^{3+} , in octahedral coordination, is split in beryl into two doublets separated by $2D = 53.6$ GHz, the splitting arising from

the trigonal distortion of the octahedron. Maser action between the doublet was observed by [61G1]. With the same application in mind, in [66S1] spin-lattice relaxation measurements were performed and they observed enhanced relaxation for Cr^{3+} dopant levels $> 1.2 \cdot 10^{20} \text{ cm}^{-3}$. They proposed that this concentration dependence was due to a contribution arising from the modulation of the exchange interaction between pairs of Cr^{3+} ions. In [60D1] the optical and EPR spectra of Fe^{3+} ions in beryl were described. There were many resonance lines in samples of emerald which could not be attributed to isolated Cr^{3+} ions. They assigned these additional lines to Cr^{3+} ion pairs. The EPR spectra of synthetic and natural samples of chromium doped beryl confirmed the presence of a large number of resonance lines, in addition to those arising from isolated Cr^{3+} ions occupying Al^{3+} sites [77H2, 78E1], in agreement with [60D1]. The angular and temperature dependences of the spectra indicate that most of the additional lines arise from three types of exchange-coupled pairs of Cr^{3+} ions occupying first, second and third nearest neighbour Al^{3+} sites, with antiferromagnetic coupling constants [78E1]. The spectra have been fitted with a spin Hamiltonian which includes anisotropic bilinear exchange, Zeeman and crystal field terms.

For isolated Cr^{3+} ions the EPR spectrum may be described by the single-ion spin Hamiltonian appropriate to axial symmetry:

$$\mathbf{H} = g_{\parallel} \mu_B B_z S_z + g_{\perp} \mu_B (B_x S_x + B_y S_y) + B_2^0 O_2^2 \quad (2)$$

where the axes are chosen so that $z \parallel c$.

The $D = 3B_2^0$ value of -0.8956 cm^{-1} was obtained by [78E1], and $-0.894(2) \text{ cm}^{-1}$ by [59G1].

The first nearest-neighbour (1NN) Cr^{3+} ion pair (a,b) is formed by two Cr^{3+} ion occupying Al^{3+} sites which are nearest neighbours along the c -axis. The appropriate spin Hamiltonian is:

$$\mathbf{H}_p = \mathbf{H}(a) + \mathbf{H}(b) + J_{\parallel} S_{az} S_{bz} + J_{\perp} (S_{ax} S_{bx} + S_{ay} S_{by}) \quad (3)$$

where $\mathbf{H}(a)$ and $\mathbf{H}(b)$ are of the single-ion form given by the relation (2).

The structure of 2NN Cr^{3+} ion pair is realized when Cr^{3+} ions replace two Al^{3+} ions which are nearest neighbours in the basal plane, and the point group symmetry about the Be^{2+} ion which is the mid-point of the Cr^{3+} - Cr^{3+} axis is D_2 (222). There are three magnetically nonequivalent 2NN pair sites in the unit cell. The appropriate pair spin Hamiltonian takes the form:

$$\mathbf{H}_p = \mathbf{H}(a) + \mathbf{H}(b) + J_x S_{ax} S_{bx} + J_y S_{ay} S_{by} + 2J_z S_{az} S_{bz} \quad (4)$$

where

$$\mathbf{H}(i) = g_{\parallel} \mu_B B_z S_{iz} + g_{\perp} \mu_B (B_x S_{ix} + B_y S_{iy}) + B_2^0 O_2^0 + B_2^2 O_2^2 \quad (5)$$

In the single ion spin Hamiltonian (5) was implicitly assumed that $g_x = g_y = g_{\perp}$.

Most of the remaining triplet lines in the $B \parallel c$ spectrum may be assigned to 3NN pairs. The two Al^{3+} sites involved are diagonally opposite in the rectangle formed by the four Al^{3+} ions and the pair has no non-trivial group symmetry.

The general pattern established above for the 1-3 NN pairs shows that the exchange interaction rapidly decreases with increasing separation, and that, in consequence, the pattern of satellite lines for particular pairs tends to collapse into the single-ion transition. In some samples which show a narrow single-ion resonance line, there appear lines additional to those from the 1-3NN pairs. These lines have been not studied in detail, but it seems reasonable to assume that they are due to 4NN and more widely separated Cr^{3+} ion pairs.

The spectra were fitted with the spin Hamiltonians (2) - (5). The parameters thus obtained are listed in Table 8. The mean antiferromagnetic exchange coupling constants of ~ 2.260 , 0.195 and 0.026 cm^{-1} were obtained for the three types of exchange-coupled pairs of Cr^{3+} ions occupying first, second and third nearest neighbour Al^{3+} sites. The spin interaction between the Cr^{3+} ions may be adequately represented by isotropic bilinear exchange and magnetic dipolar interaction. There is no evidence for a significant biquadratic exchange. For 1NN Cr^{3+} pairs in beryl the intrinsic biquadratic exchange is less than 1 % of the bilinear exchange.

The EPR and optical spectra of Fe-containing beryl were first reported by [60D1]. They observed an intense set of five lines in the EPR spectrum and several absorption lines in the visible UV region of the optical

spectrum which they assigned to isolated Fe^{3+} ions replacing Al^{3+} ions – Table 8. In [60D1] were also observed about thirty weaker lines in the EPR spectrum, some of which were tentatively assigned to Fe^{3+} ions substituting for Be^{2+} or Si^{4+} ions. The possibility that such lines could be due to exchange coupled pairs of Fe^{3+} ions, substituting Al^{3+} , has not been investigated. In [82E1] the EPR spectrum of first nearest neighbour pairs of Fe^{3+} ions substituting for Al^{3+} ions in beryl was analysed. The structure of the first nearest neighbour pair site was considered as having point symmetry $C_{3h}(\bar{6})$. It was suggested that the symmetry used previously by the same authors for analysing the spectrum of Cr^{3+} pairs [78E1] was incorrect. The appropriate spin Hamiltonian for analysing the spectrum was similar to that given by the relations (2) - (5) except that in (5) the last two terms

were replaced by $DS_{iz}^2 + \left(\frac{F-a}{180}\right)O_{4i}^0 \pm \frac{\sqrt{2}a}{9}O_{4i}^3$, these terms having their usual meanings. In [82E1] eight of

the possible thirty allowed transitions for 1NN Fe^{3+} pairs were identified. It was concluded that most of the weak lines reported by [60D1] were in fact due to 2NN and 3NN pairs. The form of the interionic coupling determined for 1NN Fe^{3+} pairs was similar to that found for Cr^{3+} pairs, that is the sum of Heisenberg antiferromagnetic exchange and the magnetic dipolar interaction. One marked difference between Cr^{3+} and Fe^{3+} pair results is that in the former case the values of D for single ions and pairs are within 1 % of each other, whereas for the Fe^{3+} pairs a value was found around 18 % larger than for single ions. It was proposed that the resonance lines attributed by [60D1] to Fe^{3+} ions in Be^{2+} or Si^{4+} sites were due to Fe^{3+} pairs [82E1].

The EPR spectrum of Co-doped flux-grown beryl ($\mathbf{B} \parallel \mathbf{c}$), at 4.2 K and 74.51 GHz, consists of sharp lines due to Cr^{3+} and Fe^{3+} ions (uncontrolled impurities) and two additional wide lines identified with two different Co^{2+} centers. In addition to identified spectra, two weaker lines near 1.35 and 3.92 T whose nature was not identified, were shown [04S1]. The first Co^{2+} center has an axial symmetry and was described by an Hamiltonian with effective spin $S = 1/2$: $\mathbf{H} = \mu_B \mathbf{g} \mathbf{S} \mathbf{B} + \mathbf{I} \mathbf{A} \mathbf{S}$, where \mathbf{S} and \mathbf{I} are the electron and nuclear spin operators, and \mathbf{g} and \mathbf{A} are tensors of spectroscopic splitting and hyperfine structure, respectively. The directions of g_{\parallel} and A_{\parallel} for the center coincided with the z -axes of the AlO_6 polyhedron – Table 8. The observed spectrum was assigned to Co^{2+} ions occupying the octahedral Al^{3+} site. It was assumed that the intricate structure of the spectrum is a result of the superposition of lines from exchange coupled pairs of Co^{2+} on the main line. In [89E2] the intricate structure of Co^{2+} spectrum at $\mathbf{B} \parallel \mathbf{c}$ was explained by the presence of two inequivalent magnetic species in the unit cell. According to [04S1] this statement seems to be erroneous. The second Co^{2+} center was described by an effective spin $S = 1/2$ and has three inequivalent magnetic complexes in the unit cell with axes z , y and x , coinciding with $[2\bar{1}\bar{1}0]$, $[01\bar{1}0]$ and $[0001]$ directions, respectively. Because of the overlapping of the spectra of three complexes and the exchange coupled pairs of ions, only approximate parameters were determined – Table 8. The observed symmetry of Co^{2+} was consistent with that of Be^{2+} [04S1].

After γ -irradiation of Co-doped beryl ($\cong 0.1$ wt % CoO), at 77 K two additional centers were observed [89S2]. The first is an O^- hole on the oxygen of the SiO_4 tetrahedron at which Al^{3+} substitute Si^{4+} and the second one $\text{Al}^{2+} \rightarrow \text{Be}^{2+}$ – Table 8.

The exchange coupled pairs of Cr^{3+} and Ti^{3+} in beryl was also studied by [81K1]. It was suggested that the 4th and 5th nearest neighbour pairs wherein the ions are positioned at $\cong 9.2$ Å along the c - and a -axes seem to contribute most significantly to the distortion of the main line from that of isolated Co^{2+} ion [04S1].

8.1.3.3.7 Heat capacity

Cordierite

The temperature dependences of the heat capacities, for high and low cordierites, as well as cordierite glass are plotted in Fig. 19a [93C1]. There is no measurable difference in heat capacity between the two structural states of cordierite. The heat capacity is a linear function of the H_2O content in hydrous cordierite, $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18} \cdot n\text{H}_2\text{O}$ – Fig. 19b – with a partial molar heat capacity value of 43.8(8) J/(mol H_2O) K. The data are consistent with a statistical-mechanical model of the behaviour of H_2O in cordierite that allows the heat capacity of hydrous cordierite to be extrapolated to higher temperatures. The model representation of the heat capacity is the sum of the heat capacities of anhydrous cordierite and the ideal gas H_2O plus a constant factor R , the gas constant (8.314 J/mol K).

Beryl

The heat capacity of beryl having the composition $\text{Be}_3(\text{Al}_{0.986}\text{Cr}_{0.014})_2\text{Si}_6\text{O}_{18}\cdot 0.36\text{H}_2\text{O}$ has been measured at $5 \leq T \leq 340$ K – Fig. 20 [86H2]. The C_p vs T data, for $200 \text{ K} \leq T \leq 1800 \text{ K}$, can be represented by the relation: $C_p = 1625.842 - 0.425206 T + 12.0318 \cdot 10^{-5} T^2 - 20180.94 T^{-0.5} + 6.82544 \cdot 10^6 T^{-2}$ where T is in kelvins. The heat capacity of beryls is unexpectedly high at low temperatures ($T < 30$ K) for a compound with such a low mean atomic weight.

The Debye temperature of two beryls were calculated from elastic constants [73Y1] by [86H2]. Values $\Theta_D = 795.6$ and 799.1 K, respectively were obtained. The heat capacity, for $\Theta_D \approx 800$ K, can be represented reasonably well up to about 16 K by a Debye function. From such a function a heat capacity was estimated for beryl that is only ≈ 19 % of the measured heat capacity at 16 K. Even considering the heat capacity of water, there is a large difference. No explanation for the deviation of measured heat capacities from theoretical estimation was given [86H2].

8.1.3.3.8 XANES data

Cordierite, beryl

The normalized Fe-K edge XANES spectra of the cordierite are shown in Fig. 21 [00G1]. Since the studied natural cordierites contain only, or predominantly, Fe^{2+} in sixfold coordination, the spectra were virtually identical in the edge and post-edge regions, while a careful analysis of the pre-edge region showed differences. The pre-edge spectra were fitted by three Gaussians with nearly the same energies (7112.5(1) eV; 7113.5(2) eV; 7114.3(1) eV). A strong enhancement of the Gaussian at about 7114.3 eV was observed in some cordierites^{31,32} (for footnotes composition see Table 3). The total pre-edge intensity of these two cordierites is slightly higher than that in cordierite^{33,34}. These differences could suggest the presence of a small percentage of Fe atoms on a different coordination state in cordierites^{31,32}.

Al K-edge absorption near-edge structure (XANES) spectra of beryl and cordierite were studied [95L1]. The Al K-edge is located at 1567 eV for cordierite and 1568.3 eV for beryl. The XANES data obtained in a number of aluminosilicates show that the Al-K edge shifts by about 1.6 eV with increase of the coordination number of Al, from 1566.7 eV for $^{[4]}\text{Al}$ (averaged for eight samples) to 1568.3 eV for $^{[6]}\text{Al}$ (averaged for 17 samples).

8.1.3.3.9 Optical properties

Cordierites

The optical spectra of natural cordierites were studied [00G1]. More recent data are reviewed [00G1]. As seen in Fig. 22, Fe^{2+} ions produce a doublet consisting of two overlapping bands appearing in the α -polarization orientation ($E \parallel c$) between 11000 and 8000 cm^{-1} , and a strong, single band near 10000 cm^{-1} in the γ -polarized and β -polarized spectra [00G1]. The doublet consists of two bands situated at about 10000 and 8000 cm^{-1} in cordierite³⁴ (for composition see Table 3) and they are shifted 100...300 cm^{-1} to higher energy in the cordierite³². In the visible region, a very broad band centered at about 20000 cm^{-1} which was assigned to Fe^{2+} - Fe^{3+} charge transfer [77G1, 84V1], appears in the β - and γ -polarized spectra. Sharp, intense bands related to the internal stretching bands of molecular H_2O were present in the IR and NIR spectra between 3000 and 8000 cm^{-1} . They are superimposed on a relatively weak and broad band. In [77G1] the doublet in the α -polarized optical spectra was assigned to spin allowed transitions between split low-symmetry $^5\text{T}_2$ - and ^5E -states of Fe^{2+} ions on the octahedral site. This assignment was confirmed by [00G1] – Fig. 22. The strong band in γ -polarized and β -polarized spectra was attributed to Fe^{2+} ions on a site other than the octahedron [00G1]. In [77G1] this band, together with a minor spectral feature at ~ 4500 cm^{-1} was attributed, to a channel position in the center of six-membered ring. In [84V1] the optical spectra were interpreted as indicating that Fe^{2+} replaces Al^{3+} or Si^{4+} . According to [00G1], the above spectroscopic data are most consistent with a small amount of Fe^{2+} (i.e. 0.02 of Fe^{2+} pfu) being located on a tetrahedral Al_1 site in cordierite, where charge balance is achieved by placing Na in the center of the six-membered rings.

The IR spectra of cordierite in early stages were analyzed [58P1, 66N1] in order to clarify the role of water [59S1, 64S1, 67F1, 77G1, 84A1]. Then, IR studies were also devoted to analyze the structural transition from

high- to low-cordierite [69F1, 69L1, 83P1, 89G2, 89R1]. In [89G1] the stoichiometric Mg-cordierite glass was devitrified by annealing isothermally in air at 1290°C and different period of time. The IR spectra thus obtained are shown in Fig. 23 [89G2]. On increasing the annealing time of the glass, an additional band can be observed on the high energy side of the 580 cm⁻¹ mode. The splitting of the phonon mode near 580 cm⁻¹ (for annealing time longer than 20 min) is due to the changing selection rules during the transition from the P6/mcc high cordierite phase to the Cccm low cordierite phase. No line splittings or discontinuities of the full width at half maximum or integrated intensities were observed in the 770 cm⁻¹ to 850 cm⁻¹ range. The peak frequencies of the modes near 770 cm⁻¹ and 580 cm⁻¹ are plotted as a function of annealing time in Fig. 24a. The frequency of the 770 cm⁻¹ mode changes linearly with the logarithm of the annealing time, $\Delta\omega_{770\text{cm}^{-1}} \propto \ln t \propto Q_{\text{od}}$ where Q_{od} is the order parameter. The 580 cm⁻¹ mode shows a marked discontinuity in the absorption frequency at an annealing time around 40 min, coinciding with the phase transition from hexagonal to modulated phase. As only the structural short-range parameter q_1 changes during this transition, $\Delta\omega_{580\text{cm}^{-1}} \propto A Q_{\text{od}} + B q_1$, where A and B are constants. The first-order character of the hexagonal to modulated transition can be deduced from integrated intensities of the 568 cm⁻¹ mode versus annealing time – Fig. 24b. This band is symmetry forbidden in hexagonal cordierite and appears stepwise during the transition [89G2].

The phase transition of K-bearing cordierite, $\text{K}_{0.2}\text{Mg}_2\text{Al}_4\text{Si}_4\text{O}_{18}$ from hexagonal to modulated and orthorhombic cordierite was also analysed [89R1]. The structural states of K-bearing cordierite appear to be very similar to the pure-Mg cordierite.

The similarity of Co- and Mn-cordierite IR spectra is obvious, which is to be expected due to the very close structural and crystal chemical relationship – Fig. 25. The main difference is that the absorption bands in the Co-cordierite spectra are not so well resolved as those in Mn-cordierite [99K1]. This can be connected with crystallization effects. The band system around 1000 cm⁻¹ in the IR spectrum of Mn-cordierite, generally assigned to Al–O stretching vibrations, shows several maxima which are typical for “intermediate” and ordered cordierite, while in Co-cordierite spectrum only shoulders on the main absorption peak can be detected which are characteristic for hexagonal cordierite [69L1, 89G2]. The band at ~ 170 cm⁻¹, in the energy range of lattice vibrations, is sensitive to the local symmetry, as the spectrum of Mn-cordierite shows two well separated peaks, while in the Co-cordierite spectrum only one much broader peak is observed. For the assignment of the IR absorption band at 170 cm⁻¹ two models seem to be appropriate: due to a mode in which structural units (e.g. TO_4 tetrahedra) of the framework vibrate with respect to each other, or that is due to a “translational motion” of the 3d-ions, i.e. a phonon whose eigenvector is dominated by the displacement of the 3d ions [99K1]. Finally, it was concluded that the peak at 170 cm⁻¹ is very likely due to motion of a structural unit such as TO_4 tetrahedra (see also section 8.1.3.3.3).

The IR method was used also for the analysis of H_2O behaviour in cordierite [00K2]. It was shown that the interaction between H_2O and the silicate framework is very weak [76L1, 94W3]. In [77G1] ν_1 and ν_3 mode energies were reported for type I H_2O at ~ 3650 and ~ 3689 cm⁻¹, respectively. The wave number of ν_1 and ν_3 of free H_2O in solid inert matrix differs by ~ 100 cm⁻¹ [00K2]. First principle calculations on the H_2O molecule also give a difference of about 100 cm⁻¹, higher than the difference between ν_1 and ν_3 of “type I H_2O ” (~ 40 cm⁻¹). The wave number difference $\Delta\bar{\nu}$ between ν_3 and ν_1 of “type II H_2O ” is 58 cm⁻¹ which is also small. Here, however, H_2O interacts with an alkali metal (K, Na) located at (0,0,0) in the center of six-membered rings and therefore need not to have $\Delta\bar{\nu}$ of the free H_2O molecule. In addition to the above discrepancy, the IR spectra reported by [67F1, 77G1] contain two additional modes at ~3710 and ~ 3600 cm⁻¹ that were not considered in their analysis. In [00K2], by polarized single crystal Raman spectra at RT and 5K and polarized IR spectra at RT natural cordierites were studied in the wave number region of CO_2 symmetric stretching vibration and the H_2O stretching vibrations. According to [00K2] the CO_2 molecules are preferentially aligned parallel to the x-axis, consistent with the results from X-ray diffraction [77C1, 85A1] and optical studies [82A1, 82A2, 84A1, 85A1]. A linear relationship was found between the CO_2 content and the Raman intensity ratio of the normalized CO_2 stretching mode against a Si–O stretching mode. This permits a determination of the CO_2 contents in cordierite using micro-Raman measurements. The internal stretching modes between 3500 and 3800 cm⁻¹ were assigned to various types of H_2O molecules occurring in the channel cavity. Three different orientations of H_2O molecules that have no interactions with alkali cations located at (0,0,0) in the six-membered tetrahedral rings, were classified in a static model as class I H_2O molecules. The H–H vector for two of them is parallel to [001] and their molecular planes lie in the xz and yz crystal plane. The third type has its H–H vector directed along the x -axis and its molecular plane lies in the xz plane. Two other types of H_2O have interactions with alkali cations

located at (0,0,0). They are classified as class II H₂O and are distinguished themselves by the number of H₂O molecules bonded to the alkali atoms. The formation of weak hydrogen bonds, at low temperatures, may explain the appearance of some Raman stretching modes below 200 K. The H₂O molecules of class I-type I/II are probably dynamically disordered about [001], and hopping between orientations in the xy and xz planes down to 5 K. Class II H₂O may also be disordered, but more studies are required to describe its dynamic behaviour [00K2] (see also section 8.1.3.3.1).

Beryl, bazzite

The effect of several types of impurities on the vibrational spectrum of beryl was studied by infrared spectroscopy [84K2, 87K1] in the 800...1300 cm⁻¹ range. Other IR studies focussed on the spectra of molecular impurity H₂O (and CO₂) in beryl [67W1, 84A1, 87V1, 89S1]. The anharmonicity of infrared vibration modes has been studied in beryl crystals analysing the temperature dependence of the reflectivity [72G2]. It was suggested that only three phonon interactions cause the anharmonicity of the internal modes whereas the anharmonicity of the external modes which have an ionic character, was caused by cubic and quartic terms.

Polarized Raman spectra on beryl were obtained by [74A1, 76A1, 90H1]. The polarized Raman spectra, at room temperature, for a synthetic flux grown emerald (0.73 wt % Cr₂O₃) are given in Fig. 26 [90H1]. The spectra were analysed comparatively to those of natural samples having different content of magnetic impurities. The factor group analysis predicts the following number of Raman active modes: 7A_{1g} (xx+yy,zz), 13E_{1g} (xz,yz) and 16E_{2g} (xy,xx-yy). The A_{1g} modes are exclusively associated with motions of silicate rings. The E symmetry present pairs of bands separated by up to 50 cm⁻¹ [76A1, 90H1]. These pairs arise to a first approximation from the same mode in each of two silicate rings in the unit cell, i.e. for several silicate modes the coupling with motion involving Be or Al remains small. As compared to the purest beryl crystal available, plotted in Fig. 26, the Raman spectra of other samples show significant differences. The data suggest that the Si-O stretching vibrations are quite sensitive to impurities in both Raman and IR [84K2, 87K1] spectroscopies.

The spectral changes in natural beryl crystals as compared to pure beryl around 520 cm⁻¹ (E_{1g}) and 400 cm⁻¹ (E_{2g}) are probably related to impurities substituting for Al in crystals, as these spectral regions show displacements toward lower Raman shifts for the crystal bazzite where Al is almost completely replaced by Sc. The polarized Raman spectra of bazzite are shown in Fig. 27 [90H1]. The (cc) polarized spectrum compares very well with that of beryl. In the other polarizations, changes are observed due to substitution of Al by Sc. In the E_{1g} polarization, the band observed at \approx 520 cm⁻¹ is shifted to 451 cm⁻¹ in bazzite. Also, in the E_g polarization the strongest shift appears for the bands around 412...423 cm⁻¹ in beryl and 377 cm⁻¹ in bazzite [90H1].

There are many optical studies on beryl crystals. The optical and fluorescence spectra of emerald show two sharp lines separated by 68 cm⁻¹ at \sim 14700 cm⁻¹ [65B1, 65W1]. These were assigned to transitions between the ⁴A₂ ground state and a ²E excited state. The separation of the two lines reflects the splitting of the ²E state by the trigonal component of the crystal field in the same way as for the R lines of ruby. In [65W1] was reported that for deep green samples of emerald there are, in addition to the two strong R lines, some weaker satellite lines which were assigned to Cr³⁺ ion pairs by analogy with the situation in ruby. The separation of these satellite, from the single ion lines, is much less than for ruby, suggesting a smaller exchange coupling constant.

The reflectance spectra of beryl were reported in [72G1, 74A1]. These differ in some interpretation of finer features. The optical spectrum of iron doped beryl is characteristic for the Fe³⁺ ion [60D1].

The effect of raising temperature on spin allowed dd transitions of octahedral Cr³⁺ was studied in Cr³⁺ bearing beryl. The spectra – Fig. 28 – show, in the near UV to near IR spectral regions, two broad and strong band systems typical of spin allowed Cr³⁺ dd-transitions, derived from ⁴A_{2g} \rightarrow ⁴T_{2g} (U-band) or from ⁴A_{2g} \rightarrow ⁴T_{1g} (Y-band) in octahedral fields [94T1]. In low symmetry fields of distorted octahedra these two transitions may be split due to abolishing of the degeneracy of the upper T-states. The split components may have different polarization behaviour due to symmetry selection rules. The above splitting was observed, especially at low temperatures, for the U band in emerald – Fig. 28. Thus, the shape of the spectra in Cr³⁺ bearing beryl are complicated due to band splitting, prominent in case of U-band in π polarization, at 77 K, and due to the appearance of three narrow bands at \approx 14660 cm⁻¹, \approx 15150 cm⁻¹ and \approx 15350 cm⁻¹ caused by spin forbidden transitions of Cr³⁺. They shift to the red on heating. At the lowest temperature achieved, 77 K, a shoulder at 17400 cm⁻¹ appears at the high energy wing of the U-band in π -polarization. At room temperature, this component band, marked in figure by an arrow, creates an asymmetry in the high-energy slope of the U-band – Fig. 28b. Band splitting indicated by a shoulder or band asymmetry, is also obvious for the Y-band in σ -

polarization, especially at low temperature – Fig. 28b. As for intensities, the highest increase on raising temperature is observed for the Y-band in π -polarization, where the integrated intensity increased by a factor of 2.2 between 77 and 597 K. U- and Y-bands for σ -polarization increase by only 1.3, whereas the integral intensity of the U-band in π -polarization remains unchanged, an effect created by a combination of band width increase and absorption coefficient α_{\max} decrease – Fig. 28b. The three above mentioned spin forbidden bands sharpen and strongly increase in the linear absorption coefficient on cooling.

The blue colour of natural beryl (aquamarine) was attributed to absorption bands Fe^{2+} impurity in the near infrared [68W1, 71S1, 76P1, 77P1, 78G1, 82B1]: the σ polarized band at around 12000 cm^{-1} ($E \perp c$), π -polarized bands at around 10000 cm^{-1} and 12000 cm^{-1} ($E \parallel c$) and a band at around 16000 cm^{-1} in deep blue beryl. The π -polarized bands were first attributed to Fe^{2+} in channel site, and σ -polarized band to Fe^{2+} in the sixfold-coordinated Al^{3+} site [68W1, 71S1, 77P1]. On examining the ^{57}Fe NGR and ESR spectra, it was concluded that the π -polarized bands arose from Fe^{2+} in the sixfold-coordinated site and suggested that the σ -polarized band arises from Fe^{2+} in tetrahedral site [76P1]. The deficiencies of some of these assignments were pointed out by [78G1]: Fe^{2+} ion produces absorption bands in pairs because of the Jahn-Teller effect or geometric distortions of coordination polyhedron; the molar absorptivity is too high for the Al^{3+} site [77G2]; typical tetrahedral Fe-O bond distances are near 1.98 \AA [69S1], whereas Fe^{2+} must be accommodated into the 1.6 \AA Be or Si site. From structural similarities between cordierite and beryl, the optical-absorption study of cordierite [77G1] was taken as the basis for interpretation of the beryl spectra [89I1]. It was shown, in the cordierite spectrum [77G1] that two overlapping lines at 995 and 1170 nm arose from Fe^{2+} in the sixfold-coordinated site. Thus, the π -polarized bands of beryl arose from Fe^{2+} in the sixfold-coordinated Al^{3+} site, in agreement with [76P1], but the σ -polarized band arose from Fe^{2+} in the channels. In beryl, the band at around 16000 cm^{-1} has been attributed to an $\text{Fe}^{2+}\text{-Fe}^{3+}$ intervalence interaction [71S1, 78G1].

The optical absorption spectra of natural green and blue beryl [82B1] showed only a single Fe band at $\approx 12000\text{ cm}^{-1}$ ($k \parallel c$). Thus, in these sample, Fe^{2+} is in the sixfold-coordinated site and $\text{Fe}^{2+}\text{-Fe}^{3+}$ intervalence interactions are absent. It was suggested [82B1] that the single band asymmetry arose from the superposition of two bands. Analysing the polarized spectra of light-green beryl single crystal, for $k \perp c$, a band at around 12000 cm^{-1} was analysed later [89I1]. For $E \perp c$, the maxima are at 11750 cm^{-1} and for $E \parallel c$ they are at 12750 cm^{-1} . The band at 11750 cm^{-1} was called A_σ and the other at 12750 cm^{-1} A_π . The band position changes continuously from 11750 cm^{-1} (A_σ band, $\theta = 90^\circ$) to 12750 cm^{-1} (A_π band, $\theta = 0^\circ$), where θ is the angle between the electrical field direction E and the c -axis. The lineshape analysis showed that the band at $\approx 12000\text{ cm}^{-1}$ is the result of the superposition of two σ - and π -polarized bands. The different contributions of the A_σ and A_π bands to the lineshapes of light blue, blue and green beryls show that these bands are due to Fe^{2+} at two different sites in the structural channels. There were attributed to water-free Fe^{2+} (A_σ) and to Fe^{2+} -associated with type II water (A_π) [89I1].

Irradiation with γ -rays cause a decrease of the intensity of the 12000 cm^{-1} band [89I1]. The kinetics analysis suggests a model in which Fe^{3+} is reduced to Fe^{2+} by release of holes from Fe^{3+} into the valence band. Subsequently holes are retrapped by Fe^{2+} or annihilated by the recombination of electron and hole at a single deep trapping center. The untrapping parameter shows Arrhenius-type behaviour. The retrapping and recombination parameters show a behaviour proportional to $T^{1/2} - T_0^{1/2}$, where T_0 ($\approx 473\text{ K}$) is the temperature where these parameters become zero. This behaviour was explained considering a free-electron distribution of hole velocities and potential barrier of the trap.

The polarized absorption spectra of Co-bearing beryls $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ single crystals, obtained by hydrothermal and flux grown methods were studied [89E2, 01T1]. As seen in Fig. 29 the presence of broad bands in the 7000 cm^{-1} to 25000 cm^{-1} region was shown. These appear at energies typical of spin allowed transitions of Co^{2+} ions. The band with maximum intensity, around 8700 cm^{-1} , with a noticeably asymmetrical shape, results from vibronic coupling. For three studied samples [89E2, 01T1] all the bands except that at $\approx 13300\text{ cm}^{-1}$ ($E \perp c$) and absorption lines caused by H_2O molecules in channels, maintain near the same intensity ratio. In [89E2] was suggested that Co enters in the beryl structure as both, Co^{2+} (Al-site) and to a lesser extent as Co^{3+} (Be and Al sites). According to [01T1] the near-constant intensity ratio for different samples suggested that 7400 cm^{-1} ($E \perp c$), 8700 cm^{-1} ($E \parallel c$), 17800 cm^{-1} ($E \parallel c$) and 22300 cm^{-1} ($E \perp c$) all arise from a single site. Therefore it was suggested that the octahedral Co^{2+} alone causes the bands common to the spectra of the studied beryl by [89E2, 01T1]. Later on, a combined study of EPR and optical measurements shows that the situation is more

complicated [04S1]. Three groups of bands, belonging to three types of Co centers, were distinguished. The first group of bands with maxima of 22220 ($E \perp c$), 17730 ($E \parallel c$) and 9090 ($E \parallel c$), 7520 ($E \perp c$) cm^{-1} is due to Co^{2+} in octahedral site of Al^{3+} . The second group of bands at 18940, 18250, 17700 ($E \perp c$), 18300, 17700, 17000 ($E \parallel c$) and 8830 ($E \perp c$) 7350 ($E \parallel c$) cm^{-1} and 5320 ($E \perp c$), 3880 ($E \parallel c$) cm^{-1} is caused by Co^{2+} in tetrahedral site of Be^{2+} . A weak wide band in flux and gas-transport obtained single crystals, in the region 12500...8300 cm^{-1} ($E \parallel c$, $E \perp c$) is related to Co^{3+} in octahedral Al^{3+} site. For a beryl obtained by hydrothermal method, bands at 13200 ($E \perp c$), 10900 ($E \parallel c$) and 8500 ($E \perp c$) cm^{-1} are caused by an uncontrolled impurity of Cu^{2+} ions. In the approximation of trigonal field, and taking into account interconfiguration or spin-orbit interaction [51T1, 52T1], the energy levels of Co^{2+} have been calculated in octahedral and tetrahedral coordination. There was a good agreement between the experimental and calculated data. The polarization dependence of the optical absorption bands was explained in terms of spin-orbit interaction [04S1].

The refractive indices of cordierites were analyzed as function of the ratio $f = (\text{Fe} + \text{Mg})/(\text{Fe} + \text{Mn} + \text{Mg})$ – Fig. 30. These show regular trends only after heating at 800°C [80S1]: $n_\alpha = 1.5223(2) + 0.0282(4)f$, $n_\beta = 1.5246(2) + 0.0348(4)f$, $n_\gamma = 1.5268(2) + 0.0403(6)f$. Similar data were also reported by [76L2] namely $n_\alpha = 1.5212 + 0.029f$, $n_\gamma = 1.5270 + 0.037f$. The heating increased generally $2V_\alpha$ [80S1]. Prior to heating, $2V_\alpha$ correlates inversely with H_2O whereas after partial dehydration at 800°C, $2V_\alpha$ correlates inversely with the Na content and, less certainly with the average radius of the ions in the octahedral sites [41F1, 80S1].

Some refractive indices are given in Table 9.