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REFINED CRYSTAL STRUCTURE OF PHENACITE Be_2SiO_4

W. H. Zachariasen

Physics Faculty, University of Chicago
Argonne National Laboratory, USA

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The exact values of 21 coordinate and 42 thermal parameters of the phenacite structure are given. The interatomic distances and the anisotropy of the thermal motion of the atoms are discussed.

The crystal structure of the mineral phenacite (Be_2SiO_4) was determined by W. L. Bragg in 1927 [1]. The solution of a structural problem with 21 coordinate degrees of freedom in the middle of the 20's was an outstanding achievement. Doubts may only be expressed in relation to the siting of the Be atoms, the scattering power of these being very small. However, a study of the intensities of x-ray diffraction lines obtained from the isostructural mineral willemite (Zn_2SiO_4) confirmed the validity of Bragg's coordinates for the Be atoms [2].

Recently the author studied extinction effects in a small spherical sample of phenacite. In this investigation the exact values of 21 coordinate and 24 thermal (temperature) parameters of the phenacite structure were obtained. The values of these parameters are being published for the first time in the present article.

The symmetry space group of phenacite is $R\bar{3}$. The rhombohedral unit cell contains six "molecules" of Be_2SiO_4, with all the atoms in general positions. We used a triple hexagonal unit cell containing 18 of these "molecules." The dimensions of this cell were a = 12,472, c = 8,252 Å; the general position, referred to the hexagonal axes, was $(0, 0, 0)$ $(^1/_3, ^2/_3, ^1/_3)$ $(^2/_3, ^1/_3, ^2/_3)$ $\pm$ (x, y, z) $(-y, x-y, z)$ $(y-x, -x, z)$.

All the measurements were made on a sample of almost perfect spherical shape, $1.97 \cdot 10^{-2}$ cm in radius. A complete set of diffraction intensities was obtained for $\sin\theta/\lambda \leq 0.72$ Å^{-1}, using MoKα radiation and a stationary detector and crystal. All the symmetry-related reflections were measured independently and averaged; the experimental standard errors calculated from these served as a basis for the weighting scheme used in refining the structure. At all stages of refinement we used the complete set of experimental quantities $|F_{hkl}|$ without any exceptions; we took the Bragg parameters of the structure as the initial approximation. The initial refinement was carried out with isotropic temperature factors, and without introducing any corrections for extinction. This refinement gave an R factor of 0.117 (allowing for the weighting), but the temperature constant for the silicon was negative. After introducing corrections for extinction [3] and allowing for the anisotropy of the thermal vibrations, the R factor fell to 0.031.

Up to this point we used the theoretical f curves for the neutral atoms taken from the Inter-

TABLE 1. Modified f Curves

$\sin\theta/\lambda$	Si	Be	O	$\sin\theta/\lambda$	Si	Be	O
0	13.49	3.70	8.28	0.40	7.26	1.48	2.91
0.05	13.06	3.46	8.07	0.45	6.85	1.43	2.56
0.10	11.95	2.89	7.52	0.50	6.44	1.38	2.35
0.15	10.74	2.35	6.74	0.55	5.98	1.30	2.16
0.20	9.70	1.98	5.88	0.60	5.53	1.22	2.02
0.25	8.90	1.76	5.05	0.65	5.10	1.13	1.87
0.30	8.26	1.63	4.25	0.70	4.70	1.05	1.76
0.35	7.74	1.55	3.49				

TABLE 2. Coordinates of the Basis Atoms of Phenacite

Atom		I	II	III	IV
Si	*x*	0.199	0.1955±2	0.19557±4	0.19559±3
	y	0.989	0.9840±2	0.98401±4	0.98402±3
	z	0.750	0.7503±2	0.74933±5	0.74993±4
Be_{I}	*x*	0.20	0.1932±10	0.1939±2	0.19397±14
	y	0.99	0.9840±10	0.9840±2	0.98412±14
	z	0.42	0.4170±13	0.4155±3	0.41547±18
$\mathrm{Be}_{\mathrm{II}}$	*x*	0.19	0.1937±10	0.1938±2	0.19386±14
	y	0.99	0.9821±10	0.984±2	0.98234±14
	z	0.08	0.0870±13	0.0845±3	0.08454±18
O_{I}	*x*	0.213	0.2104±6	0.2096±1	0.20959±8
	y	0.120	0.1216±5	0.1212±1	0.12116±8
	z	0.750	0.7503±7	0.7502±2	0.75021±10
O_{II}	*x*	0.320	0.3335±6	0.3335±1	0.33350±8
	y	0	0.0002±6	0.0003±1	0.00030±8
	z	0.750	0.7508±7	0.7499±2	0.74991±10
$\mathrm{O}_{\mathrm{III}}$	*x*	0.131	0.1229±6	0.1223±1	0.12230±8
	y	0.926	0.9120±6	0.9124±1	0.91239±8
	z	0.917	0.9145±7	0.9148±2	0.91484±10
O_{IV}	*x*	0.130	0.1230±6	0.1223±1	0.12224±8
	y	0.926	0.9129±6	0.9133±1	0.91326±8
	z	0.583	0.5852±7	0.5850±2	0.58506±10
R			0.117	0.031	0.021

I – from the data of [1].

II – coordinates after the first refinement. Isotropic thermal motion. Extinction not considered.

III – allowing for extinction and anisotropy of the thermal motion; *f* curves taken from International Tables.

IV – same as III, but using the modified *f* curves of Table 1.

TABLE 3. Phenacite. Thermal Parameters ($\times 10^4$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si	83	78	122	37	0	0
σ	2	2	4	2	2	2
Be_{I}	129	118	207	47	2	2
σ	10	10	17	9	10	10
$\mathrm{Be}_{\mathrm{II}}$	140	116	197	49	−2	−6
σ	10	10	17	9	1	1
O_{I}	149	110	134	74	0	2
σ	6	6	10	5	6	6
O_{II}	96	103	185	48	−4	2
σ	6	6	10	5	6	6
$\mathrm{O}_{\mathrm{III}}$	112	111	127	40	7	3
σ	6	6	10	5	6	6
O_{IV}	112	112	132	38	−4	−3
σ	6	6	10	5	6	6

national Tables. Analysis of the resultant data revealed that agreement might be considerably improved by making a slight correction to the theoretical scattering powers of the atoms. A refinement based on the modified *f* curves represented by Table 1, in fact, reduced the R factor to 0.021.

The original Bragg parameters of the structure (referred to the hexagonal system) and the results of the present investigation are shown in Table 2. The final values of the parameters for the anisotropic thermal vibrations of the parameters are given in Table 3.

INTERATOMIC DISTANCES

It was made perfectly clear in Bragg's original paper in 1927 that the structure of phenacite had a number of interesting characteristics. The structure constitutes a three-dimensional network of SiO_4 and BeO_4 tetrahedra, the dimensions of these being almost equal. Each O atom is divided between three tetrahedra, but two tetrahedra never have more than one common vertex. In Figs. 1 and 2 we have made an attempt at indicating the high anisotropy of the bands between the tetrahedra. In the direction of the c axis, groups of three atoms lying at a distance of c/3 from each other lie almost exactly one under the other and form rows. There are three different types of such rows. One row is composed of metal atoms, as indicated by the coordinates in the last column of Table 2. The second row is formed by the atoms O_{III}, O_{IV} (coordinates in Table 2) and O_I' with coordinates x =

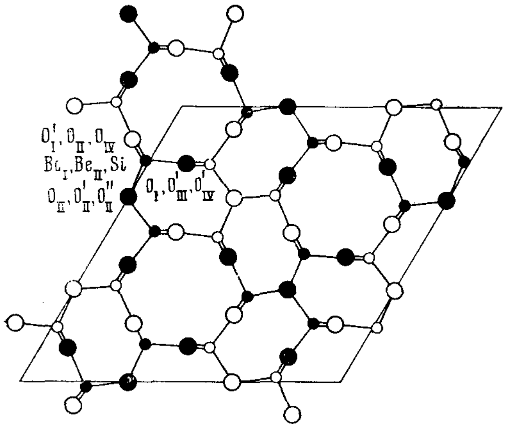

Fig. 1. Projection of the structure of phenacite on the (001) plane. The diameter of the open channels with the three-fold axis passing through them is 4.4 Å. Atoms in the structure lying c/3 apart almost entirely overlap in this projection. Along the c axis stretch rows of atoms of three different types: One is formed from the metal atoms, the second from O'_I, O_{III}, O_{IV}, and the third from O_{II}, O'_{II}, O''_{II}. The coordinates of all the atoms indicated in the figure are given in the text.

0.12116, y = 0.91157, z = 0.24979. Along the third row stretch the equivalent atoms O_{II}, O'_{II}, and O''_{II}, with coordinates (0.33350; 1.00030; 0.74991), (0.33303; 0.99987; 0.41658), and (0.33347; 0.99983; 0.08324). This aspect of the structure leads to the appearance of chains of tetrahedra parallel to the c axis, transforming this direction into one of low compressibility. In Fig. 1 we also observe large open channels, with three-fold axes passing within them. The atoms indicated in Figs. 1 and 2 as O_{III}, and O'_{IV} respectively have the coordinates (0.20991; 0.12230; 0.08516) and (0.20898; 0.12224; 0.41494).

The stress which occurs in the structure along the c axis is due to the short metal–metal distances: Si–Be_I = 2.7600; Si–Be_{II} = 2.7613; and Be_I–Be_{II} = 2.7310 Å. Table 4 gives the interatomic distances in the tetrahedra. The standard errors obtained in the course of the refining process are unusually small: Δ(Si–O) = ±0.0009; Δ(O–O) = ±0.0011; Δ(Si–Be) = ±0.0015; Δ(Be–O) = ± 0.0017; Δ(Be–Be) = ±0.0021 Å. The only marked deviations from regularity in the tetrahedra may be attributed to the strong metal–metal repulsion in the direction of the c axis. Thus all the edges of the tetrahedra parallel to the c axis (O_{III}–O_{IV}, O'_I–O_{IV}, O'_I–O_{III}) are enlarged; there is a slight elongation of the Be_I–O_{IV} and Be_{II}–O_{III} bonds also.

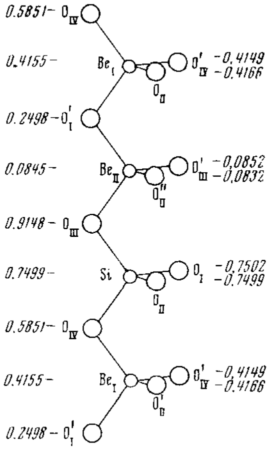

Fig. 2. Schematic representation of the chain of tetrahedra drawn out along the c axis. The shortened distances between the metal atoms and the atoms O_{II}, O'_{II}, and O''_{II} parallel to the c axis lead to a reduction in compressibility and to a diminution of the thermal vibrations in the direction of this axis. The figures alongside the symbols of the atoms indicate their z coordinates.

THERMAL MOTION OF THE ATOMS

Table 5 gives the mean square displacements of the atoms along the principal axes of the ellip-

TABLE 4. Phenacite. Interatomic Distances (Å)

Si tetrahedron		Be_I tetrahedron		Be_{II} tetrahedron	
Si–O_I	1.6301	Be_I–O'_I	1.6404	Be_{II}–O'_I	1.6310
Si–O_{II}	1.6280	Be_I–O'_{II}	1.6449	Be_{II}–O''_{II}	1.6431
Si–O_{III}	1.6337	Be_I–O_{IV}	1.6581	Be_{II}–O_{III}	1.6553
Si–O_{IV}	1.6307	Be_I–O'_{IV}	1.6371	Be_{II}–O'_{III}	1.6546
O_I–O_{II}	2.6437	O'_I–O'_{II}	2.6795	O'_I–O'_{II}	2.6828
O_I–O_{III}	2.6411	O'_I–O_{IV}	2.7667	O'_I–O_{III}	2.7640
O_I–O_{IV}	2.6438	O'_I–O'_{IV}	2.6618	O'_I–O'_{III}	2.6588
O_{II}–O_{III}	2.6655	O'_{II}–O_{IV}	2.6773	O''_{II}–O_{III}	2.6804
O_{II}–O_{IV}	2.6666	O'_{II}–O'_{IV}	2.6618	O''_{II}–O'_{III}	2.6574
O_{III}–O_{IV}	2.7213	O_{IV}–O'_{IV}	2.6674	O_{III}–O'_{III}	2.6764

The primes denote atoms related to the basic atoms by symmetry operations.

TABLE 5. Magnitudes and Orientations of the Principal Axes of the Ellipsoids of the Mean Square Deviations of the Atoms ($S_j \times 10^3$ Å, φ_j in deg)

Atom	j	S_j	ψ_1	ψ_2	ψ_3
Si	1	65±1	91±6	89±15	1±10
	2	68±1	102±9	168±9	89±16
	3	72±1	12±9	102±9	89±6
Be_I	1	82±4	69±12	25±28	102±53
	2	85±4	93±23	102±49	168±53
	3	96±3	22±11	112±11	89±14
Be_{II}	1	81±4	82±13	41±54	50±57
	2	84±4	80±13	52±55	140±57
	3	98±3	12±10	102±10	88±10
O_I	1	68±3	87±7	95±11	6±13
	2	76±2	61±5	151±6	96±13
	3	94±2	29±5	61±5	90±4
O_{II}	1	75±2	25±22	70±30	77±20
	2	78±2	77±33	151±34	65±36
	3	81±2	111±19	70±34	29±33
O_{III}	1	66±3	97±5	97±8	9±9
	2	77±2	118±6	151±7	99±9
	3	92±2	29±6	119±6	87±4
O_{IV}	1	67±3	86±6	84±10	7±11
	2	77±2	120±5	149±6	83±11
	3	94±2	30±5	120±5	90±4

soids of the vibrations S_j, and also the orientation of these principal axes. The angles ψ_1, ψ_2, and ψ_3 of any particular principal axis of the ellipsoid are given with respect to the axes of a rectangular coordinate system (X along **a**; Y along **a** + 2**b**, and Z along **c**). The mean values of the mean square displacements of all the atoms (Si 0.068, Be 0.088, and O 0.079 Å) are small in comparison with those which might have been expected on the basis of the hardness of phenacite. The mean square displacements vary from atom to atom in accordance with an $m^{-1/4}$ law, where m is the mass of the atom.

The anisotropic manner in which the tetrahedra are united into a three-dimensional network is due to the general anisotropy of the thermal vibrations of all the atoms in the structure. A special feature of this anisotropy is that the mean square displacements parallel to the c axis are much smaller than those in the perpendicular directions; the maximum displacements coincide with the normals to the walls of the open prismatic channels embracing the three-fold axes of the structure.

The immediate surroundings of the Si and Be atoms are almost isotropic, since the corresponding tetrahedra are distorted very little. Hence the reason for the anisotropy of the vibrations of these atoms lies in their interaction with the atoms of the next coordination sphere. The immediate surroundings of the O atoms are extremely anisotropic, since all three bonds (two with Be and one with Si atoms) are almost coplanar. The planes of these three bonds are parallel to the c axis for the O_I, O_{III}, and O_{IV} atoms and normal to the c axis for the O_{II} atoms. It is natural to expect that the S_3 direction will be normal to the plane of the three bonds; we see from the data presented that this is in fact the case (Table 6).

The value of S_3 = 0.081 Å for the O_{II} atom may seem too small when compared with the corresponding constants for the other oxygen atoms. The reason for the diminution of S_3 is that the third principal axis of the ellipsoid of thermal vibrations of the O_{II} atom is parallel to the c axis, along which steric hindrances are presented to the thermal vi-

TABLE 6

Atom	S_3, Å	Observed			Predicted		
		ψ_1^0	ψ_2^0	ψ_3^0	ψ_1^0	ψ_2^0	ψ_3^0
O_I	0.094	29	61	90	25	65	90
O_{II}	0.081	111	70	29	90	90	0
O_{III}	0.092	29	119	87	31	121	90
O_{IV}	0.094	30	120	90	32	122	90

brations. We see from Table 5 that for the O_I, O_{III}, and O_{IV} atoms the direction S_1 coincides with the c axis.

We may suppose from quite general considerations that the S_1 direction should coincide with the O–Si bond, which is stronger than the O–Be one. This prediction is valid, and only for the O_{II} atom does the corresponding quantity lie within the limits of experimental error, which is due to the character of the general anisotropy of the thermal motions. The effect of the general anisotropy of the thermal motions may also be characterized more coarsely. If we only take nearest neighbors into consideration, then the anisotropy of the thermal motions of the oxygen atoms in the structure of phenacite is characterized thus: $S_1 = 0.07\underset{\circ}{4}$ (along the O–Si bond), $S_2 = 0.076$ and $S_3 = 0.088$ A (along the normals to the plane of the O–Si bond and the two O–Be bonds).

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LITERATURE CITED

1. W. L. Bragg, Proc. Roy. Soc., A113, 642 (1927).
2. W. L. Bragg and W. H. Zachariasen, Z. Kristallogr., 72, 517 (1930).
3. W. H. Zachariasen, Acta Crystallogr., 23, 558 (1967).