

AN X-RAY DIFFRACTION STUDY OF THE ELECTRON-DENSITY DISTRIBUTION AND ELECTROSTATIC POTENTIAL IN PHENAKITE Be_2SiO_4 *

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Deformation electron-density maps show that the bonds in Si tetrahedra are of multicenter stressed type. During formation of a crystal some of the valency electrons from the Si atom are displaced towards the O atoms, while others participate in intraatomic level reconstruction; the latter effect makes itself felt in the form of a region of excess electron density around the Si atom. In the Be tetrahedra, there are two-center covalent bonds in which electron transfer to the O atoms occurs. The electrostatic-potential distribution is such that the Be atoms are in a continuous region of positive (nuclear) potential, which leads to their mutual repulsion. Near the Si atoms, electron (negative) potentials predominate. In the large hexagonal channels passing through the structure along the c axis, there is a continuous region of excess nuclear potential, which causes marked polarization of the electron density near the Si on the channel side.

Crystals belonging to the phenakite structural type have some useful properties that are employed in solid electrolytes, phosphors, and related areas in materials science, so they have been extensively studied for some years [1-3]. All the properties are ultimately related to the electron-density and crystal-field distributions. Recent major improvements in diffraction techniques and advances in methods of processing and representing data have made it possible to examine these characteristics directly (see for example review [4]). The information substantially supplements the usual crystallochemical description and can be employed in interpreting results obtained by other methods. It is also important for construction of models. The present study deals with a precision X-ray analysis of the electron distribution and electrostatic potential in the namesake of the phenakite structural type series: phenakite Be_2SiO_4 itself.

Bragg [5] first determined the structure of this mineral, which was subsequently refined by Zakhariassen [6]. Space group $R\bar{3}$, the framework consists of SiO_4 and BeO_4 tetrahedra, within which chains can be recognized running along the c axis in which two beryllium tetrahedra alternate with a silicon one. The c parameter is therefore the sum of the vertical edges of three tetrahedra (2Be and 1Si).

There are six parallel chains of Be and Si tetrahedra running along the 3 axes; these form a hexagonal tube having a channel of hexagonal cross section in projection along the xy plane, diameter $\sim 5.5 \text{ \AA}$. Each face of the prism is formed by the vertical edges of Be and Si tetrahedra. The tubes are linked together via the vertices of the tetrahedra and constitute a framework, in which the removal of the Si orthotetrahedra does not disrupt the three-dimensional links between the Be ones. Sets of three adjacent Be-Si tubes are linked together by 3_1 and 3_2 screw axes. This linkage results in channels of rhombic cross section, the number of them being three times as large as the hexagonal ones.

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Details of the bonds in each of the tetrahedra are of interest, since they reflect not only the pair interactions but also collectively the multiatom effects responsible for the detailed structure. The distribution of the electron density and electrostatic potential in the hexagonal channels is also of interest; their large geometrical dimensions allow impurity atoms to enter and diffuse in them. These topics will be considered here. Also, bond analysis of the Si and Be may be useful in elucidating the geochemical behavior of silicon and beryllium.

Spherical specimens were prepared from a pure natural phenakite crystal for precision X-ray diffraction. From these we selected one of diameter 0.02 ± 0.005 cm, which gave the best diffraction pattern and provided the minimal spread in the intensities for symmetrical equivalent reflections. The measurements were made at room temperature with a Syntex PI four-circle diffractometer with graphite monochromator ($\text{Mo } K_\alpha$) over a hemisphere in reciprocal space by $\theta/2\theta$ scanning. The scan angle varied from 2 to 3° as the scattering angle θ increased. The survey rate was varied over the range 2-24 deg/min depending on the intensity. The background intensity was measured to left and right at points separated from the maximum by half the scanning angle. The instrumental stability was monitored periodically (every 30 reflections) by measuring the intensity of the 360 reflection; there were no significant deviations in the experiment lasting 200 h. For each group of equivalent reflections the internal divergence factor $R_{\text{in}} = \Sigma(I - I_{\text{av}}) / \Sigma I_{\text{av}}$ was calculated; the mean over the entire data set was 0.017, which showed that there were only small effects related to anisotropy. No absorption correction was applied because $\mu r = 0.07$.

The unit-cell parameters derived from 12 reflections were: $a = 12.485(3)$, $c = 8.264(3)$ Å, $\gamma = 120^\circ$, $d_{\text{calc}} = 2.95$ g/cm³, and $\mu = 7.237$ cm⁻¹.

The structure was refined with an Eclipse S/200 computer on the basis of the full-matrix least-squares method in the anisotropic approximation [7]. The initial data were provided by [6] (in our study, the choice of the x and y axes was opposite to that of [6]). The refinement was based on spherically symmetrical scattering amplitudes for Be^{2+} , Si^{4+} , and O^- from [8] in the following manner. First, the entire data set was used to refine 21 positional parameters and 42 thermal ones for all the atoms together with the scale factor K ($R_1 = 0.0266$, $R_2 = 0.0405$, $S = 4.2475$)*; we used the weighting scheme $w = \sigma_s^{-2}(F_e)$, where $\sigma_s^2(F_e)$ is the statistical variance in the structure amplitude. Extinction correction in accordance with [9] caused the refinement parameters to deteriorate, which was attributed to the absence of this effect from this specimen, so extinction was subsequently neglected. Then we excluded any effect on the structure parameters from factors related to inadequacy in the ionic curves for the real electron structure by restricting the data set to remote reflections having $\sin \theta/\lambda > 0.85$ Å⁻¹. The main contribution to the scattering in this region of reciprocal space comes from the inner shells, which can be taken as spherically symmetrical [10]. At the same time, the refinement was restricted to 324 reasonably strong reflections whose structure amplitudes satisfied $F \geq 12$; this led to $R_1 = 0.0203$, $R_2 = 0.0244$, and $S = 1.982$. Further, from this set of reflections we deleted 12 for which $F_e - F_t \geq 10\sigma$ and $F_e - F_t \leq 3\sigma(F_e)$, and in accordance with the Abrahams-Keve criterion [11] we used a weighting scheme of the form $w^{-1} = \sigma_s^2(F_e) + (0.01F_e)^2$ ($R_1 = 0.0178$, $R_2 = 0.0220$, and $S = 1.290$).

The wider range of reflections with $\sin \theta/\lambda$ 0.7-0.996 Å⁻¹ was used to refine the coordinates and thermal parameters only for the Be_1 and Be_2 atoms, which produce comparatively slight scattering at large θ , together with the scale factor.

$$* \sin \theta/\lambda \geq R_1 = \frac{\Sigma(|F_e| - |F_t|)}{\Sigma |F_e|}; R_2 = \frac{\Sigma w(|F_e| - |F_t|)}{\Sigma w |F_e|}; S = \left\{ \frac{\Sigma w(|F_e| - |F_t|)^2}{n - m} \right\}^{1/2},$$

where F_e are the experimental structure amplitudes and F_t are the theoretical ones, with n the number of reflections and m the number of parameters to be refined.

Table 1

Basal-Atom Coordinates and Anisotropic Thermal Corrections for
Phenakite Be_2SiO_4

Atom	Coordinates	I	II	Atom	Coordinates	I	II
Si	x/a	0,98394 (4)	0,98402 (3)	O ₁	x/a	0,12104 (13)	0,12116 (8)
	y/b	0,19561 (4)	0,19559 (3)		y/b	0,20967 (13)	0,20959 (8)
	z/c	0,75004 (5)	0,74993 (4)		z/c	0,74972 (13)	0,75021 (10)
Be ₁	x/a	0,98290 (14)	0,98412 (14)	O ₂	x/a	0,00007 (13)	0,00030 (8)
	y/b	0,19422 (15)	0,19397 (14)		y/b	0,33346 (15)	0,33350 (8)
	z/c	0,41568 (13)	0,41547 (18)		z/c	0,75016 (8)	0,74991 (10)
Be ₂	x/a	0,98397 (15)	0,98234 (14)	O ₃	x/a	0,91341 (12)	0,91239 (8)
	y/b	0,19423 (14)	0,19386 (14)		y/b	0,12231 (12)	0,12230 (8)
	z/c	0,08424 (13)	0,08454 (18)		z/c	0,91475 (15)	0,91484 (10)
	x/a			O ₄	x/a	0,91235 (11)	0,91326 (8)
	y/b				y/b	0,12222 (12)	0,12224 (8)
	z/c				z/c	0,58504 (14)	0,58506 (10)

Atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Si	0,190 (12)	0,208 (13)	0,175 (10)	0,100 (9)	-0,004 (7)	0,015 (8)
Be ₁	0,371 (13)	0,369 (31)	0,385 (27)	0,118 (26)	0,036 (23)	0,008 (24)
Be ₂	0,366 (29)	0,442 (32)	0,347 (26)	0,227 (26)	0,003 (23)	-0,060 (24)
O ₁	0,360 (25)	0,531 (33)	0,238 (25)	0,280 (23)	-0,026 (15)	-0,020 (17)
O ₂	0,400 (26)	0,281 (26)	0,396 (16)	0,193 (27)	-0,051 (21)	-0,000 (20)
O ₃	0,306 (30)	0,261 (25)	0,306 (22)	0,040 (18)	0,009 (17)	-0,007 (17)
O ₄	0,346 (30)	0,317 (25)	0,248 (20)	0,075 (20)	-0,019 (17)	-0,030 (17)

Note: I this study, II Zakhariassen's coordinates [6] with modified f curves ($R = 0.021$);

$$T = \exp \left[-\frac{1}{4} (B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*) \right]$$

Table 2

Interatomic Distances in Phenakite, Å

Si-Tetrahedron		Be ₁ -Tetrahedron		Be ₂ -Tetrahedron	
Si — O ₁	1,631 (2)	Be ₁ — O ₁	1,638 (2)	Be ₂ — O ₁	1,647 (2)
— O ₂	1,630 (2)	— O ₂	1,641 (2)	— O ₂	1,645 (2)
— O ₃	1,631 (1)	— O ₃	1,659 (2)	— O ₃	1,659 (2)
— O ₄	1,637 (1)	— O ₄	1,650 (3)	— O ₃	1,643 (3)
Mean	1,632	Mean	1,647	Mean	1,649
O ₁ — O ₂	2,646 (3)	O ₁ — O ₂	2,686 (2)	O ₁ — O ₂	2,685 (2)
— O ₃	2,635 (2)	— O ₄	2,766 (2)	— O ₃	2,773 (2)
— O ₄	2,644 (2)	— O ₄	2,663 (2)	— O ₃	2,666 (2)
O ₂ — O ₃	2,668 (2)	O ₂ — O ₄	2,682 (2)	O ₂ — O ₃	2,684 (2)
— O ₄	2,670 (2)	— O ₄	2,657 (2)	— O ₃	2,667 (2)
O ₃ — O ₄	2,725 (2)	O ₃ — O ₄	2,678 (2)	O ₃ — O ₄	2,671 (2)
(O—O) _{av}	2,665	Mean	2,689	Mean	2,691

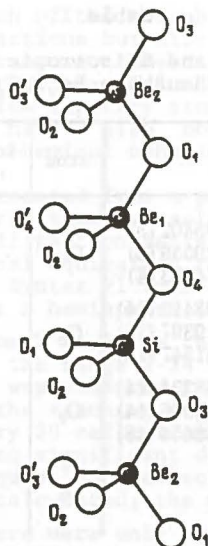


Fig. 1. Disposition and numbering of atoms in part of phenakite structure.

Then the parameters for these atoms were fixed, and we used 216 reflections having $0.9 \leq \sin \theta/\lambda \leq 0.996 \text{ \AA}^{-1}$ to refine the structure parameters for the Si and O atoms together with K . The final results were: $R_1 = 0.0152$, $R_2 = 0.0162$ and $S = 0.978$. Table 1 gives the atomic coordinates and anisotropic thermal parameters, which are compared with the data of [6], while Table 2 gives the interatomic distances; Fig. 1 gives the disposition and numbering of the atoms.

The details of the electron-density distribution were derived from the deformation density [10]:

$$\delta\rho(\vec{r}) = \frac{1}{V} \sum_{\vec{q}} \delta F(\vec{q}) \exp(-i\vec{q}\vec{r}),$$

where $\delta F = F_e - F_t$, $\vec{q}$ is the scattering vector, and V is the unit-cell volume. The moduli of the F_e were determined from the diffraction measurements, while the phases were calculated theoretically from the high-angle refinement. The F_t were constructed from relativistic atomic scattering amplitudes [8] via the high-angle positional and thermal parameters. That reference state (i.e., F_t) corresponds to an ensemble of noninteracting spherical atoms lying at the same points as the atoms in the crystal and vibrating in the same way. The summation included all reflections having $\sin \theta/\lambda \leq 0.8 \text{ \AA}^{-1}$, which are related to the valency-electron distribution [10]. The construction method implies the significance of the deformation density, which characterizes the electron-charge transfers in the system as a whole when the atoms are bonded. Here $\delta\rho$ is directly related via Poisson's equation to the deformation potential:

$$\delta\varphi = -\frac{4\pi}{V} \sum_{\vec{q}} \frac{\delta F(\vec{q})}{q^2} \exp(-i\vec{q}\vec{r}),$$

which shows how far the potential produced by the electrons in the crystal differs from that for an ensemble of spherically symmetrical atoms (the minus sign incorporates the negative electron charge).

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Fig. 2. 2D-DEDD maps of planes of the Si tetrahedron containing O_1 -Si- O_3 (a) and O_2 -Si- O_4 (b). The solid lines here and subsequently join points having excess deformation electron density, while the dashed lines join ones with deficient density, and the dot-dash lines are those of zero density. Intervals between lines $0.1 \text{ e} \cdot \text{\AA}^{-3}$.

Information is extracted from $\delta\rho$ and $\delta\phi$ by constructing planar sections (maps), whose forms and symbols have been considered in [12]. We use these symbols here. For example, 2D-DEDD denotes a two-dimensional dynamic electron-density diagram, i.e., one broadened by the thermal motion, while 2D-PEDD is the two-dimensional pattern for the deformation potential. Some dozens of such diagrams were constructed to derive the details of the electron-density and crystal fields. The most interesting and characteristic features are considered below.

We begin the discussion of the electron-density distribution with the Si tetrahedron. Figure 5 shows two of the 2D-DEDD, which contain the O_1 -Si- O_3 and O_2 -Si- O_4 atoms lying in almost mutually perpendicular planes. The diagrams show the specific electron distribution around the Si, which is characterized by continuous excess DED.



Fig. 3. 2D-DEDD maps of planes of the Be₁ tetrahedron containing O₁-Be₁-O₄ (a) and O₂-Be₁-O₄ (b). Intervals between lines: a) 0.09 e·Å⁻³; b) 0.08 e·Å⁻³.

The Si tetrahedron lacks individual directions for the covalent bonds, and the electron cloud is highly delocalized. Some of the electron density is displaced towards the oxygen atoms, but there is a large peak with a value of 0.57 e·Å⁻³ of excess DED around the Si, a peak that is displaced towards the O₁-O₃-O₄ face of the tetrahedron, which is parallel to the large hexagonal channel. Such a disposition of this peak means that the DED is of two-humped character on the Si-O lines in certain sections. The excess peaks near the O are 0.18-0.45 e·Å⁻³, and the displacement of the maxima from the lines of the Si-O bonds indicates the direction of the stress in the tetrahedron. This is confirmed by diagrams that include the faces of Si tetrahedron: O₁-O₃-O₄ and O₁-O₂-O₃. On these, the centers of gravity of these peaks lie on the bisectors of the angles of the triangle composed of O atoms, with the peaks joined by a region of excess electron density of about 0.05 e·Å⁻³. There is a DED peak at the center of the O₁-O₃-O₄ face that reaches 0.28 e·Å⁻³ and that is associated with the above polarization (Fig. 2) of the electron density on the Si atom towards that face, while

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Fig. 4. 2D-DEDD maps passing along the c axis: a) section through $\text{Si-Be}_2\text{-O}_4$; b) section through the points (000), (001), and Be_1 . Intervals between lines $0.1 \text{ e} \cdot \text{\AA}^{-3}$.

on the other faces, the DED at the same points lie in the range $0.1\text{-}0.2 \text{ e} \cdot \text{\AA}^{-3}$. On the lines joining the O atoms there are DED minima, the largest of which is of depth $-0.30 \text{ e} \cdot \text{\AA}^{-3}$ and lies near the $\text{O}_3\text{-O}_4$ edge of the tetrahedron parallel to the z axis, which has the largest length ($2.725 \text{ \AA}$, Table 2); the values of the others range from $0.05 \text{ e} \cdot \text{\AA}^{-3}$ ($\text{O}_1\text{-O}_4$ edge) to $0.20 \text{ e} \cdot \text{\AA}^{-3}$ ($\text{O}_1\text{-O}_2$ edge). The turning points in these negative regions are also displaced from the lines of the tetrahedron edges.

In the Be_1 and Be_2 tetrahedra, the electron distributions are qualitatively the same (Figure 3 shows 2D-DEDD for Be_1). The electron shells of the Be atoms are somewhat polarized in the xy plane (Fig. 3), as is evident from the DED minima elongated in this plane (perpendicular to the plane of Fig. 3a) and of depth -0.38 (Be_1) and $-0.5 \text{ e} \cdot \text{\AA}^{-3}$ (Be_2). The centers of gravity do not coincide with the nuclei but are displaced in the Be_1 tetrahedron towards O_4 , and in Be_2 towards the $\text{O}_2\text{-O}_3$ edge. In contrast to the Si, there is no excess DED near the Be, it being displaced towards the O atoms and distributed in somewhat the same fashion as around these atoms in the Si tetrahedron. There are also broad DED peaks surrounding the O atoms with maxima of $0.1\text{-}0.49 \text{ e} \cdot \text{\AA}^{-3}$, which are usually displaced from the lines joining the Be and O atoms. Sections taken through the faces of

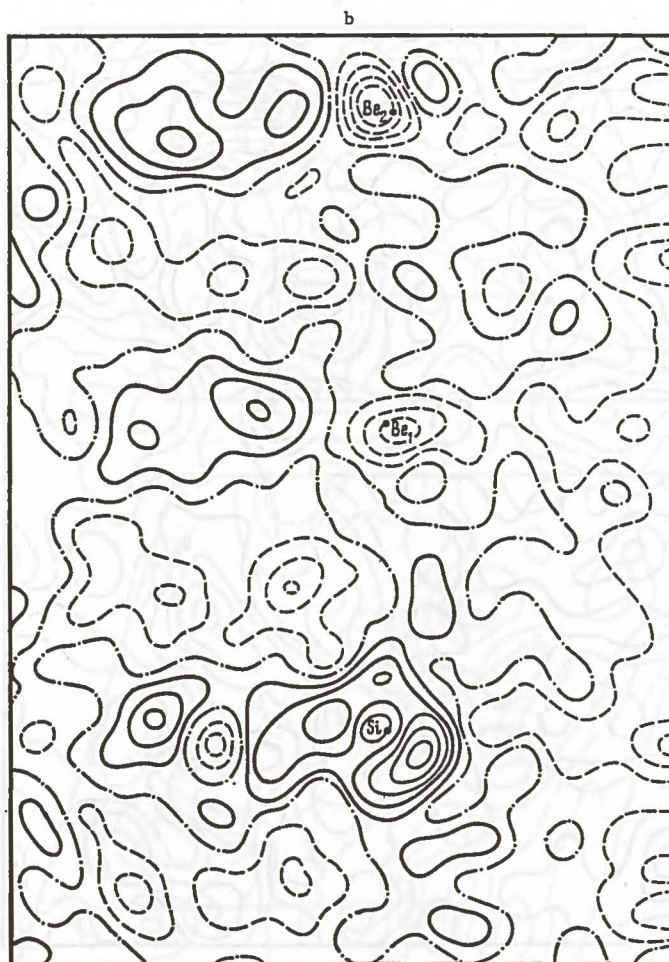


Fig. 4 (continued).

these tetrahedra showed that these peaks are not connected by electron-density bridges in these planes, in contrast to the Si tetrahedron. They are separated by regions of small negative DED ($-0.1 \text{ e} \cdot \text{\AA}^{-3}$). A characteristic feature of both Be tetrahedra is the DED minima of -0.39 (Be_1) and $-0.28 \text{ e} \cdot \text{\AA}^{-3}$ (Be_2) near the most elongated edges, which are parallel to the z axis; O_1-O_4 ($2.766 \text{ \AA}$), and O_1-O_3 ($2.773 \text{ \AA}$). Around the short edges $\text{O}_2-\text{O}'_4$ ($2.657 \text{ \AA}$) and $\text{O}_2-\text{O}'_3$ ($2.666 \text{ \AA}$), negative DED peaks also occur, these are -0.38 and $-0.18 \text{ e} \cdot \text{\AA}^{-3}$ respectively.

Let us now consider the details of the electron distribution along the z axis of the unit cell. Figure 4a shows a DED section passing through $\text{Si}-\text{Be}_2-\text{O}_4$ (the other atoms lie outside the plane of section but near it). The $\text{O}-\text{Be}_2$ bond is more ionic than $\text{Si}-\text{O}$. There are continuous bands of negative DED, whose value ranges from zero to $-0.35 \text{ e} \cdot \text{\AA}^{-3}$, perpendicular to the z axis and enclosing both Be atoms. An analogous band enclosing the Si atom is interrupted near the latter by the adjacent excess DED. Consequently, the O atoms are separated by DED minima of depth from -0.2 to $-0.3 \text{ e} \cdot \text{\AA}^{-3}$, which reflects the layered distribution noted above. The DED is almost zero along the line joining the cations, although there are directly adjacent regions of excess electron density. The channel of rhombic section running to the left from this line has alternating minima and maxima.

The other section (Fig. 4b) runs through the origin and Be_1 . The deviations of the Si and Be_2 from the plane of section do not exceed 0.01 Å. The oxygen atoms out of the plane of the section (not more than 0.06 Å from it) act as excess DED peaks in the left-hand half of the figure. To the right of the Si, Be_1 , and Be_2 runs a hexagonal channel passing through the structure. The above DED peak near the Si, which is displaced towards the channel, is clearly seen, as is the electron transfer towards the more electronegative O atoms. This section has two features. Firstly, the DED in the channel is negative throughout the unit cell; this is also seen in other sections whose DED maps are not shown here. Secondly, as in Fig. 4a, the DED is zero between the cations along the z axis. There are only small peaks in the excess electron density of $\sim 0.12 \text{ e} \cdot \text{Å}^{-3}$ slightly to the side of the lines joining the cations. There are also regions of negative DED separating the O atoms along the z axis.

This pattern shows that phenakite has multicenter bonds, whose description requires crystal orbitals (Bloch wave functions). The differing number of electrons on the Si and Be atoms lead to differences in interaction with the immediate environment (O atoms in the tetrahedra) and with the more remote environment. The structure has stresses that are particularly prominent along the z axis. For example, the Si- Be_1 , Si- Be_2 , and Be_1 - Be_2 distances are 2.763, 2.762, and 2.739 Å correspondingly, while the other Si(Be)-Be distances have a mean of 2.900 Å, so they are fairly short, while the edges of the tetrahedra parallel to this axis are elongated by comparison with the average O-O distance. Figure 5a shows the 2D-PEDD for the same plane as the DED of Fig. 4b; the electronic (negative) part of the electrostatic potential predominates at the Si atom, value $0.52 \text{ e} \cdot \text{Å}^{-1}$. The gradient varies with direction, and in particular the minimum in $\delta\phi$ on formation of the crystal is displaced from the nucleus of the Si atom towards the hexagonal channel, which is accompanied by electron-density polarization in that direction. One consequence of this is the large DED peak noted above.

The two Be atoms are in regions of excess nuclear (positive) potential penetrating the faces of the adjacent tetrahedra, which is direct evidence for electrostatic repulsion between these cations. The $0.36 \text{ e} \cdot \text{Å}^{-1}$ peak in the positive region is half-way between Be_1 and Be_2 , but to the side of the line joining them. There are parallel changes in magnitude and sign for $\delta\rho$ and $\delta\phi$ (Figs. 4b and 5a).

The deformation potentials are negative at all the O atoms (Fig. 5b), while their values range from -0.04 to $-0.09 \text{ e} \cdot \text{Å}^{-1}$. This section passes through the origin and the O atoms, and here the parallel changes in $\delta\rho$ and $\delta\phi$ do not occur: in the regions between the atoms, where the DED is negative, there is excess electrostatic potential. This emphasizes the importance of considering the multiparticle character of the interaction in phenakite.

The two 2D-PEDD in Fig. 5 illustrate the crystal field in the hexagonal channel. Along the axis and throughout the unit cell, there is a continuous region of excess positive potential ($\sim 0.30 \text{ e} \cdot \text{Å}^{-1}$), in which there are three local maxima of $0.36 \text{ e} \cdot \text{Å}^{-1}$ at heights $z = 0.25, 0.50$, and 0.75 . The channel thus provides conditions for impurity ions to diffuse freely.

Our results may be compared with the DED for the isostructural Li_2BeF_4 [13], as the two are largely analogous, although the Be-F bonds are less covalent than Si-O, while Li-F is more ionic than Be-O. The similarity may be useful in explaining the properties of other crystals with a phenakite structure: Zn_2SiO_4 , which is used in phosphors [2], or Li_2GeO_4 and Li_2MoO_4 , which are used as solid electrolytes [14]. In particular, the DED diagrams indicate the localization of the impurity ions and the diffusion paths they take. The data may be useful for models for these processes.

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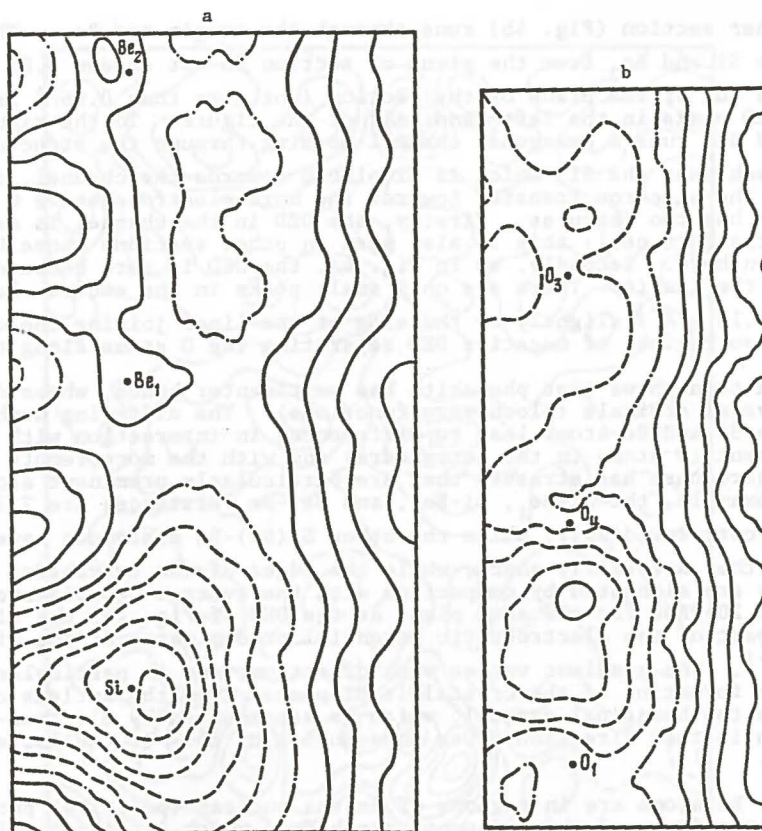


Fig. 5. 2D-PEDD maps in planes passing through the points (000), (001), and Be₁ (a) and (000), (001) and O₃ (b). The solid lines join points with excess positive (nuclear) electrostatic potential, while the dashed lines show excess negative potential (electronic), and the dot-dash lines are of zero potential. Intervals between lines 0.09 e·Å⁻¹ (a) and 0.07 e·Å⁻¹ (b).

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