

Electron Density and Bonding in Ring Silicates: Beryl, Cordierite, Diopase *

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The electron density and bonding in the silicates beryl, cordierite and diopase has been investigated. The replacement of Be, Si and Al atoms in the identical structural fragments leads to a $\delta\rho$ -redistribution and changes the σ -bond character from slightly polar to strongly polar. The condensation of $[\text{SiO}_4]$ -tetrahedra in the rings leads to the accumulation of electron density near bridge oxygens. This phenomenon is expressed especially in diopase (pure ring silicate). Therefore, the electron density picture may be considered as a supplementary independent criterion for classification of crystal structures. The experimental $\delta\rho$ -maps for H_2O molecules in diopase are in good agreement with theoretical ones. The $\delta\rho$ -distribution of 3d-electrons and bonding in the Jahn-Teller distorted Cu-octahedron can be interpreted from crystal-field-theory point of view.

Key words: Electron density; Bonding; Ring silicates.

The investigation of the experimental electron density distribution obtained by precise X-ray data [1] offers the possibility to analyse the chemical bonding and its peculiarities in crystals, the atomic charges, the principles of classification of crystal structures and other crystal chemical concepts on a more fundamental level. The comparison of the experimental $\delta\rho$ -maps with theoretical ones is also very useful. A review of recent data on $\delta\rho$ -distributions in silicates [2] shows the relevance of this approach and the insufficiency of data concerning certain groups, in particular ring silicates.

New data on orthorhombic iron-rich low-cordierite $\text{Na}_{0.04}(\text{Al}_2\text{Si})(\text{Mg}_{1.13}\text{Fe}_{0.78}\text{Mn}_{0.05}) \cdot [\text{Al}_2\text{Si}_4\text{O}_{18}] \cdot 0.2 \text{H}_2\text{O} \cdot 0.06 \text{CO}_2$ and trigonal diopase $\text{Cu}_6\text{Si}_6\text{O}_{18} \cdot 6 \text{H}_2\text{O}$ are presented in this work. Together with hexagonal beryl $\text{Na}_{0.04}\text{Be}_{2.98}\text{Al}_2[\text{Si}_6\text{O}_{18}] \cdot 0.3 \text{H}_2\text{O}$ [2, 3] these three minerals are classified as ring silicates [4] possessing different symmetry of the tetrahedral anionic group $[\text{T}_6\text{O}_{18}]$. The cations Al, (Mg, Fe, Mn) and Cu have octahedral coordination. The minor impurity of water molecules in beryl and cordierite is established within the channels. At the same time, water molecules are considered as important structural elements in diopase, forming rings of 6 H_2O like $[\text{Si}_6\text{O}_{18}]$ (Figures 1 a–c).

The experimental and data-treatment conditions are given in Table 1. The models used for refinement were based on the precise determination of the cordierite structure by Armbruster [5] and by Armbruster and Bürgi [6], and of the diopase structure by Belov et al. [7]. The results of high-order refinement were the

Table 1. Crystallographic and experimental data.

	Beryl	Cordierite	Diopase
<i>a</i> , Å	9.222 (3)	17.155 (5)	14.597 (2)
<i>b</i> , Å	9.222 (3)	9.777 (4)	14.597 (2)
<i>c</i> , Å	9.204 (1)	9.339 (1)	7.796 (14)
Sp. group	P6/mcc	C ccm	R $\bar{3}$
<i>r</i> _{sph} , cm	0.012	0.0125	0.01
No. refl., meas. (<i>I</i> ≥ 1.96 σ_I)	4971	6324	3878
Max. no. equiv.	12	4	3
Aver. stat., <i>R</i> _{int}	2.3	2.5	3.5
No. indep. refl.	752	1982	1593
Abs. corr., μ_r	0.1	0.33	0.7
Ext. corr., <i>R</i> _x (Zachariasen)	1566	6138	8414
Angle range for high-order refl., $\sin \theta/\lambda$	0.8–1.08	0.65–1.08	0.75–1.08
No. reflection	338	1058	625
<i>R</i> _{hkl}	0.73	1.18	1.90
<i>R</i> _{whkl}	0.79	1.19	2.00
<i>S</i> _{whkl}	1.020	1.023	0.862

Diffractionmeter P $\bar{1}$ "Syntex" $\lambda\text{Mo-K}\alpha$, graphite monochromator, 2θ - θ -step scan, 2–24 degree/min, $\sin \theta/\lambda_{\text{max}} = 1.08 \text{ \AA}^{-1}$, MINEXTL-complex of crystallographical programs [9]; independent-atom crystal model.

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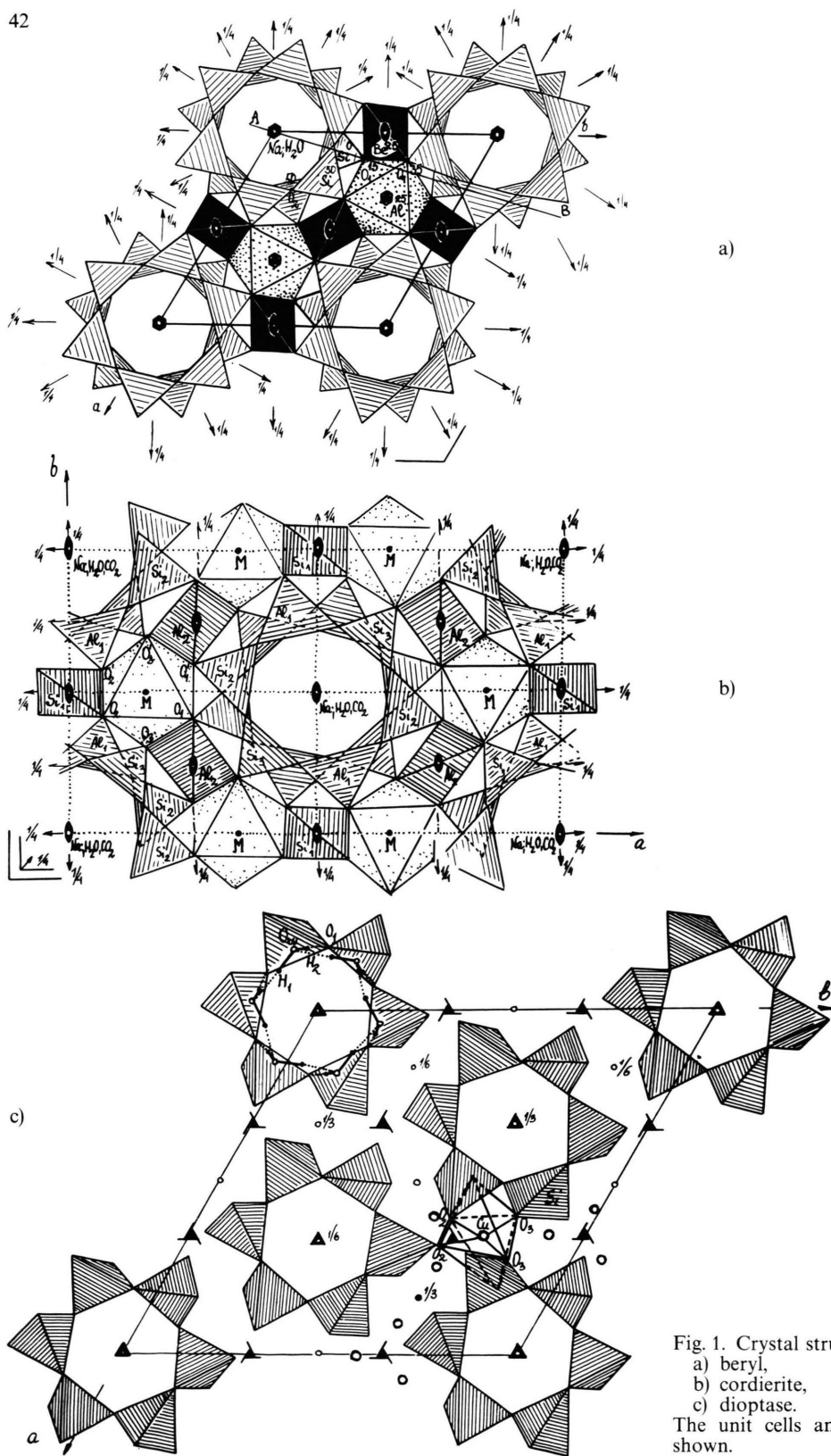


Fig. 1. Crystal structures in (001)-projection:
 a) beryl,
 b) cordierite,
 c) diopside.
 The unit cells and symmetry elements are shown.

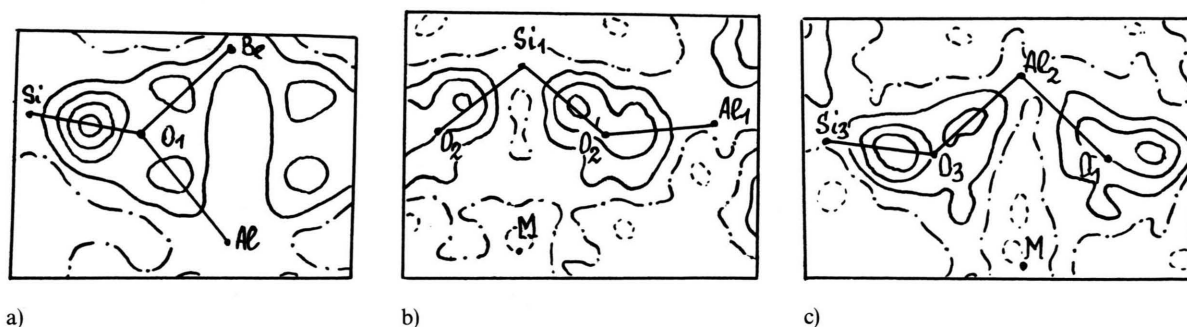


Fig. 2. $\delta\rho$ -maps for identical structural fragments with $0.1 \text{ e}\text{\AA}^{-3}$ contour interval: a) Si, Be-tetrahedra, Al-octahedron, $\text{O}_1\text{--O}_1'$ common edge (beryl), b) Al_1 , Si_1 , M, $\text{O}_2\text{--O}_2'$ (cordierite), c) Al_2 , Si_3 , M, $\text{O}_3\text{--O}_1$ (cordierite).

base for calculations of deformation electron density ($\delta\rho$) maps (Figures 2–6). The $\sigma(\delta\rho)$ -maps were calculated in accordance with [8]. The values of errors on the atoms are for diopside $0.4 \text{ e}\text{\AA}^{-3}$ on Cu, $0.3 \text{ e}\text{\AA}^{-3}$ on Si and $0.1 \text{ e}\text{\AA}^{-3}$ on O, for cordierite $0.06 \text{ e}\text{\AA}^{-3}$ on (Mg, Fe), $0.05 \text{ e}\text{\AA}^{-3}$ on Si, $0.04 \text{ e}\text{\AA}^{-3}$ on Al and $0.02 \text{ e}\text{\AA}^{-3}$ on O, and for beryl $0.1 \text{ e}\text{\AA}^{-3}$ on Si and Al, $0.02 \text{ e}\text{\AA}^{-3}$ on Be and $0.05 \text{ e}\text{\AA}^{-3}$ on O; in the region of chemical bonds the error is $0.1\text{--}0.2 \text{ e}\text{\AA}^{-3}$.

Let us consider the $\delta\rho$ -distribution of the three minerals: a) for the identical structural fragments, b) for different types of $[\text{T}_6\text{O}_{18}]$ -rings, c) for H_2O molecules, and d) for octahedra with Al, (Mg, Fe) and Cu as central atoms. The latter deserves special interest owing to Jahn-Teller distortion.

The crystal structures of beryl and low-cordierite are very similar and have identical structural fragments. The reason for the lower symmetry (orthorhombic instead of hexagonal) of cordierite is considered to be the double substitution in the tetrahedra of the beryl crystal structure: two Si in the $[\text{T}_6\text{O}_{18}]$ -ring by Al and three Be by two Al and one Si (Figures 1 a, b). The replacement of the central atoms in the tetrahedra and the octahedron in the structural fragment consisting of three polyhedra leads to remarkable differences in the $\delta\rho$ -maps for these two minerals (Figures 2 a–c). The $\delta\rho$ -maxima of $0.2 \text{ e}\text{\AA}^{-3}$ on the Be–O bond in beryl (Fig. 2a) are apparently displaced towards the oxygen atoms. Hence, Be–O σ -bonds have more polar character than the $\text{Si}_1\text{--O}$ σ -bond in cordierite (Si_1 is situated in the Be-position), whereas the $\delta\rho$ -peak of $0.4 \text{ e}\text{\AA}^{-3}$ (Fig. 2b) lies in the middle of the bond. The same is true for the $\text{Al}_2\text{--O}$ bond (Figure 2c). In accordance with the change of the electronegativity of the elements we can also observe the $\delta\rho$ -redistribution around the oxygen: the small maxi-

mum of $0.1 \text{ e}\text{\AA}^{-3}$ is on the (Mg, Fe)–O bond, the bigger maxima of $0.2\text{--}0.35 \text{ e}\text{\AA}^{-3}$ are on Si, Al–O bonds (Figures 2b, c). In contrast to cordierite, the $\delta\rho$ -peaks in beryl are almost equal ($0.2 \text{ e}\text{\AA}^{-3}$) between Al–O in the octahedron and Be–O in the tetrahedron with increased concentration of $\delta\rho$ ($0.4 \text{ e}\text{\AA}^{-3}$) on Si–O bonds. It is possible to recognize on $\delta\rho$ -maps Si–O ($0.35\text{--}0.4 \text{ e}\text{\AA}^{-3}$) and Al–O ($0.20\text{--}0.25 \text{ e}\text{\AA}^{-3}$) bonds in cordierite, whereas in the $[\text{Al}_2\text{Si}_4\text{O}_{18}]$ -ring the $\delta\rho$ -maxima on the bonds are “averaged”.

Three $[\text{T}_6\text{O}_{18}]$ -rings with different symmetry are presented on Figures 3 a–c. The puckered diopside ring was collected from Si–O–Si' fragments. The general rule for the $\delta\rho$ -distribution in $[\text{T}_6\text{O}_{18}]$ -units is the electron density accumulation near the bridge oxygens. The values of $\delta\rho$ -peaks $0.3\text{--}0.4 \text{ e}\text{\AA}^{-3}$ are nearly equal in highly symmetrical beryl-rings and correlate with bond lengths (Table 2). The $\delta\rho$ -map in cordierite has a more dispersed appearance, in agreement with the lower symmetry and the presence of both Si and Al atoms in the ring. The $\delta\rho$ -maxima on the bridge oxygens in diopside are much higher ($0.6\text{--}0.8 \text{ e}\text{\AA}^{-3}$; the shorter Si– O_1 bond corresponds to the largest maxima) than the ones in the first two minerals. On the other hand, comparison of the $\delta\rho$ -maxima near bridge and nonbridge oxygens inside $[\text{TO}_4]$ -tetrahedra in beryl and cordierite shows the absence of any significant difference (Figures 4 a–c). In contrast to cordierite, in diopside this difference is remarkable ($0.2\text{--}0.3 \text{ e}\text{\AA}^{-3}$, Figure 4e). This has apparently crystal chemical reasons. According to Godovikov [10], beryl and cordierite can be classified as framework structures formed by linkage of Si-, Al- and Be-tetrahedra. The $[\text{Si}_6\text{O}_{18}]$ -units in the diopside crystal structure are completely isolated from each other. The redistribution of $\delta\rho$ inside the $[\text{SiO}_4]$ -tetra-

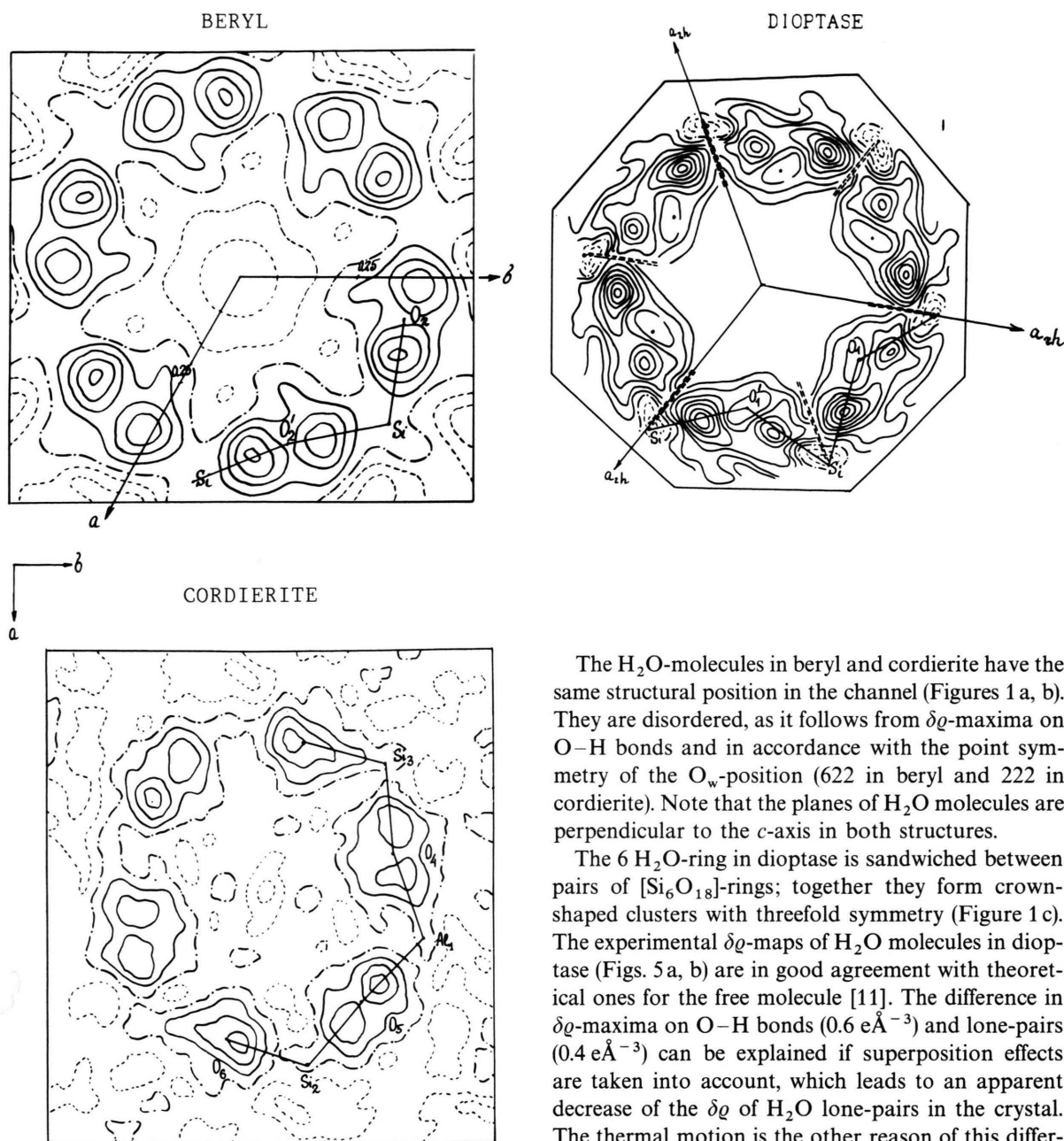


Fig. 3. $\delta\rho$ -maps through the $[T_6O_{18}]$ -rings with $0.1 \text{ e}\text{\AA}^{-3}$ contour interval: a) beryl, symmetry $6/m$; b) cordierite, symmetry $2/m$; c) diopside, symmetry 3 , line border double-dotted.

hedra in favour of the bridge oxygen is necessary in order to maintain the puckered pure ring-silicate unit for the rigidity of the structure, though with more effort.

The H_2O -molecules in beryl and cordierite have the same structural position in the channel (Figures 1 a, b). They are disordered, as it follows from $\delta\rho$ -maxima on O–H bonds and in accordance with the point symmetry of the O_w -position (622 in beryl and 222 in cordierite). Note that the planes of H_2O molecules are perpendicular to the c -axis in both structures.

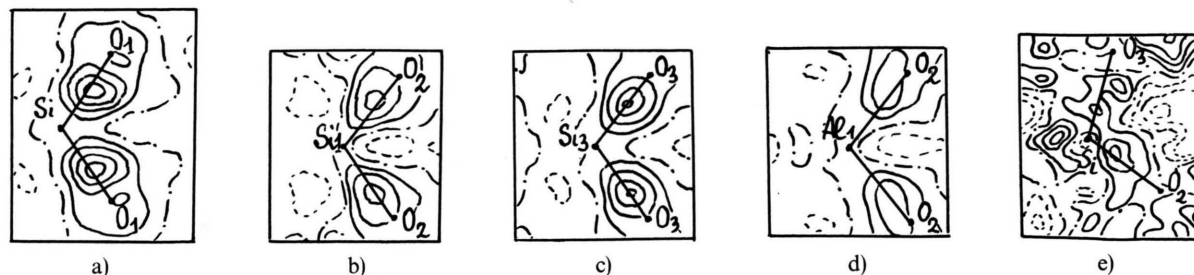
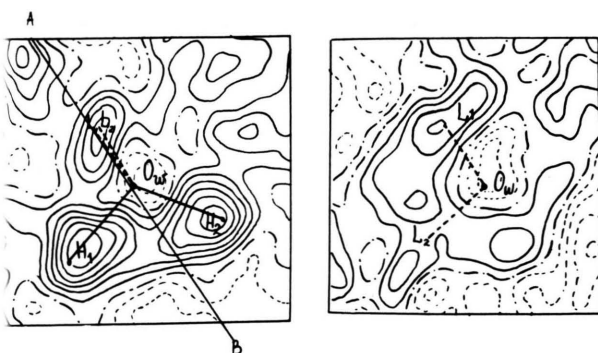
The $6 H_2O$ -ring in diopside is sandwiched between pairs of $[Si_6O_{18}]$ -rings; together they form crown-shaped clusters with threefold symmetry (Figure 1 c). The experimental $\delta\rho$ -maps of H_2O molecules in diopside (Figs. 5 a, b) are in good agreement with theoretical ones for the free molecule [11]. The difference in $\delta\rho$ -maxima on O–H bonds ($0.6 \text{ e}\text{\AA}^{-3}$) and lone-pairs ($0.4 \text{ e}\text{\AA}^{-3}$) can be explained if superposition effects are taken into account, which leads to an apparent decrease of the $\delta\rho$ of H_2O lone-pairs in the crystal. The thermal motion is the other reason of this difference in $\delta\rho$.

The $\delta\rho$ -maps of the O_w-O_w bond (Table 2) in the $6 H_2O$ -ring are in good agreement with theoretical ones [13], calculated for the same distance of about $2.6 \text{ \AA}$.

The water-molecule rings have ice-like configuration, although the lone-pair positions are different in ice and diopside: they are statistically disordered in the former and ordered outside the ring in the latter.

Beryl	Cordierite	Diopside
Be-tetrahedron	Si ₁ -tetrahedron	Si-tetrahedron
Be-O ₁ × 4 1.657 (1)	Si ₁ -O ₂ × 4 1.630 (1)	Si-O ₁ 1.615 (2)
Si-tetrahedron	Si ₂ -tetrahedron	O ₁ ' 1.651 (2)
Si-O ₁ × 2 1.623 (1)	Si ₂ -O ₁ × 2 1.638 (1)	O ₂ 1.596 (2)
O ₂ 1.595 (1)	O ₅ 1.587 (1)	O ₃ 1.528 (2)
O ₂ ' 1.600 (1)	O ₆ 1.609 (1)	Cu-octahedron
Al-octahedron	Si ₃ -tetrahedron	Cu-O ₂ 1.937 (2)
Al-O ₁ × 6 1.909 (1)	Si ₃ -O ₃ × 2 1.640 (1)	O ₂ ' 1.857 (1)
	O ₄ 1.574 (1)	O ₃ 1.880 (1)
	O ₆ 1.616 (1)	O ₃ ' 1.989 (2)
	Al ₁ -tetrahedron	O _w 2.464 (4)
	Al ₁ -O ₂ × 2 1.776 (1)	O _w ' 2.633 (4)
	O ₄ 1.710 (1)	Hydrogen bonds
	O ₅ 1.609 (1)	O _w ...O _w ' 2.684 (6)
	Al ₂ -tetrahedron	O _w -H ₁ 0.970 (4)
	Al ₂ -O ₁ × 2 1.758 (1)	H ₁ -O _w 1.773 (4)
	O ₃ × 2 1.755 (1)	O _w -O ₁ 2.635 (4)
	M-octahedron	O _w -H ₂ 0.904 (5)
	M-O ₁ × 2 2.121 (1)	H ₂ -O ₁ 1.741 (2)
	O ₂ × 2 2.126 (1)	H ₁ -H ₂ 1.524 (1)
	O ₃ × 2 2.133 (1)	*O _w -H ₁ -O _w ' 115.0 (2)°
		*O _w -H ₂ -O ₁ 169.8 (2)°
		*H ₁ -O _w -H ₂ 108.8 (4)°

Table 2. The main interatomic distances (Å) in polyhedra and hydrogen bonds.

Fig. 4. $\delta\rho$ -maps for $[TO_4]$ -tetrahedra with nonbridging oxygens at $0.1 \text{ e}\text{\AA}^{-3}$ contour interval: a) beryl, b-d) cordierite, e) diopside.Fig. 5. $\delta\rho$ -maps of the H_2O molecule in diopside with $0.1 \text{ e}\text{\AA}^{-3}$ contour interval: a) $H_1-O_w-H_2$ plane, b) section perpendicular to the $H_1-O_w-H_2$ plane. A-B is the trace of this section. L_1, L_2 are ideal lone-pair positions.

The Cu-octahedron in diopside shows Jahn-Teller distortion (Table 2) with four equatorial oxygen atoms and two apical water molecules. The 3d energy levels of Cu^{2+} in a field of tetragonal symmetry D_{4h} split into four sublevels: $e_g(d_{xz}, d_{yz})$, $b_{2g}(d_{xy})$, $b_{1g}(d_{x^2-y^2})$, $a_{1g}(d_{z^2})$. The $\delta\rho$ -maxima of $0.2-0.3 \text{ e}\text{\AA}^{-3}$ (Figs. 6a, b) on Cu-O lines near oxygens can be considered as indication of a σ -bond. The smeared $\delta\rho$ -peak of $0.6 \text{ e}\text{\AA}^{-3}$ (Fig. 6b) directed towards O_w is connected with the a_{1g} -level and partially with the e_g -level. Four $\delta\rho$ -minima directed towards the equatorial O ligands are connected with the b_{1g} -level, which is less occupied by electrons (Fig. 6a). Four $\delta\rho$ -maxima of $0.2-0.6 \text{ e}\text{\AA}^{-3}$ in the same section are connected with the b_{2g} -

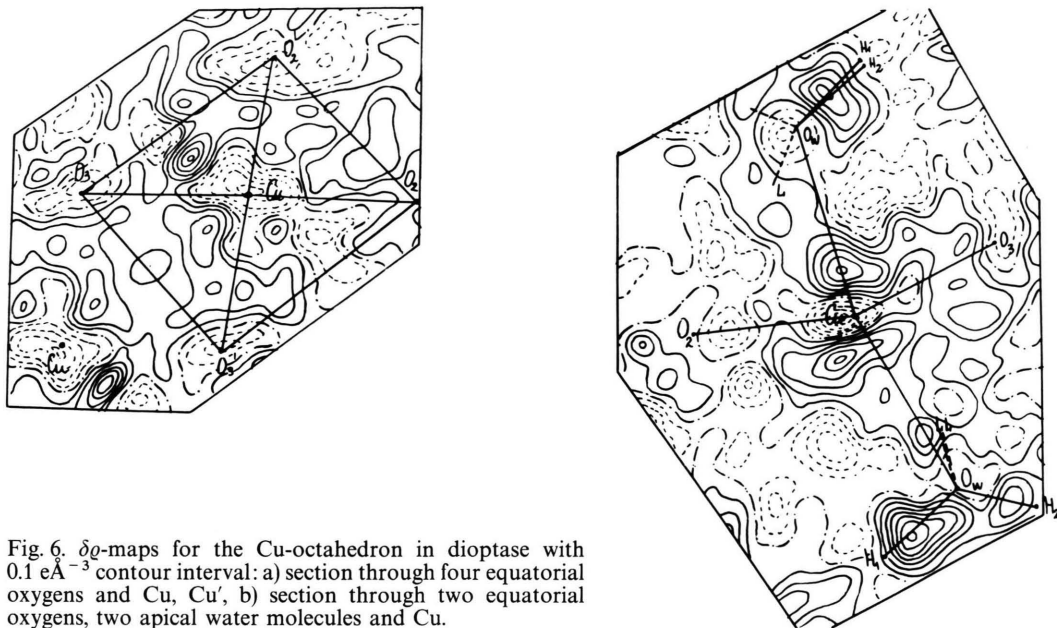


Fig. 6. $\delta\rho$ -maps for the Cu-octahedron in diopside with $0.1 \text{ e}\text{\AA}^{-3}$ contour interval: a) section through four equatorial oxygens and Cu, Cu', b) section through two equatorial oxygens, two apical water molecules and Cu.

level. The difference in the values may be explained by the electrostatic interaction with ions from the second coordination sphere. The largest maximum of $0.6 \text{ e}\text{\AA}^{-3}$ is observed near the $\text{O}_3\text{--O}_2$ edge screened outside by two silicon atoms from the $[\text{Si}_6\text{O}_{18}]$ -ring. The main features of the $\delta\rho$ -distribution in the Cu Jahn-Teller octahedron in diopside are close to that in chalkantite $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ [14].

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