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THE CRYSTAL STRUCTURE OF HEMIHEDRITE

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ABSTRACT

Hemihedrite is a triclinic mineral having the composition $ZnF_2[Pb_5(CrO_4)_3SiO_4]_2$ with cell dimensions $a=9.497$ Å, $b=11.443$ Å, $c=10.841$ Å, $\alpha=120°30'$, $\beta=92°06'$, $\gamma=55°50'$. Three-dimensional counter data were collected and the structure was solved from the Patterson function and refined to an R factor of 0.04. The structure is similar to those of the tsumebite series and contains a zinc coordinated by four oxygens and two fluoride ions; the lead environments are quite varied. Chromium and silicon are regularly four-coordinated by oxygen. Evidence from the crystal structure determination tends to cast some doubt on the morphological interpretation that the species is acentric.

INTRODUCTION

The new mineral hemihedrite was found in Arizona and is described in the preceding paper. The present investigation deals with the crystal structure, its determination and the compositional problems which it brought to light. The chemical formula for hemihedrite was thought to be $ZnPb_5(CrO_4)_3O_3$ at the outset of this structure determination. This composition was significantly modified when it was realized that the proposed composition of hemihedrite could not provide atoms necessary to occupy sites which emerged during the course of the structure determination. New chemical work showed that the predicted elements fluorine and silicon were indeed present. The composition based on the refined structure was established as $ZnF_2[Pb_5(CrO_4)_3SiO_4]_2$.

CRYSTAL DATA

Hemihedrite, triclinic, $ZnF_2[Pb_5(CrO_4)_3SiO_4]_2$

$a=9.497(3)$ Å	$\alpha=120.50(4)°$
$b=11.443(5)$	$\beta=92.10(4)$
$c=10.841(4)$	$\gamma=55.84(3)$
$V=787.183$ Å^3	$\rho_0=6.42$ gm/cc
Space group: $P1$ or $P\bar{1}$	$\rho_2=6.39$ gm/cc

Numbers in parentheses are standard deviations and refer to the last decimal places.

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EXPERIMENTAL

A number of crystals of hemihedrite were ground to spheres and the one selected for data collection had a radius of 0.052 mm. The unit cell had been previously selected (preceding paper) and its parameters refined using data obtained from Weissenberg photographs taken on all three axes with CuKα radiation (a = 1.5418 Å) and calibrated with NaCl powder (a = 5.6402 Å at 22°C). These data were used in conjunction with diffractometer measurements to refine the cell parameters by least squares. Intensity data were collected on a Picker four-circle automatic diffractometer. Of the 3607 reflections obtainable with CuKα radiation, 2790 were collected, of which 2428 were considered to be observed on the basis that their intensities were greater than 1.5σ. The intensities were corrected for absorption by linear interpolation of the spherical corrections taken from the *International Tables for X-ray crystallography, Vol. II*, pp. 304 and 305 (1959), with a μR of 6.4.

STRUCTURE DETERMINATION

The intensities were reduced to structure factors and a three-dimensional Patterson function was calculated which indicated that the Pb structure was essentially centric. The Patterson was solved routinely by choosing a vector, assuming it to be a double Pb–Pb interaction, and searching the Patterson manually for two single Pb–Pb interactions separated by twice the double interaction vector. This established the positions of two Pb atoms and a third was located manually by selecting another vector and assuming it to be a double interaction between a third Pb and one of the known Pb's. After several trials a vector was found for which this assumption was valid and the position of the third Pb established. These three atoms were used to calculate a three-dimensional multiple minimum function from which the remaining two Pb atoms were obtained. A second multiple minimum function was calculated, based on the five Pb atoms, which clearly showed four additional positions, but one of these was at a center of symmetry. The position at the center of symmetry was ignored and one Zn and two Cr atoms inserted into the other three positions, giving a conventional R factor of 0.31. A difference Fourier synthesis was calculated which (1) indicated that the atom which had been put in as Zn was actually Cr, (2) indicated that there was Zn in special position at 0, $\frac{1}{2}$, 0 and that there were no other special position atoms, (3) indicated shifts for the other atoms, and (4) showed 16 oxygen-like atoms which formed four independent tetrahedra, three around the three Cr atoms and the fourth coordinating an atom whose scattering power appeared to be about twice that of an oxygen. The application of these findings with the fourth tetrahedral atom assumed to be Cr reduced the R factor to 0.21. Three cycles of full matrix least-squares refinement with isotropic temperature factors reduced R to 0.06. The temperature factor of the fourth Cr assumed the anomalously high value of 3.0. A difference Fourier then revealed a seventeenth oxygen-like atom in the region of the special position Zn. A fourth least squares cycle with this atom added, the fourth Cr changed to $\frac{1}{2}$Zn, the addition of correction for anomalous dispersion resulting from the Pb, Zn, and Cr atoms, and all 27 atoms varied isotropically, reduced R to 0.05.

The structure model at this point was based on the apparent centric nature of the structure and the originally assumed composition, $2[ZnPb_5(CrO_4)_3O_3]$, modified by the appearance of the additional oxygen-like atoms to give $2[ZnPb_5(CrO_4)_3F_4O]$. All atoms occurred in centric pairs except the Zn atoms where the presence of one at a center of symmetry forced the other to be disordered in the centric refinement. The possibility that the structure is actually noncentric is very strongly suggested by the crystal morphology and an attempt was made to test this possibility by refining the structure in the space group $P1$. At this point it was necessary to go to a block diagonal least-squares procedure. The least-squares refinement was preceded by three cycles of difference Fourier synthesis which began with one Zn atom as the only noncentric part of the structure and ended with all atoms shifted into slightly acentric positions, the mean difference in positional parameters from the centric case being about 0.009. Two least-squares cycles produced poorer agreement ($R=0.06$) and the number of parameters was nearly doubled. While this result is not conclusive because of the difficulties inherent in making the shift from a centric to a noncentric refinement and the shift from full matrix to block diagonal least-squares, the very satisfactory centric refinement tends to indicate that the structure is not significantly acentric.

The assumed composition $2[ZnPb_5(CrO_4)_3F_4O]$ requires disorder of the general position Zn. Moreover, the distance from this position to the oxygen-like atoms surrounding it is about 1.64 Å. A normal Zn–F or Zn–O distance is greater than 1.9 Å. These difficulties are avoided if the fourth tetrahedral position is assumed to be occupied by silicon rather than zinc. The Si–O distance is about 1.63 Å for independent tetrahedra, and the scattering power of Si is very close to that observed for this position. This assumption obviates the necessity to postulate disorder of Zn in the general position. The composition of the crystal of hemihedrite from which the data were collected is therefore indicated to be $ZnF_2[Pb_5(CrO_4)_3SiO_4]_2$. Substitution of a full Si atom for the half Zn and centric full matrix least-squares refinement of isotropic F and O atoms and the five Pb atoms, three Cr atoms, and Si atom with anisotropic temperature factors for one cycle reduced the R factor to 0.041. At that point the refinement was terminated. The resulting atomic param-

TABLE 1. ATOMIC PARAMETERS FOR HEMIHEDRITE[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pb(1)	0.2591 (1)	0.1116 (1)	0.2594 (1)	0.0060 (1)	0.0051 (1)	0.0040 (1)	−0.0031 (1)	−0.0009 (1)	0.0016 (1)
Pb(2)	.2616 (1)	.0862 (1)	.6568 (1)	.0043 (1)	.0039 (1)	.0039 (1)	−.0021 (1)	−.0007 (1)	.0019 (1)
Pb(3)	.9306 (1)	.2442 (1)	.0306 (1)	.0052 (1)	.0045 (1)	.0041 (1)	−.0028 (1)	−.0010 (1)	.0022 (1)
Pb(4)	.7307 (1)	.4165 (1)	.7513 (1)	.0078 (2)	.0070 (1)	.0058 (1)	−.0045 (1)	−.0028 (1)	.0044 (1)
Pb(5)	.3171 (1)	.4530 (1)	.5316 (1)	.0072 (1)	.0071 (1)	.0048 (1)	−.0052 (1)	−.0030 (1)	.0040 (1)
Zn	.0000	.5000	.0000	.0051	.0047	.0036	−.0031	−.0015	.0024
Cr(1)	.9591 (4)	.0752 (4)	.3555 (4)	.0067 (6)	.0053 (6)	.0045 (4)	−.0042 (5)	−.0017 (4)	.0026 (4)
Cr(2)	.5642 (4)	.1758 (4)	.1535 (4)	.0047 (6)	.0047 (5)	.0040 (4)	−.0023 (5)	−.0012 (4)	.0028 (4)
Cr(3)	.4470 (4)	.3246 (4)	.8369 (4)	.0041 (5)	.0041 (5)	.0040 (4)	−.0022 (5)	−.0008 (4)	.0019 (4)
Si	.0229 (6)	.4516 (6)	.6594 (5)	.0033 (8)	.0010 (8)	.0010 (6)	−.0008 (7)	.0001 (5)	.0004 (6)

	x	y	z	B		x	y	z	B
F	0.1425 (25)	0.2488 (24)	0.9318 (21)	0.87 (32)	O(9)	0.5990 (24)	0.2969 (24)	0.9141 (21)	1.87 (31)
O(1)	.7535 (27)	.2193 (27)	.4835 (23)	2.12 (36)	O(10)	.4559 (31)	.3985 (29)	.7442 (26)	2.45 (41)
O(2)	.1079 (35)	.0778 (34)	.4436 (29)	2.38 (49)	O(11)	.2385 (27)	.4815 (26)	.9767 (23)	.97 (35)
O(3)	.9940 (26)	.1184 (25)	.7361 (22)	1.92 (33)	O(12)	.4794 (21)	.1360 (20)	.7183 (18)	1.54 (25)
O(4)	.9677 (28)	.1120 (27)	.2294 (23)	2.36 (37)	O(13)	.2089 (25)	.3053 (24)	.5120 (21)	1.60 (32)
O(5)	.5101 (26)	.1407 (25)	.2712 (21)	1.54 (33)	O(14)	.0421 (25)	.3859 (24)	.7677 (21)	1.20 (32)
O(6)	.4318 (24)	.1992 (23)	.0573 (20)	2.16 (30)	O(15)	.9931 (20)	.3717 (20)	.2568 (17)	.92 (25)
O(7)	.7772 (27)	.0082 (26)	.0274 (22)	2.06 (34)	O(16)	.8475 (27)	.4788 (26)	.6134 (23)	1.18 (35)
O(8)	.5405 (24)	.3585 (23)	.2686 (20)	1.76 (29)					

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[a] Standard deviations in parentheses refer to the last digits. Atomic numbering is shown in Fig. 3.

TABLE 3. COMPARISON OF THE STRUCTURES OF TSUMEBITE AND HEMIHEDRITE. THE CELL AND PARAMETERS OF HEMIHEDRITE ARE CONVERTED TO THOSE OF ITS $P2_1/m$ PSEUDOCELL FOR COMPARISON.[a]

Name	Tsumebite				Hemihedrite			
Formula	$CuOHPb_2PO_4SO_4$				$Zn_{0.5}PbFPb_4(CrO_4)_3SiO_4$			
Space group	$P2_1/m$				$P\bar{1}$			
Unit cell		a 7.85 Å.	b 5.80 Å.	c 8.70 Å.		a' 7.86 Å.	b' 5.72 Å.	c' 9.34 Å.
		x	y	z		x'	y'	z'
Atomic positional parameters	Cu(1)	0.000	0.000	0.000	Zn	0.000	0.000	0.000
	Cu(2)	.000	.500	.000	Pb(3)	.069	.388	.031
	Pb(1)	.729	.250	.250	Pb(1)	.741	.224	.259
					Pb(4)	.731	.196	.249
	Pb(2)	.288	.250	.393	Pb(2)	.262	.223	.343
					Pb(5)	.317	.309	.468
	P	.032	.750	.340	Cr(1)	.041	.753	.356
					Si	.023	.732	.341
	S	.454	.750	.171	Cr(2)	.436	.762	.154
					Cr(3)	.447	.740	.163

[a] The $P2_1/m$ pseudocell parameters for hemihedrite are related to those of the triclinic cell by: $x' = 1.000 - x$, $y' = 2y + x - z - 1.000$, $z' = z$.

eters are given in Table 1 and the structure factors are listed in Table 2.[1] The atomic scattering factors used were those for atoms of Zn, Cr, Si, and O and for the F^- ion which are given in the International Tables for X-ray Crystallography, Vol. III, pp. 202–204 (1962) and for the Pb atom given on page 212 of the same volume.

DESCRIPTION OF THE STRUCTURE

The structure of hemihedrite contains pseudosymmetry much higher than the indicated $P\bar{1}$ symmetry. The symmetry of the structure ap-

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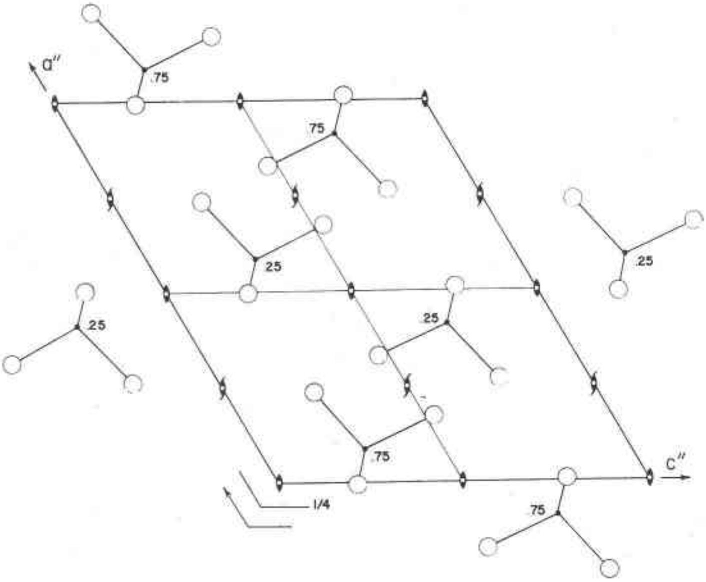
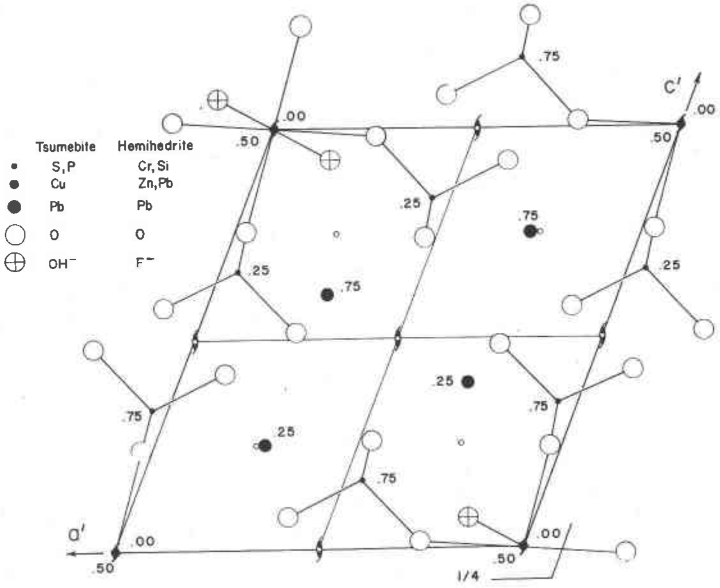
[1] To obtain a copy of Table 2, order NAPS Document #00366 from National Auxiliary Publications Service, c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022; remitting $2.00 for microfiche or $5.00 for photocopies, in advance, payable to CCMIC-NAPS.


a''
.75
.75
.25
.25
.25
.25
.75
.75
c''
1/4

(a)


Tsumebite
Hemihedrite
S,P
Cr,Si
Cu
Zn,Pb
Pb
Pb
O
O
OH⁻
F⁻
.75
.00
.50
c'
.00
.50
.25
.75
.25
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1/4

(b)

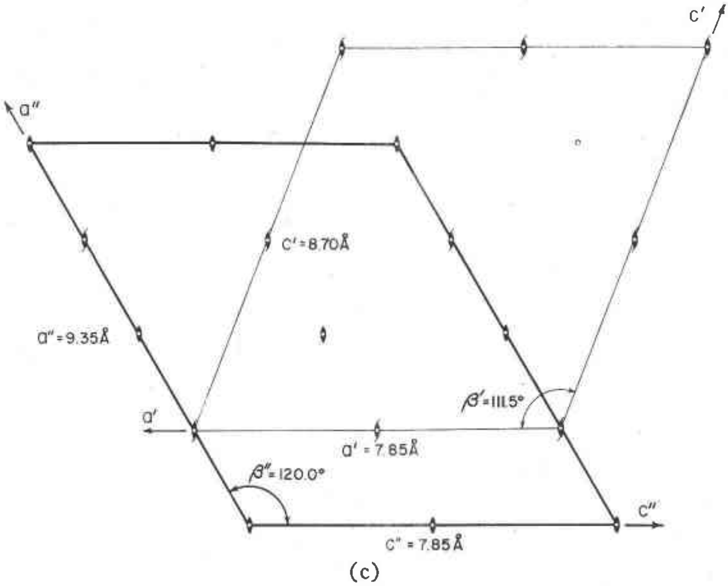

FIG. 1. (a) The $C2/m$ pseudocell of hemihedrite. The a''–c'' plane of the pseudocell is approximately normal to the b axis of hemihedrite. Solid circles represent Cr or Si; open circles represent oxygen. (b) The $P2_1/m$ pseudocell which is found in both hemihedrite and tsumebite. (c) Relationship between the $C2/m$ cell (lower left) and the $P2_1/m$ cell (upper right).

proaches that of the space group $C2/m$ if only the tetrahedral anions are considered, as is shown in idealized form in Figure 1a. When the whole structure is considered the $C2/m$ pseudosymmetry remains only if large distortions are allowed. If the largest distortions are not allowed, the pseudosymmetry is reduced so that it approaches that of the space group $P2_1/m$ as is shown in Figure 1b. The representation of Figure 1b is the structure of the mineral tsumebite (Nichols, 1966) as well as being an idealized version of that of hemihedrite in projection perpendicular to the b axis. The two pseudocells are related as shown in Figure 1c where the cell dimensions of the $P2_1/m$ cell are designated by single-primed letters and those of the $C2/m$ cell by double-primed letters.

The $P2_1/m$ pseudosymmetry defines a pseudocell related to the actual triclinic cell in that the triclinic b axis is halved and the new a' and c' axes are the projections of the a and c axes of the triclinic cell on a plane approximately perpendicular to b. The $P2_1/m$ pseudocell has the approximate dimensions: $a' = 7.86$ Å, $b' = 5.72$ Å, $c' = 9.34$ Å, and $\beta' = 112.9°$. The relationship between the triclinic cell and the $P2_1/m$ pseudocell is

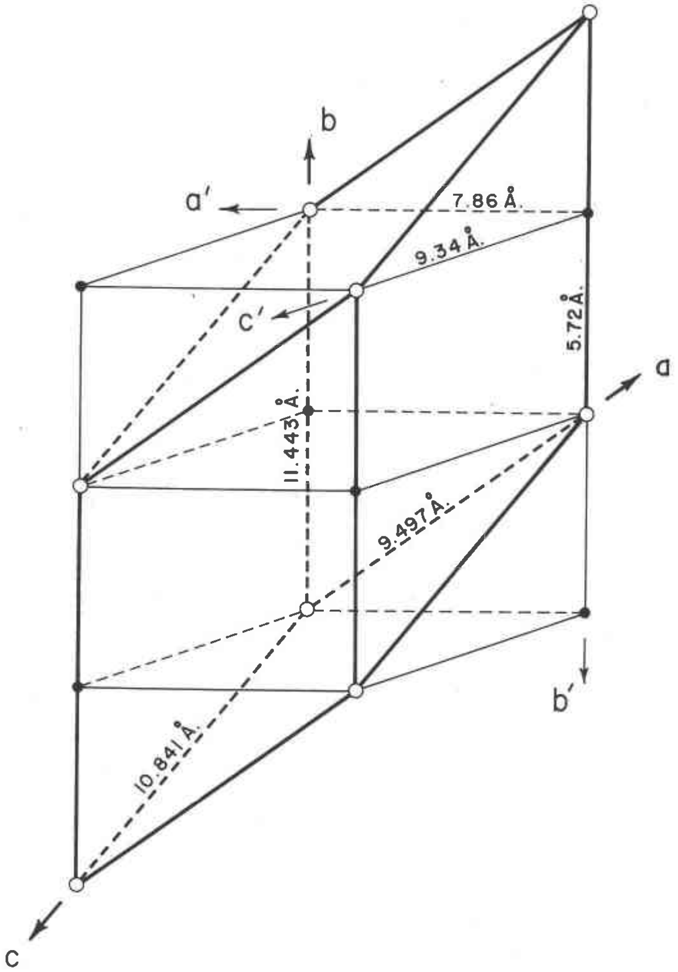

FIG. 2. Relationship between the triclinic cell (heavy lines) and the $P2_1/m$ pseudocell (light lines) of hemihedrite. Solid circles represent position of zinc; open circles locate position of center of Pb_3 couple.

shown in Figure 2. The triclinic axial directions are designated by unprimed letters and those of the $P2_1/m$ pseudocell by primed letters.

Fanfani and Zanazzi (1967) have shown that a series of minerals exists in which the structures are closely related to that of tsumebite. The series contains minerals in the space groups $P2_1/m$ and $P2_1/c$. The unit-cell dimensions and atomic positional parameters of tsumebite are compared with the dimensions of the $P2_1/m$ pseudocell and the positional parameters of comparable atoms of hemihedrite in Table 3. The structural similarity of the two minerals is emphasized by comparing their chemical compositions as follows:

Tsumebite	Cu_2	$(OH)_2$	Pb_4	$(SO_4)_2$	$(PO_4)_2$
Hemihedrite	$Zn_{0.5}Pb$	F	Pb_4	$(CrO_4)_2$	CrO_4SiO_4

The actual hemihedrite structure is shown in projection in Figure 3. It is apparent that the two structures are essentially the same and that hemihedrite should be considered as a member of Fanfani and Zanazzi's tsumebite structural series. Thus the series can be extended in the low symmetry direction at least to a structure of space group $P\bar{1}$.

The reduction of symmetry is caused by the small positional distortions which are evident in Table 3, and by the presence of a Si atom related by pseudosymmetry to a Cr atom and the Zn atom similarly related to two

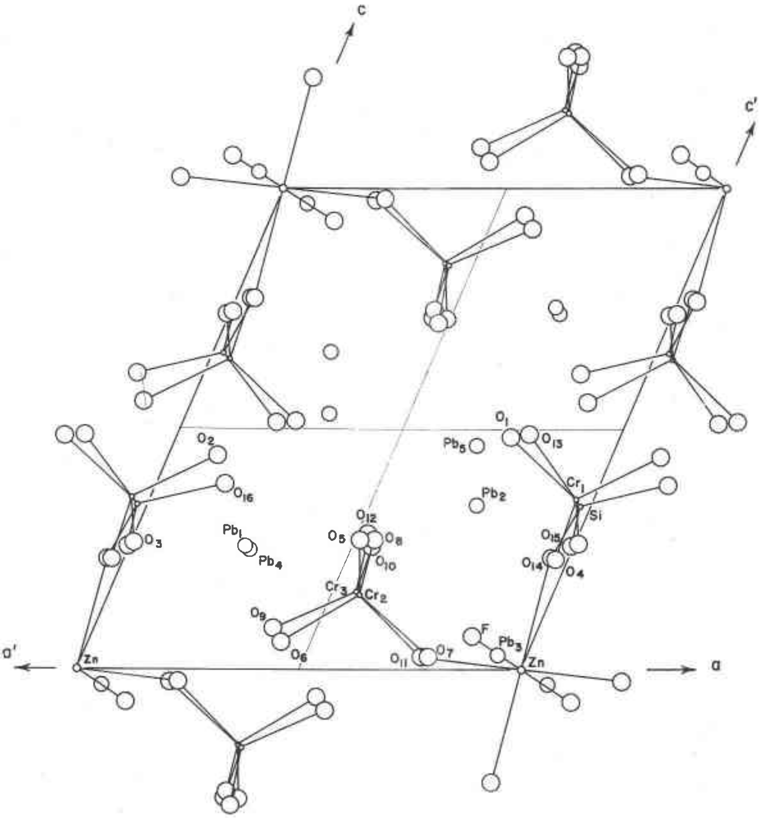

FIG. 3. The structure of hemihedrite viewed in projection from the $-b$ direction.

TABLE 4. INTERATOMIC DISTANCES AND ANGLES.

i *j*	d_{ij}	*i* *j*	d_{ij}	*i* *j*	d_{ij}	*i* *j* *k*	Angle (*ijk*)
Cr(1)–O(1)	1.65(3)Å	Pb(1)–O(4)	2.772Å	Pb(4)–O(10)	2.726Å	O(2)–Cr(1)–O(4)	110.3(1.5)°
Cr(1)–O(2)	1.68(4)	Pb(1)–O(5)	2.574	Pb(4)–O(11)	2.640	O(2)–Cr(1)–O(1)	109.6(1.5)
Cr(1)–O(3)	1.67(3)	Pb(1)–O(13)	2.320	Pb(4)–O(3)	2.790	O(2)–Cr(1)–O(3)	111.1(1.4)
Cr(1)–O(4)	1.64(3)	Pb(1)–O(15)	2.622	Pb(4)–O(14)	2.785	O(4)–Cr(1)–O(1)	111.8(1.4)
		Pb(1)–O(6)	3.109	Pb(4)–O(16)	2.462	O(4)–Cr(1)–O(3)	107.8(1.3)
Cr(2)–O(5)	1.69(3)	Pb(1)–O(9)	3.375	Pb(4)–O(6)	3.063	O(1)–Cr(1)–O(3)	106.1(1.3)
Cr(2)–O(6)	1.60(3)			Pb(4)–O(9)	3.309		
Cr(2)–O(7)	1.68(2)	Pb(2)–O(2)	2.677	Pb(4)–O(9)	3.329	O(7)–Cr(2)–O(5)	112.2(1.3)
Cr(2)–O(8)	1.68(2)	Pb(2)–O(12)	2.425	Pb(4)–O(2)	3.336	O(7)–Cr(2)–O(6)	107.1(1.3)
		Pb(2)–O(5)	2.767			O(7)–Cr(2)–O(8)	110.6(1.2)
Cr(3)–O(9)	1.60(2)	Pb(2)–O(3)	2.474	Pb(5)–O(5)	2.623	O(5)–Cr(2)–O(6)	110.2(1.2)
Cr(3)–O(10)	1.64(2)	Pb(2)–O(14)	2. 349	Pb(5)–O(10)	2.783	O(5)–Cr(2)–O(8)	105.3(1.2)
Cr(3)–O(11)	1.70(3)	Pb(2)–F	2.425	Pb(5)–O(13)	2.350	O(6)–Cr(2)–O(8)	111.5(1.2)
Cr(3) -O(12)	1.70(3)	Pb(2)–O(1)	3.115	Pb(5)–O(15)	2.674		
		Pb(2)–O(13)	3.395	Pb(5)–O(16)	2.285	O(12)–Cr(3)–O(9)	111.3(1.1)
Si–O(13)	1.63(3)			Pb(5)–O(8)	2.922	O(12–Cr(3)–O(10)	111.0(1.3)
Si-O(14)	1.64(3)	Pb(3)–O(7)	2.391	Pb(5)–O(8)	3.080	O(12)–Cr(3)–O(11)	110.3(1.2)
Si–O(15)	1.65(2)	Pb(3)–O(11)	2.649	Pb(5)–O(1)	3.304	O(9)–Cr(3)–O(10)	107.5(1.4)
Si-O(16)	1.62(3)	Pb(3)–O(3)	2.670	Pb(5)–O(4)	3.343	O(9)–Cr(3)–O(11)	109.1(1.3)
		Pb(3)–O(15)	2.393	Minimum Non		O(10)–Cr(3)–O(11)	107.5(1.4)
Zn–O(11)	2.17(3)	Pb(3)–F	2.352	bonded Distances			
Zn–O(14)	2.09(3)	Pb(3)–O(4)	3.099	Pb–Cr	3.367	O(13)–Si–O(14)	109.5(1.3)
Zn–F	2.05(3)	Pb(3)–O(4)	3.116	Pb–Zn	3.173	O(13)–Si–O(15)	103.1(1.2)
		Pb(3)–O(10)	3.133	Pb–Si	3.275	O(13)–Si–O(16)	113.0(1.3)
Pb(1)–O(7)	2.791	Pb(3)–O(9)	3.197	Zn-Si	3.440	O(14)–Si–O(15)	113.1(1.2)
Pb(1)–O(2)	2.796			Cr–Si	3.543	O(14)–Si–O(16)	105.0(1.3)
Pb(1)–O(12)	2.645	Pb(4)–O(1)	2.531	Cr–Cr	4.144	O(15)–Si–O(16)	113.4(1.2)
		Pb(4)–O(8)	2.527				
						O(11)–Zn–O(14)	91.5(1.0)
						O(11)–Zn–F	94.3(1.0)
						O(14)–Zn–F	96.6(1.0)

[a] Standard deviations given in parentheses are computed by the method of Cruickshank and Robertson (1953) and refer to the last digits. Atomic numbering is shown in Fig. 3.

Pb atoms (Pb_3 and its centric partner). The Zn and Pb_3 atoms are also the most important cause of the triclinic symmetry of the cell since in any $a'-c'$ plane the Zn alternates with the Pb_3 pair along the a' and c' axes as shown in Figure 2. Thus the larger triclinic cell is required to describe a periodic array.

Bond distances and angles are given in Table 4. The mean Cr–O distances for the three CrO_4 tetrahedra are 1.658, 1.659 and 1.661 Å and the O–Cr–O angles range from 105.3° to 112.2°. The mean Si–O distance is 1.637 Å and tetrahedral angles range from 103.1° to 113.4°. The Zn atom is octahedrally coordinated by two CrO_4 oxygens at 2.17 Å, two SiO_4 oxygens at 2.09 Å, and two fluorines at 2.05 Å. The angles are within 6.6° of 90° and the Zn octahedron is less distorted than that of Cu in tsumebite. The Pb–O distances are extremely variable ranging upward from 2.29 Å, and the coordination is also variable and depends upon the distance taken as a maximum for a Pb–O bond.

DISCUSSION

As pointed out, Fanfani and Zanazzi (1967) have recognized a series of five secondary lead minerals which have the same basic structure. The addition of hemihedrite to this group extends the series on the low symmetry side. The structure of hemihedrite also suggests that the series may be extendable on the high symmetry side since it contains both $P2_1/m$ and $C2/m$ pseudosymmetries. If some latitude is allowed in the boundaries of the series, the mineral dolerophanite appears to be a good example of the high symmetry extension.

Dolerophanite has the cell dimensions $a = 9.39$ Å, $b = 6.30$ Å, $c = 7.62$ Å, and $\beta = 122.7°$ and space group $C2/m$ (Palache, Berman, and Frondel, 1951). For comparison, the unit cell of tsumebite converted to the orientation required for the symmetry $C2/m$ as shown in Figure 1c, gives the cell dimensions $a'' = 9.35$ Å, $b'' = 5.80$ Å, $c'' = 7.85$ Å, and $\beta'' = 120.0°$. The structure of dolerophanite was determined by Flügel-Kahler in 1963. Figure 4 shows the structure of dolerophanite in projection down the $+b$ axis. Cu_2 is five coordinated, but bonds involving this atom have been omitted for clarity. A comparison of Figure 4 with Figure 1 shows the obvious similarity between the dolerophanite structure and that of tsumebite, as well as the differences. If dolerophanite is added to the tsumebite structural series, the series can be extended not only toward higher symmetry, but also to include a mineral which does not contain

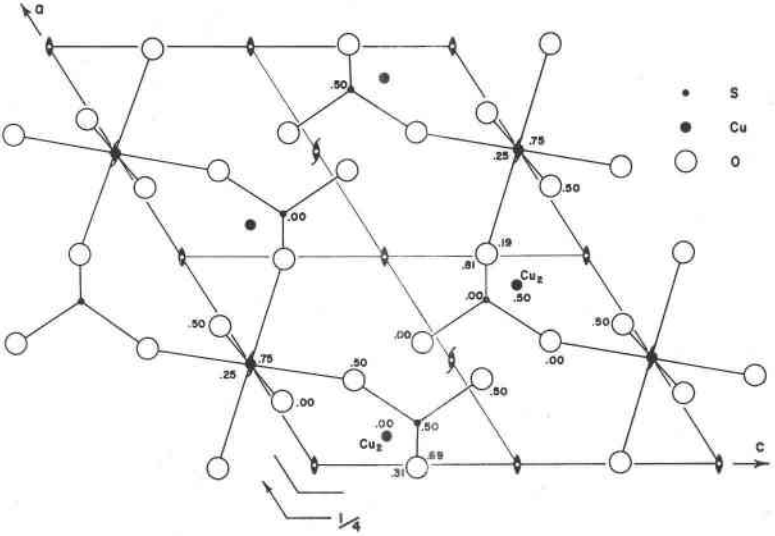

FIG. 4. The structure of dolerophanite in projection down the $+b$ axis. Bonds involving Cu_2 are omitted for clarity. Drawn from Flügel-Kahler (1963) coordinates.

lead and to include substances with cation:tetrahedral anion ratios ranging from 6:4 to 8:4.

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