

### 8.1.3.6 Diopside and $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$ system

The magnetic and related properties of diopside-type silicates are reviewed. These are included in group VIIC09 of cyclosilicates [91N1]. In addition, we discuss the magnetic behaviour of the  $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$  system. The above synthetic germano-silicates have compositions which resemble to dehydrated diopside, although they are not members of this cyclosilicate group.

#### 8.1.3.6.1 Crystal structures. Lattice parameters

##### $\text{Cu}_6\text{Si}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ , $\text{Cu}_6\text{Si}_6\text{O}_{18}$

Diopside is a natural green copper silicate hydrate,  $\text{Cu}_6[\text{Si}_6\text{O}_{18}] \cdot 6\text{H}_2\text{O}$ . It was shown that from the natural green diopside, a blue polymorph with deviating lattice parameters can be obtained by annealing just below  $400^\circ\text{C}$ . At higher temperatures ( $400\ldots 800^\circ\text{C}$ ) a dehydration to black  $\text{Cu}_6[\text{Si}_6\text{O}_{18}]$  takes place. All three varieties are structurally closely related and were called **green**, **blue** and **black** diopside, respectively. Their lattice parameters are listed in Table 1.

After attempts by [42B1, 52B1], the structure of green diopside was determined by [55H1] and refined by [77R1] and [78B1], the latter also using neutron diffraction method. A detailed analysis of the structure of various diopside varieties was made by [88B1, 89B1].

The structure of green diopside  $\text{Cu}_6[\text{Si}_6\text{O}_{18}] \cdot 6\text{H}_2\text{O}$  contains corrugated six-membered rings with symmetry  $\bar{3}$ . They alternate along the  $c$ -axis with analogous six-membered rings of water molecules which are located by hydrogen bonds between each other and between the silicate rings. Jahn-Teller distorted octahedra, elongated in the direction of the apical water molecules, are paired by common edge  $\text{O3-O3'}$  and interconnect silicate rings – Fig. 1a. They build helical columns around the  $3_1$  axis in the structure.

A study of the electron density in natural diopside based on accurate single-crystal X-ray diffraction was made [92B1]. In the above analysis, a spherical-atom model was refined from high-angle data, and dynamic Fourier deformation maps were calculated. In [02B1] the original X-ray data were reanalyzed including a multipole model refinement, static deformation electron density map calculations and determination of atomic charges and occupancies of  $\text{Cu}^{2+}$  3d orbitals. The sections of the  $\text{SiO}_4$  tetrahedron – Fig. 2a,b – are similar, both using a dynamical model [92B1] and static deformation electron-density calculations [02B1]. These show that there is a difference on bonds with bridging  $\text{O1, O1'}$  and non-bridging  $\text{O2, O3}$  oxygens. In Fig. 2a there are two peaks ( $0.8 \text{ e}\text{\AA}^{-3}$ ) closer to oxygen, consistent with the higher electronegativity of the oxygen relative to silicon and being practically on the Si–O bond lines. There are also oxygen lone pairs of smaller height. In Fig. 2b there are two peaks displaced from oxygen which are much smaller ( $0.6$  and  $0.4 \text{ e}\text{\AA}^{-3}$ ). The former is close to the bond line and the latter is outside the bond line. In the section through Si–O1–Si – see Fig. 2c – an accumulation of density across the interior of the Si–O–Si angle was found, as evidenced for one Si–O–Si bond in coesite [87G1, 95D1]. This effect was explained by the presence of additional strain in the bond and the decrease of the Si–O–Si angle in diopside ( $132^\circ$ ) as compared with coesite ( $137^\circ$ ) [02B1].

The sections in Cu octahedron are shown in Fig. 3 [02B1] for Cu-oxygen square (a), Cu-oxygen apicals (b) and through the common edge of two Cu octahedra (c). The  $0.2\ldots 0.6 \text{ e}\text{\AA}^{-3}$  peaks close to oxygens in the corners of the Cu octahedron are due to  $\sigma$ -bonds between Cu-4s- and O-2p- overlapped orbitals. In the approximation of tetragonal symmetry, the 3d electron density is concentrated in the  $a_{1g}(\text{d}_{z^2})$ ,  $e_g(\text{d}_{xz}, \text{d}_{yz})$  and  $b_{2g}(\text{d}_{xy})$  levels, whereas the  $b_{1g}(\text{d}_{x^2-y^2})$  level, corresponding to bonding orbitals in the section of the Cu square has a small electron density. The 3d orbital occupancies for the bonding  $\text{d}_{x^2-y^2}$  orbital is  $\cong 14\%$  and for the other orbitals is  $\cong 20\%$ . It was concluded that due to Jahn-Teller distortion the  $a_{1g}$ ,  $e_g$  levels are stabilized, whereas the  $b_{1g}$  level is destabilized and less populated [02B1].

It was concluded that the silicon tetrahedron contains single Si–O  $\sigma$ -bonds between Si- $\text{sp}^3$  hybrid orbitals and O-p orbitals, but there is also an accumulation of density on bridge oxygens and across the interior of the Si–O–Si angle in the isolated corrugated ring, where the chemical bonds are under strain. In the Cu octahedron there are single Cu–O  $\sigma$ -bonds. Most remarkable is the lower occupation by 3d electrons of the bonding orbitals of the Cu atom in a typical Jahn-Teller octahedron [02B1].

The static deformation density in water molecule shows two peaks with the height of 0.6 and 0.8  $e\text{\AA}^{-3}$  on H1–O4 and H2–O4 bonds. The region of lone electron pairs is more diffuse than that expected from a common  $\text{sp}^3$  hybridization. This is connected with the bond interaction of water molecules with other atoms; the apical water molecule is directed by lone pairs to the Cu atoms – Fig. 3b.

The effective charge on the Cu ion in diopside, determined from the multipoles is +1.23  $e$ , closer to the  $\text{Cu}^+$  than the  $\text{Cu}^{+2}$  state. The charge on the silicon atom is 1.17  $e$ .

The thermal properties of diopside were studied [55H1, 67N1, 70S1, 76G1, 88B1, 89B1]. In [55H1] was found that dehydration of diopside begins at  $\approx 100^\circ\text{C}$ , but that water loss is only complete at  $\approx 700^\circ\text{C}$ . They reported a concomitant change in color from emerald green to grey black. A detailed analysis of the structure changes with temperature was reported by [88B1]. The temperature dependences of lattice parameters, during hydrothermal annealing from 2 and 12 days, respectively, at 0.5 kbar water pressure are given in Fig. 4 [88B1]. The small discontinuity at  $238^\circ\text{C}$  may be an initial step for the changes described subsequently. With increasing temperature, the basic crystal structure persists but the  $a$ -axis shrinks dramatically; the  $c$ -axis shows only a slight increase. Above  $325^\circ\text{C}$  the colour change continuously from green to blue, reaching the most intensive blue at  $400^\circ\text{C}$  just before the decomposition. Both the changes in colour and lattice parameters, indicate a new phase. Above  $400^\circ\text{C}$ , the sample turns black due to simultaneous dehydration and decomposition into  $\text{CuO} + \text{SiO}_2$ . Blue diopside could be crystallized hydrothermally by keeping a sample of black dehydrated diopside for 3 weeks at  $250^\circ\text{C}$  and 2 kbar.

The structure of **black diopside** was studied by [89B1]. Since the effective aperture diameter of the  $\text{Si}_6\text{O}_{18}$  ring in diopside is only 2.1  $\text{\AA}$  [77R1], the  $\text{H}_2\text{O}$  molecule ( $\phi \approx 2.6 \text{\AA}$ ) cannot leave the structure through the channels on dehydration. As a consequence, the structure is cracked and it was not possible to obtain single crystals of black diopside by dehydrating green crystals. The structure of black diopside – Fig. 1b – therefore was determined by line profile analysis of a neutron powder diffraction pattern [89B1]. The basic structural features of black and green diopside are the same – Figs. 1a,b. The most obvious difference is, that after the removal of the water molecules, copper exhibits a deformed square coordination with four oxygen atoms instead of the Jahn-Teller octahedron. The  $a$ -axis shrinkage is much stronger than that of the  $c$ -axis. The reason is that the  $\text{CuO}_4$  squares (one is marked by heavy lines in Fig. 1) are oriented steeper in  $\text{Cu}_6\text{Si}_6\text{O}_{18}$ , thus spreading the silicate rings apart in  $c$ -direction even though no water between them is present [89B1]. The strong decrease of the  $a$ -axis is due to this steeper orientation and to the shrinkage of Cu–O distances, i.e. of the dimension of the squares. The dehydration causes changes of the bond strengths, i.e. shifts of the bond distances and affects all atoms in the structure – Table 2.

The crystal structure of the **blue diopside** is similar to that of green diopside. Although a structure determination was not carried out, some predictions were made [89B1]: (1) The lattice parameters indicate an intermediate state of the blue variety between green and black diopside and suggest a closer relationship to the green form. (2) The weakest bonds in the structure are the bonds of the  $\text{H}_2\text{O}$  molecules, i.e. both the H bridges and the Cu– $\text{H}_2\text{O}$  bonds. This means that on heating the  $(\text{H}_2\text{O})_6$  rings, as the weakest structural units, are affected first. It was concluded that on heating, the voluminous  $(\text{H}_2\text{O})_6$  ring is cracked, allowing both, a closer packing and a higher mobility of the single  $\text{H}_2\text{O}$  molecule within the cages between the silicate rings. Since the released water molecules are less available as permanent bonding partners of the Cu atoms, the coordination changes towards four, resulting in blue diopside. By increasing temperature, the water molecules have to break Cu–O bonds between the columns to leave the structure. In this way microscopic and macroscopic cracks are formed and single crystals are destroyed. In the temperature range  $400\ldots 800^\circ\text{C}$ , the energy is not sufficient to break all the strong bonds between Cu and the  $\text{SiO}_4$  tetrahedra and the water-free diopside structure is preserved metastable. The atomic coordinates of green and black diopside are listed in Table 2.

The lattice parameters of diopside, as function of water content, is plotted in Fig. 5. In Fig. 6 the lattice parameters, as function of temperature, are given [88B1]. All diopside was decomposed above  $800^\circ\text{C}$ . From curves AB and DC the thermal expansion coefficients were determined:  $T(20\ldots 380^\circ\text{C})$   $\alpha_a = 5.5 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$  and  $\alpha_c = 24.7 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ ;  $T(20\ldots 800^\circ\text{C})$   $\alpha_a = 3.9 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$  and  $\alpha_c = 5.3 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ .  $\alpha_c$  is a strongly dependent on the presence or absence of water.  $\alpha_a$  and  $\alpha_c$  vs  $T$  of  $\text{Cu}_6\text{Si}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$  include the continuous change from green to blue diopside which proceeds linearly within the experimental errors [88B1].

**$\text{CuSiO}_3$ ,  $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$** 

The crystal structure of  $\text{CuGeO}_3$  is built from single chains of  $\text{GeO}_4$  tetrahedra and  $S = 1/2$  spin chains of edge sharing  $\text{CuO}_{4+2}$  octahedra [54G1, 67V1]. It is the unique inorganic compound showing the spin-Peierls (SP) transition [93H1, 96B2]. In this compound neighbouring antiferromagnetic Heisenberg chains exhibit a spin dimerization at  $T_{\text{SP}} = 14.3$  K, resulting in an exponentially vanishing magnetic susceptibility in all crystallographic directions when decreasing the temperature. The  $\text{Cu}^{2+}$  spin condense into a nonmagnetic spin-singlet ground state. A small shift of the atomic positions, which mediates the superexchange in the magnetic chains, accompanies this magnetic dimerization. The space group transforms, below  $T_{\text{SP}}$ , from Pbm to Pbcm with a doubling of  $a$  and  $c$  lattice parameters.

Partial substitution of Ge by Si in the  $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$  system, without changing the structure, was possible for single crystals up to  $x = 0.1$  [95O1, 95P1, 95R1, 95R2] and up to  $x = 0.5$  for polycrystals [97W1].

Pure  $\text{CuSiO}_3$  was considered long time as nonexistent [56L1].  $\text{CuSiO}_3$  was later discovered as a metastable decomposition product of green diopside [99O1, 02O1]. The single chain silicate  $\text{CuSiO}_3$  is the unique example of anhydrous copper silicates apart from black diopside, having the same composition but different structure [99O1, 04W1]. At RT  $\text{CuSiO}_3$  is isotypic to the  $\text{CuGeO}_3$ . The atomic sites are given in Table 2. The competing network forming cations  $\text{Cu}^{2+}$  and  $\text{Si}^{4+}$  both share chains down [001] in the orthorhombic structure as result of almost identical length of the tetrahedral edge for  $\text{SiO}_4$  and the distance between edges of the “octahedral” basis of the  $\text{CuO}_{4+2}$  polyhedron – Fig. 7a [04W1]. On the other hand, even the misfit between the two chain periods may lead to a strained crystal structure.

Compared to the Ge homologue, the lattice parameters  $a$  and  $c$  are reduced by  $-3.5\%$  and  $-3.7\%$ , respectively, whereas  $b$  increases by about  $+3.5\%$ . The unit cell volume of  $\text{CuSiO}_3$  is reduced by  $\approx -3.8\%$ . This leads to a modification of bond angles and lengths [99O1] which should have influence on the strength of magnetic interactions generated by the superexchange between neighbouring  $\text{Cu}^{2+}$  ions via the  $\text{O}^{2-}$  ions. The most important structural modification is the reduction of the Cu–O2–Cu bond angle from  $99^\circ$  in  $\text{CuGeO}_3$  to  $94^\circ$  in  $\text{CuSiO}_3$  which is accompanied by a shrinking of the in-chain Cu–Cu distance [99O1, 00B1, 04W1]. As a consequence of the reduced chain periodicity  $c$ , the bond valence contribution of the O2 atoms to copper is increased. This increase has to be compensated by a larger separation of the O1 atoms of the copper surrounding leading to the large Jahn-Teller distortion; the  $\text{CuO}_{4+2}$  “octahedral” chains are degenerated to  $\text{CuO}_2$  ribbons. The changed atomic distances cause a rotation of these chains in the  $(ab)$  plane of  $\Delta\tau \approx 10^\circ$  shortening the  $a$ -axis and enlarging the  $b$ -axis of  $\text{CuSiO}_3$  in comparison to  $\text{CuGeO}_3$  [04W1]. In this way the  $\text{CuO}_2$  ribbons have a larger separation from each other, in the  $b$ -direction being  $b/2 = 4.39$  Å for silicate, compared to 4.23 Å for germanate. The  $ac$  layerlike character of germanate, as a consequence of its large chain separation in the  $a$ -direction, corresponding to the lattice parameter  $a = 4.80$  Å, turns over into a more three-dimensional (3D) behaviour of the silicate with only  $a = 4.63$  Å. The O2–Cu–O2 angle in  $\text{CuSiO}_3$  is close to  $90^\circ$ , namely  $95.4^\circ$ , as compared to  $99^\circ$  in  $\text{CuGeO}_3$ . This angle is considered to be important, besides the strength of the crystal field for the different magnetic interactions and ground state properties found for  $\text{CuGeO}_3$  and  $\text{CuSiO}_3$  compounds [04W1].

Both  $\text{CuGeO}_3$  [96B1, 98B1] and  $\text{CuSiO}_3$  [99O1, 04W1] should be considered as nearly planar quasi-two dimensional crystal structures with the layers being deformed into a zig-zag arrangement – Figs. 7b,c. The analysis of thermal variation of a layered structure – Table 1 – is expected to be manifested mainly in the distance between the layers. In addition, the zig-zag folding of the layers allows for efficient contraction by an enhancement of the zig-zag angle upon cooling. This describes well the main part of the temperature induced structural changes [04W1]. In both  $\text{CuMO}_3$  ( $M = \text{Ge}, \text{Si}$ ) compounds one finds a similar temperature related rotation of the  $\text{CuO}_2$  ribbons around the  $c$ -axis. The angle  $\tau$  – Fig. 7b – decreases by  $\approx 1^\circ$  in the silicate and by  $\approx 0.7^\circ$  in germanate and consequently the folding angle  $\beta = 2\epsilon$  increases upon cooling. In  $\text{CuSiO}_3$ , the periodicities along  $a$  and  $b$ -directions decrease with temperature and that down the chain direction  $c$  increases only slightly. The chain arrangement in  $\text{CuSiO}_3$  with its very short translation period is extremely stiff and obviously does not allow any large alteration with temperature [04W1]. The pronounced change in the  $b$ -axis parameter may be an evidence of a “soft”  $b$ -direction. When passing through the Néel temperature,  $T_N$ , no significant changes in lattice parameters were observed, suggesting that  $\text{CuSiO}_3$  is not a magnetically one-dimensional system.

The dependences of lattice parameters on the silicon content in the  $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$  system are plotted in Fig. 8 [96W1, 97W1]. Linear type dependences were shown, up to the solubility limit, with nearly the same slope both for small and high Si content.

### 8.1.3.6.2 Magnetic properties

#### $\text{Cu}_6\text{Si}_6\text{O}_{18}(\text{H}_2\text{O})_6$ , $\text{Cu}_6\text{Si}_6\text{O}_{18}$

The temperature dependence of the reciprocal magnetic susceptibility,  $\chi^{-1}$ , of polycrystalline diopside was reported to decrease down to  $\approx 70$  K. Above this temperature,  $\chi^{-1}$  vs  $T$  follows a linear dependence [67N1]. These authors determined the Néel temperature  $T_N \approx 70$  K and a paramagnetic Curie temperature,  $\Theta = -70$  K. The effective magnetic moment, obtained from the above data was  $p_{\text{eff}} = 1.86 \mu_B/\text{Cu atom}$ . They suggested the most likely magnetic coupling scheme from molecular field calculations based on an energy level diagram corresponding to a  $d^9$  ion in an octahedral field with square planar distortion and  $c > a$ . They concluded that the two most important exchange interactions (across the common O3–O3' edge and via corner oxygens to two other copper ions) were both antiferromagnetic and predicted that the magnetic structure would have a doubled  $c_{\text{hex}}$  dimension.

Later on, further susceptibility data for both diopside and its structurally similar black dehydrated derivative have been obtained [93W1]. The thermal variations of reciprocal susceptibilities for  $\text{Cu}_6\text{Si}_6\text{O}_{18}(\text{H}_2\text{O})_6$  and  $\text{Cu}_6\text{Si}_6\text{O}_{18}$  (where 1/6 from crystal structure was considered) are shown in Fig. 9 [93W1]. The effective copper moments are listed in Table 3. These are close to the expected spin only value,  $1.73 \mu_B/\text{Cu atom}$ . According to [93W1] the crystal structures of green and black diopside are such that in both silicates there are probably two exchange interactions which are important, namely the n.n. intrachain interaction  $J_1$  and the n.n. interchain interaction,  $J_2$ . Moreover, the geometry allows  $J_1$  and  $J_2$  to be satisfied simultaneously, whatever their sign, in other words there is no frustration. The observed antiferromagnetism rules out the case  $J_1$  and  $J_2$  positive. As will be mentioned in section 8.1.3.6.3, from the magnetic structure of black diopside determined by neutron diffraction, it results that  $J_1 < 0$  and  $J_2 > 0$ . For  $J_1$ , the angle Cu–O–Cu via the shared O corner is  $111^\circ$ . For  $J_2$  the Cu–O–Cu angles for the two oxygens of the shared edge are only  $97^\circ$ . So the indirect exchange interaction is positive when the Cu–O–Cu angle is near  $90^\circ$ . It was also suggested that  $J_2$  is substantially lower than the intrachain coupling,  $J_1$ .

In [02G1] was shown that green diopside has a magnetic structure formed by the  $\text{Cu}^{2+}$  ions which allows for a quantum phase transition between an antiferromagnetically ordered state and a quantum spin liquid. As already mentioned, the  $\text{Cu}_6\text{Si}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$  silicate structure is built up from  $\text{Si}_6\text{O}_{18}$  single rings on a lattice which sandwiches six-membered water rings down the crystallographic  $c$ -direction [55H1, 77R1, 78B1]. The magnetic  $\text{Cu}^{2+}$  ions are located between the  $\text{Si}_6\text{O}_{18}$  rings and form chiral chains along  $c$ , placed on an  $ab$ -honeycomb net and are three edge-sharing connected forming  $\text{Cu}^{2+}$  dimers. The sublattice of  $\text{Cu}^{2+}$  ions is plotted in Fig. 10a. The magnetic sublattice is characterized by an antiferromagnetic intrachain constant  $J_1$  which couples the  $\text{Cu}^{2+}$  chains and an antiferromagnetic interchain coupling  $J_2$ , leading for small  $J_2/J_1$  to an AB-type Néel ordered state with doubling of the unit cell along  $c$ . Alternatively, one might consider the diopside magnetic lattice as made up by in-plane dimers of  $\text{Cu}^{2+}$  ions, with an intra-dimer coupling strength of  $J_2$  and an inter-dimer coupling along  $c$  of  $J_1$ . For small  $J_1/J_2$  a singlet dimer state with a spin-gap and no long range magnetic order can be realized.

The phase diagram of the diopside magnetic sublattice obtained by Quantum Monte Carlo (QMC) simulation is given in Fig. 10b for  $J_2 = J(1 + \delta)$  and  $J_1 = J(1 - \delta)$ . At  $\delta_c \approx 0.3$ , a quantum phase transition occurs. The Néel temperature of the antiferromagnetic ordered phase for  $\delta < \delta_c$  is given by the left axis. The antiferromagnetic order is of AB type with a doubling of the unit cell along  $c$ . For  $\delta > \delta_c$  a gap, given by the right axis opens in the magnetic excitation spectrum and the state is a quantum spin liquid.

The temperature dependence of the magnetic susceptibility of the green diopside is shown in Fig. 10c. The data for the magnetic field aligned parallel and perpendicular to the  $c$ -axis are given in the inset. A transition to an ordered state is shown at  $T_N = 15.5$  K. The moments are aligned along the  $c$ -axis for  $T < T_N$ . The QMC simulations were compared, due to spin-rotational invariance, with the directional-averaged experimental susceptibility. The Hamiltonian parameters  $J_2 = J(1 + \delta)$  and  $J_1 = J(1 - \delta)$  appropriate for diopside were determined. The optimal value of the spectroscopic splitting factor,  $g = 2.1$ , was relatively independent on  $\delta$ . The experimental data were equally well fitted for  $\delta = 0.1$  and  $\delta = -0.1$ .

It has been suggested [93W1] that the in-chain coupling  $J_1$  might actually be ferromagnetic. A quantum phase transition to a state with alternating ferromagnetic chains was found also for  $J_1 = -0.7 J_2$ , but large deviations between experimental susceptibilities and the theoretical values were found [02G1].

### **CuSiO<sub>3</sub>**

The temperature dependence of the magnetic susceptibility for  $\text{CuSiO}_3$  in a magnetic field of 1 T is plotted in Fig. 11a [00B1]. In the region  $200 \text{ K} \leq T \leq 300 \text{ K}$  a Curie-Weiss behaviour was followed, with  $\Theta = -7.2 \text{ K}$ , indicating rather weak antiferromagnetic coupling and  $p_{\text{eff}} = 1.56 \mu_{\text{B}}/\text{Cu atom}$ . Scaling the measured susceptibility with the amount of pure  $\text{CuSiO}_3$  content, (76 wt %  $\text{CuSiO}_3$ , 13.7 wt %  $\text{CuO}$ , 10.3 wt %  $\text{SiO}_2$ ) a value  $p_{\text{eff}} = 1.79 \mu_{\text{B}}/\text{Cu atom}$  and  $g = 2.06$  was obtained. At lower temperatures,  $\chi(T)$  shows a broad maximum at  $T_{\text{max}} = 13.5 \text{ K}$  which is a hallmark for a low-dimensional spin system [64B1]. Above 8 K,  $\chi(T)$  can be fitted with the numerical results obtained for  $S = 1/2$  Heisenberg chains [98K1]. The best fit was obtained for a nn coupling  $J/k_{\text{B}} = 21 \text{ K}$  and  $p_{\text{eff}} = 1.60 \mu_{\text{B}}/\text{Cu atom}$ . According to [00B1], the quality of the fit suggests that frustration effects, i.e. antiferromagnetic interaction  $J'$  between next-nearest-neighbours (n.n.n.), is negligible. The presence of a phase transition at 7.9 K was shown [00B1, 00R1]. This is confirmed by analyzing the temperature dependence of the heat capacity – Fig. 11b. A  $\lambda$ -type asymmetric anomaly was shown at  $T_{\text{N}} = 7.9 \text{ K}$  with a jump of  $\Delta C \cong 1.50(5) \text{ J/mol K}$ . Well below  $T_{\text{N}}$ ,  $C(T)$  follows a  $T^3$  power law with  $\beta \cong 4.5 \text{ mJ/mol K}^4$ , more than one order of magnitude larger than expected for the phonon contribution – Fig. 11b – indicating that in this temperature range the heat capacity of  $\text{CuSiO}_3$  is dominated by the magnetic contribution. Such a power law is expected for long-range order 3D antiferromagnet with weak or absent anisotropy.

The influence of a magnetic field on the susceptibilities and heat capacity is plotted in Fig. 12. The  $\chi(T, H)$  curves show that the signature of the transition, at  $T_{\text{N}} = 7.9 \text{ K}$ , is smeared out, the drop in the susceptibilities is reduced and the temperature of the susceptibility maximum ( $T_{\text{max}}$ ) is shifted to lower temperatures when increasing the field [00B1]. The shift of  $T_{\text{max}}$  values indicates the suppression of the antiferromagnetic in-chain correlations, when increasing the field, in agreement with theoretical calculations for the  $S = 1/2$  Heisenberg chain [98K1] – Fig. 12 inset. The temperature dependence of  $\chi(T)$  at fixed field – Fig. 12 – and the field dependent ac susceptibilities at fixed temperatures – Fig. 13b – show broadened transitions at  $\mu_0 H_{\text{SF}} \cong 3 \text{ T}$  which look similar to a spin-flop transition. The temperature dependences of the AF transition field and spin-flop field are shown in Fig. 13a. The almost independent transition temperature and the presence of a spin-flop-like transition are strong evidence for an antiferromagnetic ordered ground state in  $\text{CuSiO}_3$  [00B1].

The analysis of the data shows that the ratio between interchain and intrachain exchange parameter ( $J_2/J_1$ ) is larger in  $\text{CuSiO}_3$  than in  $\text{CuGeO}_3$ . The weaker interchain coupling  $J_2$  and the much larger  $J_2/J_1$  ratio obviously favour the occurrence of an AF transition instead of SP transition as evidenced in  $\text{CuGeO}_3$ .

### **CuGe<sub>1-x</sub>Si<sub>x</sub>O<sub>3</sub>**

$\text{CuGeO}_3$  is a spin-Peierls system [93H1, 93H2, 95W1]. In the orthorhombic structure, composed of linear chains of  $\text{Cu}^{2+}$  ions running along the *c*-axis, the  $S = 1/2$   $\text{Cu}^{2+}$  spins in a chain are equally spaced at high temperatures and strongly coupled by antiferromagnetic intrachain interaction. The spin-Peierls (SP) transition from a uniform phase to a dimerized phase (SP-phase) which occurs at  $T_{\text{SP}} = 14.3 \text{ K}$  is evidenced by a kink in the magnetic susceptibility [93H1, 94P1]. The structural transition to the dimerized state at  $T_{\text{sp}}$  has been revealed by X-ray and elastic neutron scattering [94H1, 94P1].

The temperature dependences of the magnetic susceptibility for single crystal samples with  $x = 0$  and  $x = 0.007$  are shown in Fig. 14a [95P1]. For pure  $\text{CuGeO}_3$  the susceptibility is isotropic below  $T_{\text{SP}} = 14 \text{ K}$ . It decreases rapidly, in agreement with the expected temperature dependence for a SP system. The upturn below 6 K was associated with paramagnetic impurities [95P1]. For the sample with  $x = 0.007$  the susceptibility is anisotropic above and below  $T_{\text{SP}}$ . The SP transition was defined as the inflection point of the  $\chi$  vs  $T$  curve, at  $T_{\text{SP}} = 9 \text{ K}$ . At lower temperatures a peak is observed around 4 K when the field is oriented along the *c*-axis and a monotonous increase along the *b*-axis [95P1, 95R1]. The above behaviour was interpreted as due to 3D AF order below  $T_{\text{N}} = 4.3 \text{ K}$ , with sublattice magnetization oriented along the *c*-axis.

The magnetic phase diagram of a  $\text{CuGe}_{0.993}\text{Si}_{0.007}\text{O}_3$  single crystal along the three crystallographic directions, as obtained from ultrasonic velocity measurements, is given in Fig. 14b. In comparison with pure  $\text{CuGeO}_3$ , the diagram shows one additional phase, the antiferromagnetic Néel phase (AF). The other phases have been identified in the pure crystal to be the uniform U phase (Heisenberg AF linear chains), the SP phase and the magnetic M phase. For low Si content, the short-range SP correlations set up before the occurrence of the AF phase at lower temperatures. In the pure spin-Peierls (SP) system, the SP phase is separated from the magnetic

phase M by a first-order transition at low temperatures. For  $x = 0$ , this happens at a critical field around 12 T. In the doped system, the occurrence of the AF Néel state modifies the picture by introducing a supplementary boundary line between the AF and SP phases. The AF-SP line is of second order and the critical temperature increases weakly with the field. At higher fields the AF-SP and M-U intermingle and join progressively with the SP-U line. The AF-M line has been found to be first order like the SP-M transition boundary in pure crystal [95P1]. Magnetic anisotropy comes into play when the field is oriented along the chains, the  $c$ -axis. As seen in inset of Fig. 14b the AF-SP line is shifted to lower temperatures as the field is increased. The decrease of  $T_N$ , at low fields ( $B \parallel c$ ), is associated with the appearance of a spin-flop (SP) phase for  $B \geq 1.1$  T – Fig. 14b inset. The AF Néel phase has an easy axis along the chain ( $c$ -axis) and as the field is increased above  $B = 1.1$  T, for  $T < 3.5$  K, the spins flop in perpendicular direction. When the field is increased at  $B \approx 8$  T, there is an SF-M boundary. This boundary is not different from the one obtained for the perpendicular direction measurements ( $\perp c$ ) (AF-M) [95P1].

The magnetic phase diagram of  $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$  single crystals – Fig. 15 – was analysed [95R1]. In a gapless quasi-one-dimensional antiferromagnet, a transition towards a 3D-AF phase at low temperatures is always induced by the interchain interaction  $J_2$ , since the 1D spin correlation length,  $\xi$ , diverges as  $T \rightarrow 0$  K. In quasi-1D-AF, with a gap  $\Delta$ , the correlation length, instead of diverging as  $T \rightarrow 0$  K, tends towards a finite value  $\xi_0$  given by  $\xi_0/d = \lambda J_1/\Delta$ , where  $J_1$  is the intrachain exchange,  $d$  the chain parameter and  $\lambda$  a constant of the order 1. This forbids AF long range order (AFLRO) at small  $|J_2/J_1|$  values, which is the case of  $\text{CuGeO}_3$ . The effect of Si substitution is to reduce  $\Delta$ , as evidenced by the decrease of  $T_{SP}$  and then to increase  $\xi_0$ , proportionally to  $\Delta^{-1}$  and to allow AFLRO to set up when  $\Delta$  becomes smaller than a critical value. It was suggested that the gap vanishes for  $x = 0.02$  which allows a low-temperature divergence of  $\xi$ . This concentration corresponds to the  $T_N$  maximum. With further increase of  $x$ , one can expect that the lattice defects reduce  $\xi$  and thus  $T_N$  values [95R1].

The analysis of the effect of Si doping in  $\text{CuGeO}_3$  [95P1, 95R1, 96F1, 96W1, 97W1], show discrepancies between the data obtained in single crystals (sc's) and polycrystals (pc's). Thus,  $T_{SP}$  values are strongly reduced in sc's and the SP state is already suppressed at 2 at % Si substitution. The decrease of  $T_{SP}$  is rather weak in pc's;  $T_{SP}$  is 14.1 K even for 10 at % Si. In addition the AF state is present at lower Si content in sc's than in pc samples. The AF and SP states coexist in the doping range 2...4 at % in pc's – Fig. 16 – while this composition range is narrower in sc's. The above coexistence is also seen from the specific heat and thermal expansion measurements of pc's – Fig. 17 [97W1]. At  $T_{SP}$ , a sharp transition is observed both in magnetic specific heat,  $C_{\text{magn}}/T$ , and in thermal expansion coefficient,  $\alpha(T)$ . The size of anomalies in both cases are reduced by  $\approx 50$  % in comparison with the undoped compound [95W1]. The transition at  $T_N$  is broadened; this fact was attributed to a broadened Si distribution in sample and strong dependence of  $T_N$  on composition. In Fig. 15 the composition dependences of  $T_{SP}$  and  $T_N$  for single crystals and polycrystals are plotted. Single crystals prepared by different methods (flux grown and image furnace) have the same  $T_{SP}$ - and  $T_N$ - type variations.

The difference in the magnetic behaviour of polycrystals and single crystals was analysed in correlation with preparation conditions [97W1]. Both in pc's and sc's, the lattice parameters depend linearly on the Si content and have nearly the same value for a given composition – Fig. 8. As will be mentioned in section 8.1.3.6.6, the Raman experiments showed no difference in the phonon spectrum for sc's and pc's up to 10 at % Si (limit of the studied compositions). The half widths of the phonons in pc's are about 15 % larger than those in sc's, probably due to a higher amount of defects.

A striking difference between sc and pc samples is due to different preparation temperatures,  $\approx 1200^\circ\text{C}$  and  $1000^\circ\text{C}$ , respectively. As long as  $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$  samples with  $0 \leq x \leq 0.05$  were prepared at temperatures smaller than melting temperature,  $T_N = 1150^\circ\text{C}$ , no significant changes either in morphology or in the magnetic properties were observed. Once the melting temperature was reached, the formation of many small single crystalline grains inside the pc's appears and a steplike decrease of  $T_{SP}$  to the values observed in sc's was observed – Fig. 15. This strong effect of the melting may be attributed to a different kinematic of the oxygen inside the molten part of sample. Preparation at higher temperatures and/or reduced oxygen pressure probably leads to a slight oxygen deficiency in the samples. These oxygen deficiencies stabilize the AF state and enhance its existence range. Thus, the differences between  $T_{SP}$  values of sc's and pc's are related to different preparation temperatures. The strong suppression of  $T_{SP}$  occurs at temperatures where the samples melt and consequently the kinematic of preparation is changed. Thus, it was concluded that the intrinsic effect of Si doping may be studied on pc samples [97W1].

In [96G1] the decrease of  $T_{\text{SP}}$  due to Si doping was calculated, considering a change in hybridization between O2 and the Ge site. The smaller Si ion will attract the O2 ion leading to a decrease of the Cu–O2–Cu angle towards  $90^\circ$  and consequently a reduction of the antiferromagnetic superexchange. This effect should decrease  $T_{\text{SP}}$  drastically because each dopant at the Ge site influences two chains [96K1], in agreement with experiments on sc's but in contradiction with pc samples. In [97W1] only minor changes were found in the position of O2 and thus in the Cu–O2–Cu angle. The data indicate that the crystal structure remains unaffected by Si doping except for the change in the lattice parameters. Therefore, according to [97W1], both the AF stabilization and  $T_{\text{SP}}$  reduction observed in sc's are not an intrinsic effect of Si doping. The pc samples which can be prepared at lower temperatures and more oxidizing conditions, reflect much better the intrinsic properties of the  $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$  system.

The analysis of a magnetic properties of pc samples shows that with increasing Si content, the characteristic feature of the one-dimensional fluctuations is gradually suppressed. The maximum in  $\chi$  value, at  $T_{\text{max}} = 56$  K ( $x = 0$ ), disappears when increasing  $x$  – Fig. 16b. For the sample with  $x = 0.50$  a Curie-Weiss type behaviour is observed above 50 K. An effective moment of  $1.80 \mu_{\text{B}}$  and paramagnetic Curie temperature  $\Theta = -80$  K was determined. This suggests approximately the same coupling constant as in chain direction,  $J/k_{\text{B}} \approx 90$  K [93H1]. No long range magnetic order was observed down to  $T = 2$  K. Below 10 K,  $\chi(T)$  presents a large increase which is suppressed with increasing magnetic field, suggesting the presence of a spin-glass-like state [97W1]. The increasing Si content shifts gradually the magnetic properties from one-dimensional behaviour to a three-dimensional one.

#### 8.1.3.6.3 Neutron diffraction data

##### $\text{Cu}_6[\text{Si}_6\text{O}_{18}] \cdot 6\text{H}_2\text{O}$ , $\text{Cu}_6\text{Si}_6\text{O}_{18}$

The neutron diffraction studies on the dehydrated sample,  $\text{Cu}_6\text{Si}_6\text{O}_{18}$  (black), at 1.5 K, showed some weak magnetic extra peaks compared to the pattern taken at 130 K [93W1]. The magnetic lines were indexed considering a magnetic propagation vector  $k = (0,0,1/2)$  in the hexagonal cell. A copper moment of  $0.52 \mu_{\text{B}}$  was reported. As  $k_z = 1/2$ , the moments must be opposite for two neighbours in the same helical chain. The model which fits the experimental data is that with ferromagnetic interchain coupling and with moments along the  $c$ -axis – Fig. 18.

A single crystal neutron diffraction study on  $\text{Cu}_6[\text{Si}_6\text{O}_{18}] \cdot 6\text{H}_2\text{O}$  shows that diopside becomes antiferromagnetically ordered below  $T_{\text{N}} = 15.9(1)\text{K}$  as can be seen from the temperature dependence of the  $(2,0,1/2)_{\text{hex}}$  reflections [02B1] – Fig. 19a. The magnetic propagation vector is  $(0,0,3/2)$  on the hexagonal triple cell or  $(1/2,1/2,1/2)$  in rhombohedral indices. The Cu moments is  $0.55(1) \mu_{\text{B}}$  inclined to the triad axis by  $\pm 13(3)^\circ$ . The intrachain interaction across corner oxygens, with a Cu–O–Cu angle of  $111(1)^\circ$  is antiferromagnetic and results in a doubling of the  $c_{\text{hex}}$ -axis as predicted by [67N1]. According to [02B1], the above proposed magnetic structure [67N1] was incorrect in that the interchain interaction across the common O3–O3' edge, where the Cu–O–Cu angle is  $97^\circ$ , was also assumed to be antiferromagnetic. There are ferromagnetic interchain interactions due to weak direct exchange between Cu ions,  $2.95 \text{ \AA}$  apart, and may be related with the bridge of density via a common edge O3–O3' – Fig. 3c. The charge density and the antiferromagnetic behaviour of diopside can be correlated [02B1]. The less occupied Cu  $d_{x^2-y^2}$  orbitals are responsible for the magnetic properties of diopside. These lie in the Cu–O squares which are approximately perpendicular to  $c_{\text{hex}}$ , but which are alternatively inclined to it by a small angle. There are three (multiplied by threefold axis) pairs (joint by symmetry center) of Cu squares at the level  $z \approx 0$  and three pairs at the  $z \approx 2/3$  level along  $c_{\text{hex}}$  – Fig. 1. In Fig. 19b Cu squares at  $z \approx 0$  and  $z \approx 2/3$  are shown. Within experimental errors, the magnetic moments are perpendicular to the square planes which make an angle around  $\pm 15^\circ$  to the trial axis [02B1].

##### $\text{CuSiO}_3$

The neutron diffraction pattern shows two weak reflections of magnetic origin in the low scattering angle part of the records below  $T_{\text{N}}$  [04W1]. They can be indexed as satellites of the ordinary (110) Bragg reflection of  $\text{CuSiO}_3$  with a commensurate propagation vector of  $q = (1/2, 0, 1/8)$  with respect to the chemical Pbnm unit cell. With respect to the zero  $q_y$  component, that for the space group Pbnm the structural motive is already repeated along

the  $b$ -direction by the action of the glide mirror plane perpendicular to the  $a$ -axis with  $b/2$  glide component. The temperature dependence of the integrated magnetic neutron diffraction intensity  $I_{\text{magn}}(T)$  of the strongest  $(1/2, 1, -1/8)$  magnetic satellite follows the relation  $I_{\text{magn}} = I_0 t^{2\beta} (1 + A t^{0.5})$  with  $t = 1 - T/T_N$ ,  $\beta = 0.34(3)$ ,  $A = -0.55(3)$  and  $I_{T=0} = I_0(1 + A) = 196$  – Fig. 20 [04W1]. A value  $T_N = 8.01(5)$  K was obtained, close to that determined by magnetic measurements. The  $\beta$  value is consistent with 3D XY universality [95H1, 96P1]. The integrated magnetic reflexion intensity scales with the square of the ordered moment  $I_{\text{magn}}(T) \propto p^2$ . At  $T = 1.4$  K a value of  $p_z = 0.83(2) \mu_B$  was obtained when attributing the magnetic moment to the hole on the  $3d^9$  copper site with spin alignment along the  $z$ -direction. A slightly larger value of  $p_x = 1.09(3) \mu_B$  was determined for spin alignment along the  $x$ -direction. The analysis of the magnetic pattern suggested that the  $x$  spin alignment is favored. The in-chain coupling is expected to be ferromagnetic in nature in view of the Cu–O2–Cu valence angle of only  $95.4^\circ$  and the long-periodic magnetic modulation along  $c$ , but the next neighbour exchange coupling may be still antiferromagnetic. The low-temperature magnetic moment determined experimentally on the condition that the spin density resides fully on the Cu  $3d^9$  sites yielded too high values in comparison with the expected moment suggesting a non sinusoidal spin density modulation. The question of spin density residing partially or solely on O2 non-bonding orbitals [03G1] has been not solved by [04W1].  $\text{CuSiO}_3$  with its more densely packed succession of zig-zag sheets down the  $a$ -direction is considered to be more closer to an anisotropic 3D structure than  $\text{CuGeO}_3$ .

### **$\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$**

The neutron diffraction studies on a  $\text{CuGe}_{0.993}\text{Si}_{0.007}\text{O}_3$  single crystal have demonstrated the existence of superlattice peaks indexed with propagation vector  $k_{\text{SP}} = (1/2, 0, 1/2)$  as in pure  $\text{CuGeO}_3$  [94P1]. Fig. 21 depicts  $Q$  scans along the  $c$ -direction across scattering vector  $Q = (1/2, 3, 1/2)$ , for some temperatures [95R1, 96R1]. The temperature dependence of the intensity, at the maximum, shows a transition temperature ranging from 8.5 K to 10 K, with an average value of 9.2 K, in agreement with magnetic data (section 8.1.3.6.2). The analysis of the superlattice peak  $(0, 1, 1/2)$  shows that a magnetic Bragg peak appears below  $T_N \cong 4$  K, characteristic of a 3D antiferromagnetic ordering described by the wave vector  $k_{\text{AF}} = (0, 1, 1/2)$ . Above  $T_N$ , quasi-1D correlations subsist which coexist with the dimerized phase up to  $T_{\text{SP}}$ , above which a more classical magnetic behaviour is recovered. Thus, below  $T_N$ , the dimerized phase persists (at least partly) coexisting with the 3D antiferromagnetic phase. The two phases seem to coexist independently one from each other. The slight decrease of the  $(1/2, 3, 1/2)$  intensity observed below  $T_N$  may be associated with a decrease of the population of dimerized domains (see also section 8.1.3.6.2).

The coexistence of the AF and SP excitations as well as a splitting of the antiferromagnetic excitation peak at the magnetic zone center ( $q = 0$ ) due to orthorhombic symmetry has been confirmed by neutron scattering on  $x = 0.01$  and  $0.03$  samples [98L1]. The  $q$  dependence of the antiferromagnetic spin-wave width scales well with  $q^2$  for small  $q$  ( $q < 0.1 \text{ \AA}^{-1}$ ) values. The spin wave velocity increases when the silicon content is higher. It was suggested that it is related to the spatially averaged size of the induced moments which increases as the silicon content increases. Some magnetic properties of the  $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$  system determined by various measurements are listed in Table 3b [98L1].

#### **8.1.3.6.4 Nuclear magnetic resonance (NMR) data**

### **$\text{Cu}_6[\text{Si}_6\text{O}_{18}] \cdot 6\text{H}_2\text{O}$**

The  $^1\text{H}$  NMR study of diopside shows that the resonance pattern, at 77 K, in the  $(11\bar{2}0)$  plane, has distortions of the order of 0.0001 T which were attributed to copper-proton interactions [58S1]. As the temperature is reduced, the resonance pattern does not widen appreciably and shows only a small paramagnetic shift. At  $T \cong 21$  K, the resonance suddenly disappears. This fact was correlated with a possible antiferromagnetic transition at  $T_N = 21$  K.

### **$\text{CuSiO}_3$**

The  $\text{CuSiO}_3$  silicate was investigated by  $^{63,65}\text{Cu}$  nuclear quadrupole resonance (NQR) [00B1]. The spectrum at 4.2 K is plotted in Fig. 22. Signals at 26.88(2) MHz for  $^{63}\text{Cu}$  and 24.88(2) MHz for  $^{65}\text{Cu}$  were observed. We note that for  $\text{CuGeO}_3$  values of 34.23(2) MHz for  $^{63}\text{Cu}$  and 31.66(2) MHz for  $^{65}\text{Cu}$  were shown [94K1, 95I1]. One



possible explanation for this difference is the effect of the modified bond lengths and angles on the EFG which affect strongly the  $^{63,65}\text{V}_{\text{NQR}}$  frequencies. The ratio of intensities,  $^{63}I/^{65}I = 2.8$ , corresponds to that of natural abundance of the respective isotopes.

The  $^{29}\text{Si}$  NMR measurements [03G1] indicated that the Si–O2 path is strongly involved in magnetic exchange interactions below  $T_N$ . The corresponding O2–Si–O2 valence angle  $\gamma$  is considerably increased with temperature decrease. Its change from 15 K down to 5 K was about  $0.2^\circ$ .

### **$\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$**

The copper NMR experiments, by using a variable frequency spin-echo equipment and performed at 2 K in a dc field of 1.1 T applied along the *c*-crystal axis, revealed a striking difference between the samples having  $x = 0$  and  $x = 0.0025$  and the samples with  $x \geq 0.005$  [95R1]. The first ones show one narrow line for each Cu isotope indicating no magnetic ordering. The second ones show broad spectra splitted by the Cu hyperfine fields, corresponding to the antiferromagnetic long range order with the Cu spin direction along the *c*-axis.

#### **8.1.3.6.5 Electron paramagnetic resonance (EPR) and antiferromagnetic resonance (AFMR) data**

##### **$\text{CuSiO}_3$**

The EPR measurements on  $\text{CuSiO}_3$  for  $T \geq 12$  K show a nearly independent *g* value,  $g = 2.156(1)$  [02S1]. Like in isostructural  $\text{CuGeO}_3$  [97P1] this *g* value is consistent with a polycrystalline-averaged, effective *g* tensor of the two magnetically unequivalent  $\text{Cu}^{2+}$  ions of  $\text{CuSiO}_3$ , the  $\text{Cu}^{2+}$  sites being within strongly elongated oxygen octahedra in the orthorhombic crystal structure [99O1]. The temperature dependence of EPR intensity,  $I_{\text{EPR}}$ , is proportional to the spin susceptibility of  $\text{Cu}^{2+}$  and follows a similar trend as that of magnetic susceptibility – Fig. 11a. However, below  $T = 8.2$  K, the EPR intensity reduces rapidly to zero, indicating an ordering phenomenon. Above  $T = 8.2$  K,  $I_{\text{EPR}}(T)$  as well as  $\chi(T)$  are well described by theoretical calculations for an  $S = 1/2$  1-D Heisenberg antiferromagnet without frustration effects [98K1]. For high temperatures, the  $I_{\text{EPR}}(T)$ , like  $\chi(T)$ , follows a Curie-Weiss type behaviour. The EPR linewidth follows at high temperatures a variation  $DH = 0.5 T + 300$  Oe where  $T$  is given in K. In the region  $t = (T - T_N)/T_N$  with  $0.1 \leq t \leq 1.0$ , the broadening of the line follows a law  $\propto (T - T_N)^{-\alpha}$  with  $\alpha = 0.25$  [02S1].

##### **$\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$**

The magnetic resonance studies at low temperatures, performed on  $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$ , show a typical pattern for antiferromagnetic resonance (AFMR) in a system having orthorhombic symmetry [97N1, 98H1]. The frequency–field diagrams for samples with  $x = 0.01$  and  $x = 0.02$ , at 1.7 K, are plotted in Fig. 23 [97N1]. The temperature shifts of the resonance fields,  $B_{\text{res}}$ , at 95.5 GHz, when the magnetic field was applied parallel to the *b*-axis, is given in Fig. 24. In case of the  $x = 0.01$  sample,  $B_{\text{res}}$  shows a small shift to a lower field below  $T_{\text{SP}} \cong 11$  K and an additional shift when the temperature approaches  $T_N$ . In case of the  $x = 0.02$  sample, the shift is observed below 5 K and it shows a large change below  $T_N$  due to AF ordering. In the whole temperature range studied, only a single peak was observed. The *g* values for the samples with  $x = 0.01$  and  $0.02$ , along the *a*, *b*, and *c*-axes, are:  $g_a = 2.15$ ,  $g_b = 2.25$ ,  $g_c = 2.06$  and  $g_a = 2.15$ ,  $g_b = 2.25$ ,  $g_c = 2.07$ , respectively [97N1]. For  $T > 15$  K, the temperature dependence of the  $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$  EPR parameters do not change significantly for Si doping concentrations up to 7 % [98H1, 99G1].

#### **8.1.3.6.6 Heat capacity**

##### **$\text{Cu}_6\text{Si}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$**

The heat capacity measurements were performed on diopside in the temperature range  $2 \text{ K} \leq T \leq 30 \text{ K}$  [64E1]. A sharp anomaly was observed at 21 K which was identified as the Néel temperature – Fig. 25. The total entropy change in this transition was  $1.19 \text{ cal mol}^{-1} \text{ K}^{-1}$  which may be compared with the value of  $1.38 \text{ cal mol}^{-1} \text{ K}^{-1}$  calculated from  $R \log (2S + 1)$ , where  $S = 1/2$  for the  $\text{Cu}^{2+}$  ion. The contribution above  $T_N$  was  $\cong 2 \%$  of the total entropy change, which indicates a very small short range ordering effect [64E1].

**$\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$** 

The heat capacities,  $C_p$ , of  $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$  ( $x \leq 0.05$ ) single crystals were studied under magnetic fields up to 15 T [98H2]. Some data are given in Fig. 26. For  $x = 0.005$  a clear peak of  $C_p/T$  was observed at  $T_{\text{SP}} = 12.6$  K in a field  $H = 0$ . The  $T_{\text{SP}}$  values decrease when increasing the magnetic field. The peak height of  $C_p/T$  also decreases with magnetic field, and after taking a minimum at  $\approx 12$  T, increases again and becomes more clear with magnetic field. This behaviour was also found for a  $x = 0$  sample and the peak was shown to take a minimum at the tricritical point in the magnetic phase diagram, where uniform, dimerized and magnetic phases meet. The critical point for the  $x = 0.005$  sample is located at  $\approx 9.4$  K and  $\approx 12$  T. A small upturn of  $C_p/T$  was seen below  $\approx 3$  K in  $\mu_0 H = 0$  and 3 T. This suggests the existence of an AF ordering below 2 K. The upturn is suppressed with increasing magnetic field. A peak in  $C_p/T$  for the  $x = 0.008$  sample which is less pronounced was observed at  $T_{\text{SP}} = 11.8$  K – Fig. 26. An upturn was shown below  $\approx 3$  K ( $H = 0$ ) which suggests the existence of an AF ordering slightly below 2 K. This upturn is suppressed by a magnetic field. A similar discussion may be made also for other compositions ( $x \leq 0.05$ ) [98H2].

**8.1.3.6.7 Optical properties** **$\text{Cu}_6\text{Si}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}_6\text{Si}_6\text{O}_{18}$** 

The diffuse reflectance spectrum of powdered green diopside is plotted in Fig. 27a [67N1]. Dominating the spectrum is an intense absorption peak at  $13300 \text{ cm}^{-1}$  with a bandwidth at half maximum of  $6500 \text{ cm}^{-1}$ . The characteristic greenish-blue color results from the transmission near 500 nm, between the broad peak and the ultraviolet absorption edge. In a pure octahedral field the broad peak would be attributed to the  $E_g \rightarrow T_{2g}$  transition of the  $\text{Cu}^{2+} 3d^9$  electron configuration. The near neighbour environment nearly approximates  $C_{4v}$  (4mm) symmetry, resulting in further splitting – Fig. 27b. The doubly degenerate  $E_g$  level splits into a  $B_1$  ground state and an  $A_1$  excited state, while triply degenerate  $T_{2g}$  separates into  $B_2$  and doubly degenerate  $E$ . Since the  $\text{Cu}^{2+}$  site symmetry does not contain inversion, electric-dipole transitions are possible. Combining the representations of  $B_1$  with those of the three excited states shows that only the transition to  $E$  contains an electric-dipole operator, suggesting  $B_1 \rightarrow E$  as the origin of the absorption peak [67N1].

The ligand field spectra of the three types of diopsides are shown in Fig. 28 [88B1]. The absorption maximum at  $13800 \text{ cm}^{-1}$  of the green polymorph is shifted to  $14100 \text{ cm}^{-1}$  in the blue one and the minimum at  $20000$  to  $20500 \text{ cm}^{-1}$ . In all cases the transformation green-blue was very sluggish. By annealing experiments, in air ( $350 \dots 400^\circ\text{C}$ ), as well as by hydrothermal experiments it was not possible to retransform the blue variety to green. By annealing experiments at  $600^\circ\text{C}$ , powders of green diopside were dehydrated stepwise. The lattice parameters against water content – Fig. 5 – indicate that the dehydration proceeds sluggishly and continuously. The final water-free product  $\text{CuSiO}_3$  is black. In  $\text{Cu}^{2+}$ -oxygen compounds, green colour as a rule indicates a Jahn-Teller octahedron and violet a square coordination. The major absorption band [89B1] is shifted to higher wave numbers from green ( $13800 \text{ cm}^{-1}$ ) over blue ( $14100 \text{ cm}^{-1}$ ) to the black ( $15400 \text{ cm}^{-1}$ ) diopside. This suggests that in blue diopside the  $\text{Cu-H}_2\text{O}$  bonds are less effective than in the green form.

In [74A1] the single-crystal Raman scattering and IR reflectance spectra of  $\text{Cu}_6\text{Si}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$  were obtained and most of the Raman active and some of the IR-active modes predicted by factor group analysis were identified. The Raman study was continued by [95M1] who calculated the normal modes of vibration and their frequencies. The calculation employed a valence force potential consisting of central interactions between nearest neighbours and bond-bending interactions centered at the  $\text{Si}^{4+}$  and  $\text{Cu}^{2+}$  ions. The force constants were determined by fitting the calculated frequencies to values obtained by measuring the single crystal Raman spectra. The calculated frequencies were in reasonable agreement with experiments – Fig. 29 [95M1]. In the diopside structure, all the six atom types: Cu, Si, O1, O2, O3 and Ow have site symmetry  $C_1(1)$ , so each atom contributes three modes to each of the Raman active  $A_g$  and  $E_g$  species and the IR active  $A_u$  and  $E_u$  species. All vibrational species can involve motions of every atom type in the structure. The normal modes were divided into 35 nondegenerate optic modes, 35 doubly degenerate optic modes and two acoustic modes: one each for  $A_u$  and  $E_u$ . There are contributions from the ring, Cu and Ow. Since the crystal structure of diopside is centrosymmetric, each of the optically active vibrational species is either Raman- or IR-active but not both. The observed and calculated  $A_g$ ,  $E_g$  fundamental frequencies, as well as observed and calculated frequencies of IR active  $A_u$  and  $E_u$  modes, are given in Table 4. The calculated frequencies are in reasonable agreement with experiment, permitting

unambiguous assignment of normal modes to the observed spectral lines. Significant mixing of Cu and  $\text{H}_2\text{O}$  motions with those of the ring was found for the Raman modes below  $430\text{ cm}^{-1}$ .

The magnetic Raman spectra of green diopside were analysed as function of temperature – Fig. 30 [02G1]. Two modes at  $48$  and  $85\text{ cm}^{-1}$  ( $\cong 69\text{ K}$  and  $122\text{ K}$ , respectively) are magnetic and they exhibit temperature dependence related to the magnetic transition. They show no anisotropy concerning the scattering selection rules. The excitation energies  $69\text{ K}$  and  $122\text{ K}$  correspond, for  $\delta = +0.1$  (see section 8.1.3.6.2), to one and two inter-chain dimer excitation energy  $J_2 = J(1 + \delta)$ , as expected for one- and two-magnon scattering processes [02G1]. The lineshape of the magnetic two-magnon scattering of  $122\text{ K}$  mode is unusual; it is symmetric and not substantially broadened by either magnon-magnon scattering or density of states effects in contrast to usual two-magnon scattering in normal 3D antiferromagnets [70F1]. This behaviour indicates a small dispersion of the underlying magnon branch. Consequently, it was concluded that green diopside is relatively close to a quantum-critical point.

The well crystallized diopside has refractive indices of  $n_o = 1.644\dots 1.658$  and  $n_e = 1.697\dots 1.709$  [88B1].

### **$\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$**

Raman spectroscopy gives also useful information on the lattice effects caused by doping in the  $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$  system [95W2, 96L1, 97W1]. A linear shift of the phonon frequencies with doping up to  $x = 0.3$  was shown – Fig. 31 [97W1]. The relative changes are more pronounced than for the lattice constants. The half-width of the phonons increases with increasing Si content. For  $x = 0.5$ , the shift is stronger than the linear extrapolation obtained from lower doping and the linewidth increases indicating a more drastic change in dynamical properties and a strongly limited phonon lifetime. A new phonon line as a defect mode was observed at  $670\text{ cm}^{-1}$  growing linearly in intensity as the doping level increases. Additional defect modes are induced at  $203$  and  $305\text{ cm}^{-1}$  – Fig. 31 a.

For sc samples a symmetry analysis was possible and the appearance of symmetry-forbidden modes with increasing Si content was observed, indicating a breaking of the selection rules [97W1] – Fig. 31a. This suggests a considerable degree of local disorder induced by Si doping.

The low-frequency Raman spectrum, at  $3\text{ K}$ , for  $\text{CuGe}_{0.996}\text{Si}_{0.004}\text{O}_3$  – Fig. 32 – shows the presence of a symmetric peak at about  $13\text{ cm}^{-1}$ , while an asymmetric gap-related second-order Raman peak corresponding to the bound state in pure  $\text{CuGeO}_3$  was observed at  $\cong 27\text{ cm}^{-1}$  [98S1]. The frequency of the peak at  $\cong 13\text{ cm}^{-1}$  is almost half of that of the gap-related second-order Raman peak. When approaching  $T_{\text{SP}}$ , it softened and disappeared above  $T_{\text{SP}}$ . This peak was assigned to first-order Raman scattering from gap-excitation. The peak at  $\cong 13\text{ cm}^{-1}$  shifts to lower frequency together with its line broadening as the silicon content increased [98S1, 98S2]. The two magnetic-excitation bound state changes into a resonant state and disappears when increasing  $x$ , mainly due to the shortening of the lifetime of magnetic excitation. These features were theoretically analysed.