THE CRYSTAL STRUCTURE OF WICKENBURGITE, $Pb_3CaAl[AlSi_{10}O_{27}](H_2O)_3$, A SHEET STRUCTURE

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ABSTRACT

The crystal structure of wickenburgite, $Pb_3CaAl_2Si_{10}O_{27}(H_2O)_3$, a 8.560(3), c 20.190(6) Å, V 1281.2(9) Å^3, space group $P31c$, Z = 2, has been solved by direct methods and refined to an R index of 3.1% based on 1042 unique reflections measured with MoKα X-radiation on an automated four-circle diffractometer. There is one unique Pb^{2+} position coordinated by eight anions, four in the range 2.30–2.53 Å and four in the range 2.97–3.36 Å; bond-valence considerations indicate that all of these interactions must be considered to be bonds. The four close anions all lie on one side of the Pb^{2+} cation, indicating stereoactive lone-pair behavior. There are six distinct Si positions, all tetrahedrally coordinated by oxygen atoms, one Ca position octahedrally coordinated by three oxygen atoms and three (H_2O) groups, and two distinct Al positions, one octahedrally coordinated and the other tetrahedrally coordinated. Two sheets of stoichiometry $[CaSi_5\phi_{17}]$ and $[AlSi_5\phi_{15}]$ link by sharing tetrahedron vertices to form a thick slab orthogonal to [001], and further intrasheet linkage is provided by hydrogen bonding. Intercalated between these slabs are interrupted sheets of corner- and edge-sharing $(Pb\phi_8)$ and $(Al\phi_6)$ polyhedra. The strong bonding within the thick slabs and the weaker interslab linkage provided by the $^{[6]}$Al and $^{[8]}$Pb account for the {001} cleavage of wickenburgite.

Keywords: wickenburgite, crystal structure, lead, stereoactive lone-pair.

SOMMAIRE

Nous avons résolu la structure cristalline de la wickenburgite, $Pb_3CaAl_2Si_{10}O_{27}(H_2O)_3$, a 8.560(3), c 20.190(6) Å, V 1281.2(9) Å^3, groupe spatial $P31c$, Z = 2, par méthodes directes jusqu'à un résidu R de 3.1% en utilisant 1042 réflexions uniques, mesurées avec rayonnement MoKα et un diffractomètre automatisé. Il y a une position unique occupée par le Pb^{2+}, à coordinence huit, quatre anions étant situés à une distance entre 2.30 et 2.53 Å, et quatre autres entre 2.97 et 3.36 Å. Les considérations des valences de liaisons montrent que toutes ces interactions doivent être considérées de vraies liaisons. Les quatre liaisons les plus courtes sont regroupées sur un même côté du cation Pb^{2+}, indication de la stéréoactivité d'une paire d'électrons isolés. Il y a six positions distinctes de Si; dans tous les cas, il s'agit d'une coordinence tétraédrique avec des atomes d'oxygène. Le calcium montre une coordinence octaédrique avec trois atomes d'oxygène et trois groupes H_2O, et l'aluminium occupe un site à coordinence octaédrique et un autre à coordinence tétradrique. Deux feuillets de stoechiométrie $[CaSi_5\phi_{17}]$ et $[AlSi_5\phi_{15}]$ sont liés par partage de sommets de tétraèdres pour former une plaquette perpendiculaire à [001]. Des liaisons hydrogène complètent la connexion entre les feuillets. En intercalation entre ces plaquettes sont des feuillets interrompus de polyèdres $(Pb\phi_8)$ et $(Al\phi_6)$ à coins et à arêtes partagés. Les liaisons fortes à l'intérieur des plaquettes et les liaisons plus faibles entre celles-ci, fournies par $^{[6]}$Al et $^{[8]}$Pb, rendent compte du clivage {001} de la wickenburgite.

(Traduit par la Rédaction)

Mots-clés: wickenburgite, structure cristalline, plomb, paire d'électrons isolés stéréoactive.

INTRODUCTION

Wickenburgite was first described by Williams (1968) from several prospects near Wickenburg, Maricopa County, Arizona. It is an oxide-zone mineral associated with phoenicochroite, mimetite, cerussite, crocoite, hemihedrite, ajoite, vauquelinite, descloizite, laumontite, and shattuckite. The formula was given as $Pb_3CaAl_2Si_{10}O_{24}(OH)_6$, but the presence of (OH) as distinct from (H_2O) was only assumed. Penna & Giese (1969) proposed a structure for wickenburgite based on the space group $P\bar{6}2c$, but a detailed description was not published. As part of a general study (by LAG) of the crystal chemistry of the lead oxysalt minerals, the crystal structure of wickenburgite was examined. Fortuitously, the structure was solved independently at the University of British Columbia and the University of Manitoba; a combined description is presented here.

EXPERIMENTAL

The crystals used in this study are from the Potter–Cramer mine, near Wickenburg, Arizona. Crystals of wickenburgite are platy on (001) and have variable properties. In cross-polarized light, some crystals show uniform extinction down [001], whereas other crystals show significant birefringence and complex twinning, both secotoral and lamellar. In convergent polarized light, these crystals are biaxial, with $2V$ values of up to 10°. The crystal used here for the collection of the X-ray intensity data shows uniform extinction down [001]. The crystal was mounted on a Nicolet $R3m$ automated four-circle diffractometer, and cell dimensions (Table 1) and intensity data were

TABLE 1. MISCELLANEOUS INFORMATION: WICKENBURGITE

	UBC	UMAN
$a(\text{Å})$	8.560(3)	8.546(1)
c	20.190(6)	20.168(4)
$V(\text{Å}^3)$	1281.2(9)	1275.6(4)
Sp.Gr.	$P31c$	
Cell content	$2[Pb_3CaAl(AlSi_{10}O_{27})(H_2O)_3]$	
Rad/mono	MoKα/Graphite	
Total I	2973	2957
R(azimuthal)	7.2 → 2.6 %	11.8 → 2.3 %
R(merge) TRIG	2.1%	2.4%
HEX	3.9%	7.6%
Total $|F_o|$	861	1109
$|F_o| > 4\sigma(F)$	833	1042
Final R(obs)	5.0%	3.1%
Final wR(obs)	5.6%	3.4%

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^x, w = 1$

collected according to the procedure of Hawthorne & Groat (1985). In the following text, the data for the UBC procedure are given, followed in parentheses by the data for the UMAN procedure. A total of 2973(2957) reflections were measured over two(two) asymmetric units out to a maximum 2θ of 60°. Eleven strong reflections uniformly distributed with regard to 2θ were measured at 10° intervals of ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0 to 350°. These data were used to calculate a thin-plate empirical absorption-correction with a 10° glancing angle, the R(azimuthal) index being reduced from 7.2(11.8)% to 2.6(2.3)%; this correction was then applied to the whole data-set. As noted above, several authors have reported wickenburgite as hexagonal. We tested the possible Laue-group symmetries (compatible with the existence of a vertical c-glide, as indicated by the symmetrically absent reflections) by comparing the merging R(symmetric) values. For the Laue group $6/mmm$, four asymmetric units of data were merged to give R(symmetric) values of 3.9%(7.6%); for the Laue group $3m$, two asymmetric units were merged to give R(symmetric) values of 2.1%(2.4%). We conclude that the Laue group is $3m$. The data also were corrected for Lorentz, polarization, and background effects, averaged and reduced to structure factors. Of the 861(1109) unique reflections, 833(1042) were classed as observed $[|F_O| > 5\sigma(F)]$.

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with anomalous dispersion coefficients, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). All calculations were done with the program system SHELXTL PC Plus. The R indices are of the form given in Table 1 and are expressed as percentages. Inspection of the diffracted intensities showed that the Laue group is $3m$, rather than $6/mmm$ as required by the space groups $P6_3/mmc$ and $P\bar{6}2c$ assigned by Williams (1968) and Penna & Giese (1969), respectively. The distribution of E values indicated the absence of a center of symmetry, and systematic extinctions showed the presence of a vertical c-glide. The structure was solved by direct methods in the space group $P31c$. The solution with the maximum figure of merit revealed most of the cation positions; the remaining cation and the anion positions were located on difference-Fourier maps, and the structure was refined to ~8% for an isotropic displacement-factor model. Conversion to anisotropic displacement factors for the Pb position resulted in convergence at an R index of 5.0(3.1)%. Attempts to refine anisotropic displacement factors for the other atoms showed no improvement. This results from problems associated with the very high absorption for this mineral, together with the fact that wickenburgite

TABLE 2. ATOMIC PARAMETERS* FOR WICKENBURGITE

Site	Position	x	y	z	U_{eq}+
Pb	6c	0.2919(1)	0.2586(1)	0	12(1)
		0.2920(1)	0.2586(1)	0	11(1)
Ca	2a	0	0	0.1465(6)	22(2)
		0	0	0.1462(3)	13(1)
Al(1)**	2b	2/3	1/3	0.4852(6)	10(3)
		2/3	1/3	0.4854(4)	12(2)
Al(2)	2b	1/3	2/3	0.3678(6)	4(3)
		1/3	2/3	0.3633(4)	6(1)
Si(1)	2b	2/3	1/3	0.1339(7)	13(3)
		2/3	1/3	0.1306(4)	7(1)
Si(2)	2a	0	0	0.3731(7)	18(3)
		0	0	0.3749(4)	10(1)
Si(3)	2b	2/3	1/3	0.2889(7)	13(2)
		2/3	1/3	0.2875(4)	9(1)
Si(4)	2b	1/3	2/3	0.2022(8)	16(2)
		1/3	2/3	0.1983(4)	10(1)
Si(5)	6c	0.3871(10)	0.0591(10)	0.3782(5)	18(2)
		0.3833(5)	0.0599(5)	0.3760(2)	9(1)
Si(6)	6c	0.0618(11)	0.4121(11)	0.0982(5)	19(2)
		0.0596(5)	0.4139(6)	0.0965(2)	8(1)
O(1)	2b	1/3	2/3	0.280(2)	18(7)
		1/3	2/3	0.278(1)	13(4)
O(2)	2b	2/3	1/3	0.214(3)	34(9)
		2/3	1/3	0.209(1)	21(4)
O(3)	2a	0	0	0.456(3)	41(11)
		0	0	0.455(1)	8(3)
O(4)	6c	0.145(3)	0.501(3)	0.172(1)	26(5)
		0.150(2)	0.493(2)	0.169(1)	20(3)
O(5)	6c	0.489(3)	0.156(3)	0.107(1)	24(5)
		0.487(1)	0.159(1)	0.105(1)	15(2)
O(6)	6c	0.512(3)	0.137(3)	0.316(1)	23(5)
		0.519(1)	0.135(1)	0.314(1)	12(2)
O(7)	6c	0.134(2)	0.571(3)	0.043(1)	20(4)
		0.126(1)	0.569(1)	0.041(1)	10(2)
O(8)	6c	0.197(4)	0.035(3)	0.346(1)	36(6)
		0.191(2)	0.031(2)	0.347(1)	18(2)
O(9)	6c	0.087(3)	0.241(3)	0.075(1)	24(5)
		0.083(1)	0.243(1)	0.075(1)	7(2)
O(10)+	6c	0.229(4)	0.197(4)	0.221(2)	45(7)
		0.229(2)	0.197(2)	0.218(1)	27(3)
O(11)	6c	0.453(2)	0.214(2)	0.435(1)	15(3)
		0.447(1)	0.211(1)	0.436(1)	12(2)
O(12)	6c	0.505(2)	0.644(2)	0.400(1)	11(4)
		0.509(1)	0.639(1)	0.397(1)	16(2)

* Upper values: UBC; lower values: UMAN; + $U_{eq} = U_{eq} \times 10^3$
** Al(1); UBC: 0.97 Al + 0.03 Fe; UMAN: 0.81 Al + 0.19 Fe
+ O(10) = H_2O

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN WICKENBURGITE

	UBC	UMAN		UBC	UMAN
Pb–O(3)a	2.53(2)	2.53(1)	Si(2)–O(3)	1.68(6)	1.62(2)
Pb–O(5)	3.13(3)	3.06(1)	Si(2)–O(8),e,j x3	1.65(3)	1.62(2)
Pb–O(7)b	2.42(2)	2.36(1)	<Si(2)–O>	1.66	1.62
Pb–O(9)	2.26(3)	2.30(1)			
Pb–O(9)j	2.99(2)	2.97(1)	Si(3)–O(2)	1.51(6)	1.59(3)
Pb–O(11)k	2.46(2)	2.43(1)	Si(3)–O(6),d,f x3	1.63(2)	1.62(1)
Pb–O(12)k	3.35(2)	3.36(1)	<Si(3)–O>	1.60	1.61
Pb–O(12)l	3.15(1)	3.20(1)			
<Pb–O>	2.79	2.78	Si(4)–O(1)	1.58(4)	1.61(2)
			Si(4)–O(4),b,c x3	1.64(2)	1.64(1)
Ca–O(9),e,j x3	2.32(2)	2.32(1)	<Si(4)–O>	1.63	1.63
Ca–O(10),e,j x3	2.37(3)	2.34(1)			
<Ca–O>	2.35	2.33	Si(5)–O(6)	1.57(2)	1.60(1)
			Si(5)–O(8)	1.67(3)	1.64(2)
Al(1)–O(7)g,h,i x3	1.88(2)	1.90(1)	Si(5)–O(11)	1.63(2)	1.64(1)
Al(1)–O(11),d,f x3	1.88(2)	1.91(1)	Si(5)–O(12)d	1.64(2)	1.60(1)
<Al(1)–O>	1.88	1.91	<Si(5)–O>	1.63	1.62
Al(2)–O(1)	1.77(4)	1.72(2)	Si(6)–O(4)	1.66(3)	1.63(1)
Al(2)–O(12),b,c x3	1.71(2)	1.77(1)	Si(6)–O(5)e	1.64(2)	1.64(1)
<Al(2)–O>	1.73	1.76	Si(6)–O(7)	1.62(2)	1.61(1)
			Si(6)–O(9)	1.65(3)	1.63(1)
Si(1)–O(2)	1.62(6)	1.58(3)	<Si(6)–O>	1.64	1.63
Si(1)–O(5),d,f x3	1.61(2)	1.60(1)			
<Si–O>	1.61	1.60	Si(3)–O(6)–Si(5)	138(2)	135(1)
			Si(2)–O(8)–Si(5)	138(2)	138(1)
Si(4)–O(1)–Al(2)	180	180	Si(5)–O(12)–Al(2)	141(2)	141(1)
Si(1)–O(2)–Si(3)	180	180			
Si(4)–O(4)–Si(6)	138(2)	138(1)			
Si(1)–O(5)–Si(6)	156(2)	153(1)			

Symmetry operations: a: x, y, z–½; b: ȳ+1, x–y+1, z; c: x̄+y, x̄+1, z; d: ȳ+1, x–y, z; e: ȳ, x–y, z; f: x̄+y+1, x̄+1, z; g: y, x, z+½; h: x–y+1, ȳ+1, z+½; i: x̄+1, x̄+y, z+½; j: x̄+y, x̄, z; k: y, x, z–½; l: x̄+1, x̄+y, z–½

DESCRIPTION OF THE STRUCTURE: CATION COORDINATION

Si positions

There are six distinct Si positions, all tetrahedrally coordinated by oxygen anions. Four of these sites are at special positions (Table 2), and the remaining two occupy the general position. Some of the tetrahedra are quite distorted, and the Si–O distances range from 1.58 to 1.64 Å. The precision of the bond lengths is quite low (0.01–0.03 Å), primarily because of absorption and twinning problems; hence, although some Si–O values lie outside the range normally observed in silicates (e.g., Si(3)–O(2) = 1.51(6) Å, Table 3), the difference is not statistically significant because of the low precision. Moreover, the short and long Si–O bonds do seem to correlate with the bond-valence requirements imposed by the basic structural connectivity (Table 4).

Al positions

There are two distinct Al sites, both at special positions (Table 2) on a three-fold axis. Al(1) is coordinated by six anions in a fairly regular octahedral arrangement. Site-scattering refinement indicates the presence of a small amount of a stronger scatterer of X rays (assumed to be Fe^{3+}); the resulting site-population is 0.81 Al + 0.19 Fe^{3+}. Al(2) is coordinated

is not hexagonal or trigonal at room temperature, as shown by the complex twinning. Positional coordinates and equivalent isotropic displacement factors are given in Table 2, selected interatomic distances and angles in Table 3, and a bond-valence analysis is given in Table 4. Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 4. BOND–VALENCE* CALCULATION (v.u.) FOR WICKENBURGITE

	Pb	Ca	Al(1)	Al(2)	Si(1)	Si(2)	Si(3)	Si(4)	Si(5)	Si(6)	Σ
O(1)				0.82				1.06			1.88
O(2)					1.15		1.12				2.27
O(3)	0.31×3→					1.03					1.96
O(4)								0.97×3↓		1.00	1.97
O(5)	0.11				1.09×3↓					0.97	2.17
O(6)							1.03×3↓		1.09		2.12
O(7)	0.45		0.51×3↓							1.06	2.02
O(8)							1.03×3↓		0.97		2.00
O(9)	0.52	0.35×3↓								1.00	2.00
	0.13										
O(10)		0.33×3↓									0.33
O(11)	0.39		0.50×3↓						0.97		1.86
O(12)	0.08			0.72×3↓					1.09		1.95
	0.06										
Σ	2.06	2.05	3.02	2.97	4.41	4.11	4.20	3.97	4.12	4.03	

* calculated with the curves of Brown (1981) for the UMAN distances

by four anions in a fairly regular tetrahedral arrangement.

Ca position

There is one unique Ca position, the special Wyckoff position $2a$ on a three-fold axis. This position is surrounded by six anions; three O(9) are O^{2-}, and three O(10) are H_2O anions, at approximately equal distances from the central cation ($\sim$2.35 Å), in agreement with that expected for octahedrally coordinated Ca.

Pb position

There is one unique Pb position in wickenburgite, a general position with the z coordinate fixed at zero to fix the origin of the unit cell. The Pb atom is surrounded by eight anions between 2.26 and 3.35 Å. These Pb–ϕ (ϕ: undefined anion) distances fall into two groups: four short bonds with 2.26 < Pb–ϕ < 2.53 Å, and four long contacts with 2.99 < Pb–ϕ < 3.35 Å (UMAN results in Table 3). The four short bonds occur on one side of the central cation (Fig. 1), and all involve nonbridging anions of the tetrahedral groups; the four long contacts occur on the other side of the central cation, and most involve bridging anions of the tetrahedral groups. This type of arrangement is typical of Pb^{2+} with a stereoactive lone-pair of electrons: where stereoactive, the lone pair occupies a $5p$ (rather than a $6s$) orbital and projects into the space formed by the shift of the cation away from the central position within its coordination polyhedron.

Should the long Pb–ϕ contacts be considered as

bonds? With regard to the bond-valence sum around Pb (Table 4), the situation is not definitive. However, these weak interactions are needed if the anion sums are to be satisfactory, as omission of the two longest Pb–O(12) bonds listed in Table 3 (3.15 and 3.35 Å) results in a bond-valence sum of 1.81 v.u. around O(12). Thus all eight Pb–ϕ distances listed in Table 3 should be considered as bonds.
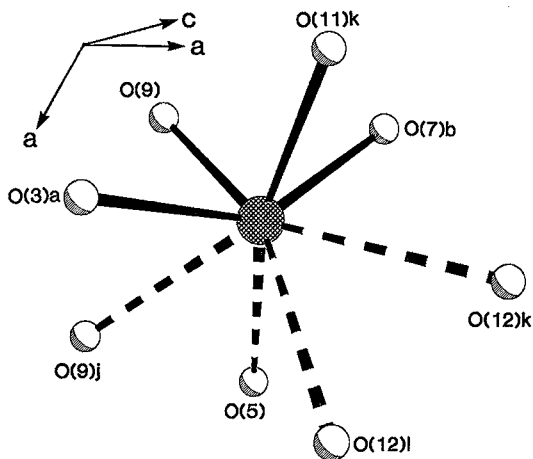

FIG. 1. The coordination polyhedron around Pb in wickenburgite; short bonds are marked by full lines, long bonds are marked by broken lines. The Pb atom is cross-hatched, and the anions are partly shaded circles.

DESCRIPTION OF THE STRUCTURE: CONNECTIVITY OF POLYHEDRA

The elegance of Nature's patterns never ceases to amaze, and wickenburgite is no exception in this regard. The Si(1), Si(4) and Si(6) tetrahedra combine with Ca octahedra (Fig. 2a) to form a corner-sharing sheet of six-membered rings of polyhedra, formally denoted by the net symbol 6^3. Smith (1977) has considered the distinct types of 6^3 nets with regard to the direction in which the constituent tetrahedra point (u: up, or d: down); this is an important factor in the linkage of such two-dimensional nets in the third dimension. The net of Figure 1a is different from those considered by Smith (1977) in that one of the nodes in each six-membered ring is occupied by an octahedron rather than a tetrahedron. However, the up–down question is still relevant; the only difference is that a
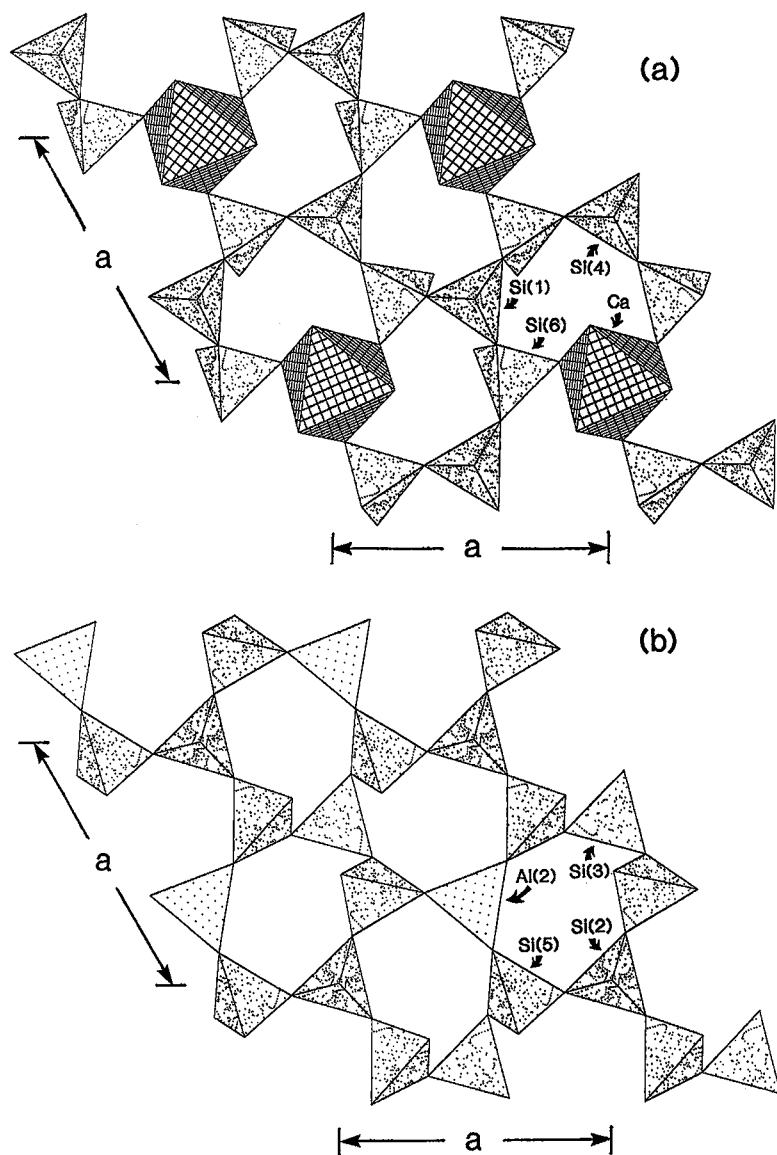
FIG. 2. Sheet elements of the structure of wickenburgite, projected along [001]: (a) the [CaSi$_5\phi_{17}$] sheet; (b) the [AlSi$_5\phi_{15}$] sheet. The (Siϕ_4) tetrahedra are random-dot shaded, the (Caϕ_6) octahedra are 4^4-net shaded, and the (Alϕ_4) tetrahedra are regular-dot shaded.
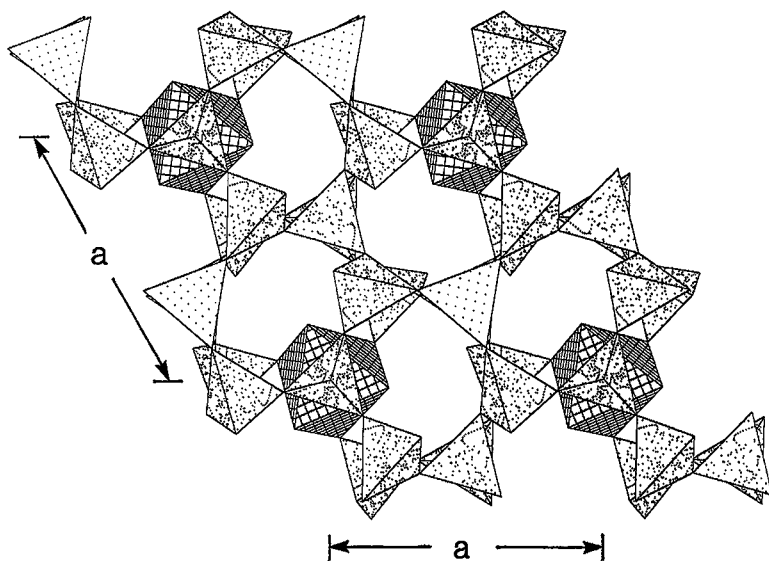
FIG. 3. The slab of tetrahedra in wickenburgite, projected along [001]; legend as in Fig. 2.

tetrahedron has one free vertex to point up or down, whereas the octahedron has three free vertices that can point in various combinations of up and down. The net in Figure 2a has the configuration *dudud*(3*u*), and the stoichiometry [CaSi$_5\phi_{17}$].

The Si(2), Si(3) and Si(5) tetrahedra combine with the Al(2) tetrahedron to form a second sheet (Fig. 2b). Again, it is based on a 6^3 net, and is an [AlSi$_5\phi_{15}$] net with the configuration *ududuu*. The two sheets of

Figure 2 link together in the *c* direction by sharing opposing tetrahedral vertices to form a thick slab (Fig. 3). As is apparent in this view, the two 6^3 sheets of the slab essentially overlie each other, and the linkage between the two sheets occurs through tetrahedra that lie on three-fold axes; hence the *T–O–T* bridging angles are constrained to be 180°, unlike the *T–O–T* bridging angles within each sheet, most of which cluster around 138° (Table 3).
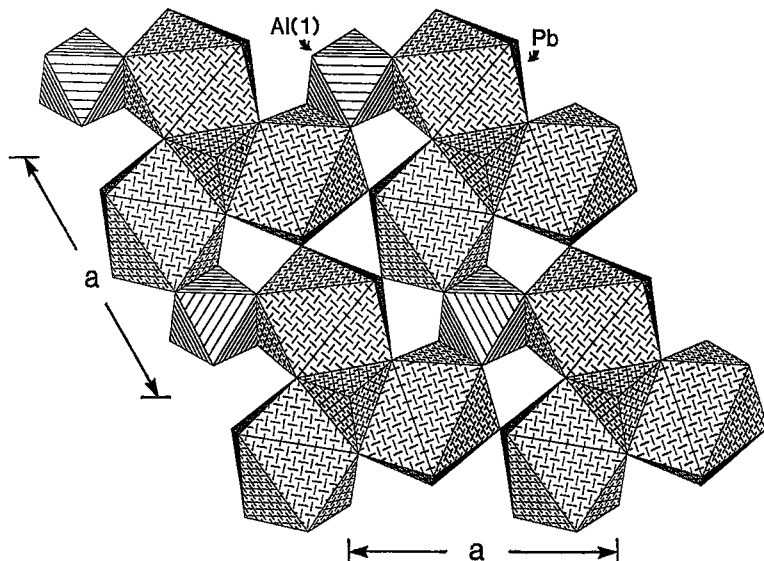

FIG. 4. The (Pbϕ_8)–(Alϕ_6) interrupted sheet of polyhedra in wickenburgite; the (Pbϕ_8) polyhedra are orthogonal-dash shaded, and the (Alϕ_6) octahedra are line-shaded.
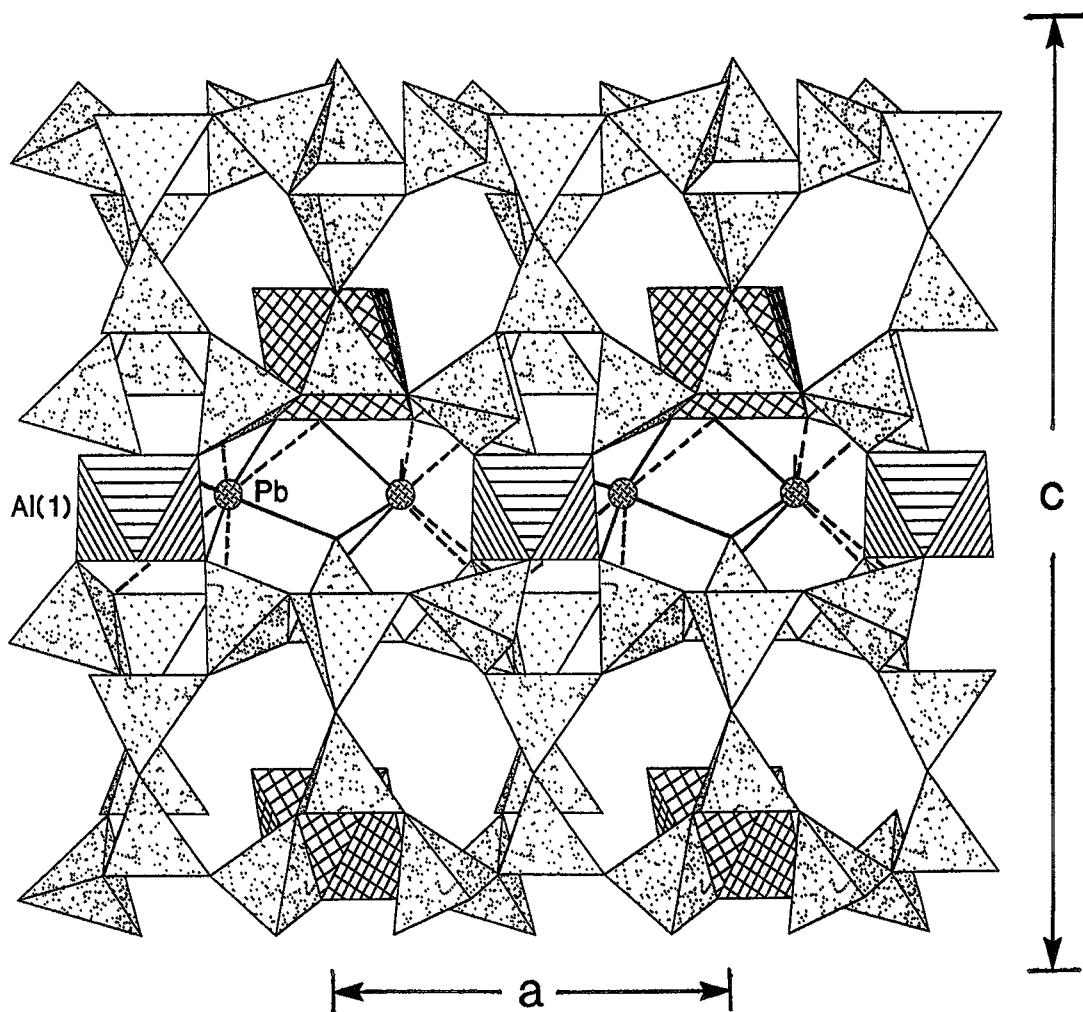
FIG. 5. The wickenburgite structure viewed orthogonal to [001]; legend as in Figs. 2 and 4. Note the alternation of slabs of tetrahedra and sheets of (Pbϕ_8) and (Alϕ_6) polyhedra.

On either side of the slab of tetrahedra are layers of (Pbϕ_8) polyhedra and Alϕ_6 octahedra (Fig. 4). The (Alϕ_6) octahedra share edges with the (Pbϕ_8) polyhedra, and the (Pbϕ_8) polyhedra share both edges and corners to form an interrupted sheet of cation and anion polyhedra.

The constitution of the entire structure is shown in Figure 5. Thick slabs of tetrahedra [+ (Caϕ_6) octahedra] alternate with sheets of (Pbϕ_8) and (Alϕ_6) polyhedra to produce a layered structure. The strong bonding within the slabs of tetrahedra contrasts with the relatively weak bonding between the slabs, and this accounts for the {001} cleavage observed in wickenburgite.

Hesse & Liebau (1993) reported the solution of the crystal structure of wickenburgite in the space group $P\bar{6}2c$; these findings were published in the form of an abstract, and hence not many details are given. However, there is sufficient information to determine that the structures and the materials are significantly different. First, the averaging statistics for different Laue groups indicate that our data are far more compatible with trigonal rather than hexagonal Laue symmetry. Secondly, our structure *cannot* have $P\bar{6}2c$ symmetry. The linkage of the tetrahedra seems to be the same in both structures. However, in our structure, Ca lies in the plane of the sheet of tetrahedra, and is octahedrally coordinated. In the structure of Hesse &

Liebau (1993), Ca is described as an interlayer cation with trigonal prismatic coordination. If Ca in our structure is displaced through one face of its coordinating octahedron into an interlayer position, it then has trigonally prismatic coordination, and requires re-arrangement of the Pb atoms. Possibly, there is some kind of (probably first-order) phase transition between the two structures. Certainly, the formula reported by Hesse & Liebau (1993), $H_2Pb_3CaAl_2Si_{10}O_{28}(H_2O)_3$, differs significantly from that reported here: $Pb_3CaAl_2Si_{10}O_{27}(H_2O)_3$, and Hesse & Liebau (1993) reported the presence of "Si–OH" groups. Thus we conclude that the crystals and their structures are somewhat different.

CHEMICAL FORMULA .

Inspection of the bond-valence table (Table 4) shows that the sum of the incident bond-valence around the O(10) anion is 0.33 v.u., whereas the corresponding sums around all the other anions are close ($\geq$ 1.86 v.u.) to 2.0 v.u., the ideal value for the O^{2-} anion. This indicates that the O(10) anion is actually (H$_2$O), and thus the formula of wickenburgite must be rewritten as $Pb_3CaAl_2Si_{10}O_{27}(H_2O)_3$.

HYDROGEN BONDING

The (H$_2$O) group [the O(10) anion] is strongly bonded (bond valence = 0.33 v.u.) to Ca, and hence must participate in a hydrogen-bonding scheme if the bond-valence requirements of the H atoms are to be satisfied. Inspection of the possible donor–acceptor distances around the O(10) site shows the O(4) and O(8) anions as hydrogen-bond acceptors. The resulting scheme is illustrated in Figure 6. There is one
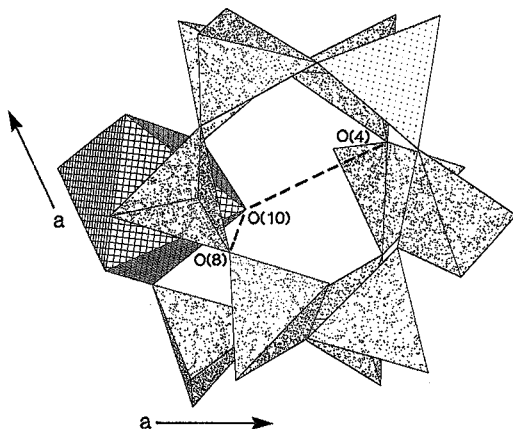
hydrogen bond from O(10) across a six-membered ring of polyhedra to the O(4) anion, and another hydrogen bond from O(10) to O(8) in the adjacent slab of tetrahedra. The hydrogen bonding thus provides additional cohesion within the slab of tetrahedra in wickenburgite.

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FIG. 6. The proposed scheme of hydrogen bonding in wickenburgite.