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LOCAL Pb^{2+}–□ DISORDER IN THE CRYSTAL STRUCTURE OF JAMESITE, $Pb_2ZnFe^{3+}_2(Fe^{3+}_{2.8}Zn_{1.2})(AsO_4)_4(OH)_8[(OH)_{1.2}O_{0.8}]$, AND REVISION OF THE CHEMICAL FORMULA

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ABSTRACT

The crystal structure of jamesite, $Pb^{2+}_2\,Zn\,Fe^{3+}_2\,(Fe^{3+}_{2.8}\,Zn_{1.2})\,(AsO_4)_4\,(OH)_8\,[(OH)_{1.2}O_{0.8}]$, triclinic, *a* 5.583(1), *b* 9.542(2), *c* 10.219(2) Å, α 109.81(2), β 90.57(2), γ 97.71(2)°, *V* 506.6(2) $Å^3$, space group $P\bar{1}$, $Z = 1$, $D_{calc.} = 5.084$ g/cm^3, has been solved by direct methods and refined to an *R* index of 4.9% based on 1609 observed (5σ) reflections measured with Mo*K*α X-radiation. There is one unique *Pb* site that is split into two subsites *Pb*(1*a*) and *Pb*(1*b*) with a separation of 0.59(2) Å and both occupied by lone-pair-stereoactive Pb^{2+}. There are two unique *As* sites both occupied by As^{5+} in tetrahedral coordination. There are five unique *M* sites occupied by Fe^{3+} and Zn; *M*(1) = Zn, *M*(2) ≈ *M*(3) = Fe^{3+}, *M*(4) ≈ *M*(5) = (Fe^{3+},Zn). Bond-valence analysis shows four anions to be (OH) and one anion to be (OH,O), leading to the revised formula given above. The polyhedra link together to form two types of heteropolyhedral chain: the *A* chain = $[M_3(TO_4)_4\phi_6]$, as found in kotoite, lindgrenite and frankhawthorneite, and the *B* chain = $[M(TO_4)_2\phi_2]$, as found in the minerals of the krohnkite, talmessite and fairfieldite groups. These chains link through an additional octahedron to form a sheet, and these sheets stack along [010] to form a heteropolyhedral framework. The Pb^{2+} cations occur in interstices of this framework. The splitting of the *Pb* site is driven by local bond-valence requirements around the O(7) anion: where OH(5) = (OH), the O(7) anion receives a H-bond; where OH(5) = O^{2-}, the O(7) anion does not receive a H-bond, and the Pb^{2+} cation is displaced toward O(7), forming a *Pb*–O(7) bond and compensating for the absence of a H-bond.

Keywords: jamesite, crystal structure, arsenate, lead mineral, Tsumeb, Namibia.

SOMMAIRE

Nous avons résolu la structure cristalline de la jamesite, $Pb^{2+}_2\,Zn\,Fe^{3+}_2\,(Fe^{3+}_{2.8}\,Zn_{1.2})\,(AsO_4)_4\,(OH)_8\,[(OH)_{1.2}O_{0.8}]$, triclinique, *a* 5.583(1), *b* 9.542(2), *c* 10.219(2) Å, α 109.81(2), β 90.57(2), γ 97.71(2)%, *V* 506.6(2) $Å^3$, groupe spatial $P\bar{1}$, $Z = 1$, $D_{calc.} =$ 5.084 g/cm^3, par méthodes directes, et nous l'avons affiné jusqu'à un résidu *R* de 4.9% en utilisant 1609 réflexions observées (5σ) et mesurées avec rayonnement Mo*K*α. Il y a un seul site *Pb* que l'on sépare en deux sous-sites *Pb*(1*a*) et *Pb*(1*b*), les deux séparés de 0.59(2) Å, et occupés par un atome de Pb^{2+} stéréoactif à cause d'une paire d'électrons isolés. Il y a deux sites uniques *As*, les deux contenant As^{5+} en coordinence tétraédrique. La structure contient cinq sites *M* uniques occupés par le Fe^{3+} et le Zn; *M*(1) = Zn, *M*(2) ≈ *M*(3) = Fe^{3+}, *M*(4) ≈ *M*(5) = (Fe^{3+},Zn). Une analyse des valences de liaison montre que quatre anions sont des groupes (OH), et un anion serait représenté par (OH,O), ce qui mène à la formule révisée citée ici. Les polyèdres sont liés et forment deux types de chaînes hétéropolyédriques: la chaîne *A* = $[M_3(TO_4)_4\phi_6]$, comme on en trouve dans la kotoïte, la lindgrenite et la frankhawthornéite, et la chaîne *B* = $[M(TO_4)_2\phi_2]$, comme on en trouve dans les minéraux des groupes de la krohnkite, la talmessite et la fairfieldite. Ces chaînes sont liées par un octaèdre de plus pour former un feuillet, et ces feuillets sont empilés le long de [010] pour former une trame hétéropolyédrique.Les cations Pb^{2+} sont situés dans les interstices de cette trame. La division du site *Pb* résulte des exigeances des valences de liaison autour de l'anion O(7): là où OH(5) est un groupe (OH), l'anion O(7) reçoit une liaison H; là où OH(5) est une atome O^{2-}, l'anion O(7) ne reçoit pas de liaison H, et le cation Pb^{2+} se déplace vers O(7) pour former une liaison *Pb*–O(7), compensant ainsi pour l'absence de la liaison H.

(Traduit par la Rédaction)

Mots-clés: jamesite, structure cristalline, arsenate, minéral de plomb, Tsumeb, Namibie.

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INTRODUCTION

Jamesite was described as a new mineral by Keller *et al.* (1981). It is triclinic with a relatively small cell, and the formula was reported as $Pb_2\ Zn_2\ Fe^{3+}{}_5\ O_4\ (AsO_4)_5$. For the quoted formula, Z is equal to 1, which means that there must be one *As* site with a multiplicity of ½. This is not possible in the space group $P\bar{1}$, as the only special position with a multiplicity of 0.5 is the Wykoff position 1*a* with point symmetry $P\bar{1}$; As^{5+} is invariably tetrahedrally coordinated by O-atoms and hence cannot occupy a Wykoff site with a point symmetry of $\bar{1}$, thus indicating that the symmetry of jamesite should be *P*1 [unless there is extensive orientational disorder of the relevant (AsO$_4$) group: Keller *et al.* 1981]. Acentric minerals of this type of composition are extremely unusual, suggesting either that the structural arrangement might also be very unusual or that the chemical composition given for jamesite is wrong. Our interest in Pb-bearing oxysalts (Cooper & Hawthorne 1994a, b, 1995a, b, 1996, Burns *et al.* 1995, Lam *et al.* 1994) led us to examine the crystal structure of jamesite; the results are reported here.

EXPERIMENTAL

The crystals used in this work are from Tsumeb, Namibia, the type locality for jamesite, and were purchased from a mineral dealer. A small crystal was attached to a glass fiber and mounted on a Siemens *P*4 automated four-circle diffractometer equipped with Mo*K*α X-radiation. Thirteen reflections (all that was visible on a 3 h rotation photograph) over the range $8 \leq 2\theta \leq 18°$ were centered, and the unit-cell dimensions were refined by least-squares from the resultant setting angles. Intensity data were collected in θ–2θ scan-mode at a fixed scan-rate of 0.4°2θ/min, as this crystal is extremely small. A total of 3123 reflections was measured over the range $4 \leq 2\theta \leq 60°$, with index ranges $\bar{7} \leq h \leq 7$, $\bar{13} \leq k \leq 12$, $0 \leq l \leq 14$. Two standard reflections were monitored every fifty-eight reflections; there were no significant changes in their intensities during data collection. The crystal was a parallelipiped measuring 6 × 24 × 80 μm; the faces were indexed on the diffractometer, and a Gaussian absorption correction was done. The data were corrected for Lorentz, polarization and background effects, and reduced to structure factors. Of the 2973 reflections, 1609 were considered as observed $[\,|F(o)| \geq 5\sigma F(o)]$.

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms were taken from the International Tables for Crystallography (1992). *R* indices are of the form given in Table 1, and are expressed as percentages. The Siemens SHELXTL PLUS (PC version) system of programs was used for this work.

TABLE 1. MISCELLANEOUS INFORMATION FOR JAMESITE

a (Å)	5.583(1)	crystal size (mm)	0.006 x 0.024 x 0.084
b	9.542(2)	Radiation	Mo*K*α/Graphite
c	10.219(2)	Total no. of *I*	3123
α °	109.81(2)	No. of $\lvert F \rvert$	2973
β	90.57(2)	No. of $\lvert F_o \rvert > 5\sigma$	1609
γ	97.71(2)	*R*(merge) %	1.3
V (Å^3)	506.6(2)	*R*(obs) %	4.9
Sp. Gr.	$P\bar{1}$	*wR*(obs)%	5.5
Z	1	min. transmission	0.487
μm (mm^{-1})	29.1	max. transmission	0.835
D_{calc} (g.cm^{-3})	5.084		

Cell contents: $Pb_2\ Fe^{3+}{}_{4.8}\ Zn_{2.2}\ (AsO_4)_4\ (OH)_{9.2}\ O_{0.8}$

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

$wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma F^2{}_o]^{1/2}$, $w = 1$

The E-statistics indicate the presence of a center of symmetry, and the structure was solved by direct methods and difference-Fourier synthesis, and refined to an *R* index of 4.9% for anisotropic-displacement parameters on the metal atoms and isotropic-displacement parameters on the anions. The *Pb* site showed extreme anisotropic displacement, and was modeled as a split site, with the site occupancies and anisotropic-displacement parameters of both components as variable. The two independently refined occupancies summed to 2.0 Pb *apfu* (atoms per formula unit) within their standard deviations; in the final cycles of refinement, the occupancies of the split sites were explicitly constrained to 2.0 Pb *apfu*. Positional and displacement parameters are given in Table 2, selected interatomic distances in Table 3, and refined site-scattering parameters in Table 4. Observed and calculated structure-factors are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

ELECTRON-MICROPROBE ANALYSIS

The crystal used in the collection of the X-ray intensity data was fixed to a plexiglass disk, carbon-coated and analyzed with a Cameca SX–50 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, a beam size of 10 μm and counting times on peak and background of 20 and 10 s, respectively. The following standards were used: Pb: PbTe; As: cobaltite; Fe: fayalite; Zn: gahnite; Ga: $GdGaO_3$; Al: kyanite; Cu: olivenite. Data were reduced using the ϕ(ρZ) procedure of Pouchou & Pichoir (1985). The chemical composition given in Table 5 is the mean of two determinations. The mean bond-lengths (Table 3) indicate all Fe to be in the trivalent state (Table 4). The unit formula was calculated on the basis of 26 anions, the H_2O content being calculated from the amount of OH in the unit formula indicated by the refined crystal-structure. The sum of the oxides is low, but the unit formula agrees very

TABLE 2. ATOMIC POSITIONS AND DISPLACEMENT FACTORS* FOR JAMESITE

Site	*x*	*y*	*z*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1*a*)	0.0601(9)	0.7276(2)	0.4179(5)	246(8)	295(16)	282(8)	180(12)	73(5)	–20(7)	123(7)
Pb(1*b*)	0.147(4)	0.754(2)	0.3972(6)	508(31)	681(67)	639(44)	314(23)	184(23)	246(30)	405(51)
As(1)	0.2083(3)	0.6789(2)	0.7648(2)	64(5)	81(7)	61(6)	59(7)	31(5)	–12(5)	16(5)
As(2)	0.3103(3)	0.0633(2)	0.7214(2)	78(5)	96(7)	75(7)	71(7)	35(5)	–12(6)	15(6)
M(1)	0	1/2	0	122(8)	97(13)	133(12)	132(12)	47(10)	–25(10)	8(10)
M(2)	1/2	0	0	65(9)	75(14)	70(13)	51(13)	24(11)	–5(11)	15(11)
M(3)	1/2	1/2	1/2	87(10)	130(16)	93(14)	45(13)	21(11)	–20(12)	51(12)
M(4)	0.2360(4)	0.1255(2)	0.2787(2)	112(8)	132(12)	123(11)	108(12)	61(8)	26(8)	53(8)
M(5)	0.4902(4)	0.4242(2)	0.8375(2)	87(7)	91(12)	91(11)	81(11)	32(8)	–17(8)	10(8)
O(1)	0.464(2)	0.805(1)	0.831(1)	124(22)						
O(2)	0.190(2)	0.534(1)	0.827(1)	133(22)						
O(3)	–0.043(2)	0.758(1)	0.808(1)	102(21)						
O(4)	0.221(2)	0.608(1)	0.591(1)	113(21)						
O(5)	0.312(2)	0.235(1)	0.702(1)	145(23)						
O(6)	0.050(2)	–0.043(1)	0.637(1)	162(24)						
O(7)	0.545(2)	–0.017(1)	0.644(1)	173(24)						
O(8)	0.301(2)	0.091(1)	0.892(1)	109(21)						
OH(1)	0.216(2)	0.674(1)	0.143(1)	114(21)						
OH(2)	0.370(2)	0.511(1)	0.316(1)	110(21)						
OH(3)	0.311(2)	0.399(1)	0.006(1)	112(21)						
OH(4)	0.211(2)	–0.051(1)	0.095(1)	108(21)						
OH(5)	0.299(2)	0.301(1)	0.454(1)	151(23)						

* *U* x 10^4

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) FOR JAMESITE

Pb(1*a*)–O(2)d	3.03(1)	*M*(1)–O(2)c,d	2.17(1)	x2
Pb(1*a*)–O(4)	2.62(1)	*M*(1)–OH(1),h	2.03(1)	x2
Pb(1*a*)–O(5)d	2.53(1)	*M*(1)–OH(3),h	2.11(1)	x2
Pb(1*a*)–O(6)e	2.56(1)	<*M*(1)–O>	2.10	
Pb(1*a*)–OH(1)	2.85(1)			
Pb(1*a*)–OH(2)	2.81(1)	*M*(2)–O(1)a,b	2.05(1)	x2
Pb(1*a*)–OH(5)d	2.44(1)	*M*(2)–O(8)c,g	2.02(1)	x2
<*Pb*(1*a*)–O>	2.69	*M*(2)–OH(4),i	1.98(1)	x2
		<*M*(2)–O>	2.02	
Pb(1*b*)–O(4)	2.84(2)			
Pb(1*b*)–O(5)d	2.78(2)	*M*(3)–O(4),b	2.04(1)	x2
Pb(1*b*)–O(6)e	2.68(2)	*M*(3)–OH(2),b	2.05(1)	x2
Pb(1*b*)–O(7)b	3.00(2)	*M*(3)–OH(5),b	1.98(1)	x2
Pb(1*b*)–OH(1)	2.50(2)	<*M*(3)–O>	2.02	
Pb(1*b*)–OH(2)	2.67(2)			
Pb(1*b*)–OH(5)d	3.01(2)	*M*(4)–O(1)b	2.17(1)	
<*Pb*(1*b*)–O>	2.78	*M*(4)–O(3)d	2.04(1)	
		M(4)–O(6)f	2.02(1)	
As(1)–O(1)	1.71(1)	*M*(4)–O(7)g	2.02(1)	
As(1)–O(2)	1.70(1)	*M*(4)–OH(4)	2.04(1)	
As(1)–O(3)	1.68(1)	*M*(4)–OH(5)	1.99(1)	
As(1)–O(4)	1.68(1)	<*M*(4)–O>	2.05	
<*As*(1)–O>	1.69			
		M(5)–O(2)	2.11(1)	
As(2)–O(5)	1.71(1)	*M*(5)–O(5)	2.00(1)	
As(2)–O(6)	1.69(1)	*M*(5)–OH(1)b	2.04(1)	
As(2)–O(7)	1.68(1)	*M*(5)–OH(2)b	2.00(1)	
As(2)–O(8)	1.68(1)	*M*(5)–OH(3)b	2.07(1)	
<*As*(2)–O>	1.69	*M*(5)–OH(3)j	2.07(1)	
		<*M*(5)–O>	2.05	
proposed H–bonding				
OH(1)....OH(4)e	2.83(2)			
OH(2)....O(3)d	2.83(1)			
OH(3)....O(8)c	2.76(2)			
OH(4)....OH(1)k	2.83(2)			
OH(5)....O(7)g	2.81(2)			

a: $x, y-1, z-1$; b: $\bar{x}+1, \bar{y}+1, \bar{z}+1$; c: $x, y, z-1$; d: $\bar{x}, \bar{y}+1, \bar{z}+1$; e: $x, y+1, z$; f: $\bar{x}, \bar{y}, \bar{z}+1$; g: $\bar{x}+1, \bar{y}, \bar{z}+1$; h: $\bar{x}, \bar{y}+1, \bar{z}$; i: $\bar{x}+1, \bar{y}, \bar{z}$; j: $x, y, z+1$; k: $x, y-1, z$

closely with the refined site-scattering values, indicating that the chemical data are representative of the crystal. Analysis of very small crystals lain on the surface or set in epoxy seems prone to low totals, presumably because of slight charging of the sample.

COORDINATION OF THE CATIONS

There is ideally one *Pb* site in the structure of jamesite. However, structure refinement showed that this site is split; *i.e.*, the cations at this site actually occupy two separate positions, designated as *Pb*(1*a*) and *Pb*(1*b*) in Table 2. The positional, displacement and site-scattering parameters of these two sites were refined, and indicate that the *Pb*(1*a*) and *Pb*(1*b*) sites are occupied by 0.72(2) and 0.28(2) Pb atoms per site, respectively. Details of the coordination of these sites are shown in Table 3. Both *Pb* sites show [7]-coordination by four O-atoms and three (OH) groups, but there is some difference in the O-atoms bonded to Pb at each site: *Pb*(1*a*) is coordinated by O(2), O(4), O(5) and O(6), whereas *Pb*(1*b*) is coordinated by O(4), O(5), O(6) and

TABLE 4. SITE-SCATTERING VALUES (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR JAMESITE

Site	Site scattering	Site population	Predicted site scattering	<*M*–O>$_{calc}$	<*M*–O>$_{obs}$
M(1)	29.1(4)*	Zn	30	2.11	2.10
M(2)	26.2(4)*	Fe^{3+}	26	2.02	2.02
M(3)	26.2(4)*	Fe^{3+}	26	2.02	2.02
M(4)	55.4(5)	1.4 Fe^{3+} + 0.6 Zn	54.4	2.04	2.05
M(5)	54.8(5)	1.4 Fe^{3+} + 0.6 Zn	54.4	2.04	2.05

* fixed at ideal occupancy in last refinement stage

TABLE 5. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA* (*apfu*) FOR JAMESITE

PbO	27.40	Pb	2.01
As_2O_5	27.94		
Fe_2O_3	23.30	As	3.99
ZnO	10.39		
Ga_2O_3	0.27	Fe	4.78
Al_2O_3	0.09	Zn	2.09
CuO	0.21	Ga	0.05
H_2O*	(5.06)	Al	0.03
TOTAL	94.66	Cu	0.04
		Σ	6.99
		OH	9.20

not detected: Mg, P, Ca, Mn, Cd

* calculated for OH = 9.20 *apfu* as indicated from crystal-structure refinement.

O(7). Clearly, the reason for this difference in *Pb* coordination is driving the splitting of the *Pb* site. These two different coordinations are shown in Figure 1. The *Pb*(1*a*)–*Pb*(1*b*) separation is 0.59(2) Å, and this displacement of the two sites leads to breaking of the *Pb*(1*a*)–O(2) bond and formation of the *Pb*(1*b*)–O(7) bond (Fig. 1). Each site shows a strong asymmetric (one-sided) coordination by its associated anions, indicative of strong stereoactive lone-pair behavior of Pb^{2+} at each site.

There are two unique *As* sites, both lying in general positions (Table 2). The <*As*–O> distances are both 1.69 Å, and the variation in individual bond-lengths falls well within the range typical for tetrahedrally coordinated As^{5+}. This assignment is confirmed by the site-scattering values and the well-behaved anisotropic-displacement parameters.

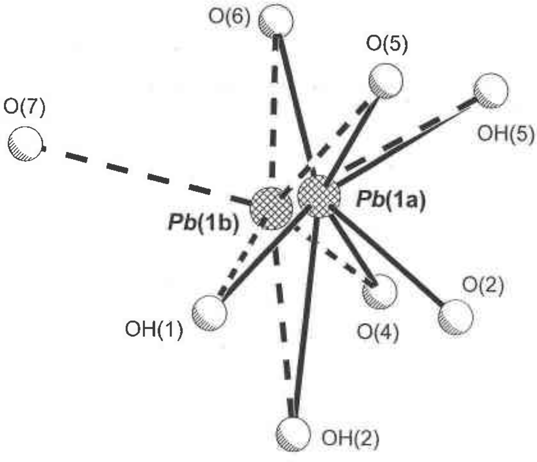

FIG. 1. The coordination of Pb^{2+} in jamesite (oblique view); Pb atoms are the large cross-hatched circles, O-atoms and (OH) groups are the highlighted circles, the Pb(1*a*)–ϕ (ϕ: unspecified anion) bonds are the full lines, and the Pb(1*b*)–ϕ bonds are the broken lines.

There are five unique sites labeled *M*(1)–*M*(5) in the structure; three of these [*M*(1), *M*(2), *M*(3)] lie on special positions (*i.e.*, on a center of symmetry) and two [*M*(4) and *M*(5)] lie on general positions. All *M* sites are octahedrally coordinated, with <*M*–O> bond-lengths lying in the range 2.02–2.10 Å; these mean bond-lengths are typical for octahedra involving medium-sized trivalent and divalent cations. The unit formula (Table 5) shows that Fe + Zn + (Ga + Al + Cu) sums to ~7.00 *apfu*, and hence these cations must occupy the *M* sites, the Fe being in the trivalent state. The refined site-scattering values for these sites are given in Table 4. The site-scattering at *M*(1) indicates that this site is occupied by Zn, and the sum of the constituent-cation and -anion radii is in accord with this assignment. The site-scattering at *M*(2) and *M*(3) indicates that these sites are occupied by Fe^{3+}, and the sum of the constituent radii are in accord with these assignments. The refined site-scattering values at *M*(4) and *M*(5) indicate occupancy by both Fe^{3+} and Zn; site populations were thus assigned from the refined site-scattering values, and the observed and calculated mean bond-lengths are in accord with the assignments. Final site-populations are given in Table 4.

STRUCTURE TOPOLOGY

Two *M*(5) and one *M*(1) octahedra link by sharing edges to form a compact trimer (see labeled octahedra in Fig. 2a). The trimer is repeated in the [100] direction by translation, linking to form a chain of the form $[M_3\phi_{10}]$ that is also found in the structures of kotoite (Effenberger & Pertlik 1984), lindgrenite (Hawthorne & Eby 1985) and frankhawthorneite (Grice & Roberts 1995). This octahedron chain is decorated by tetrahedra to form what we designate as the *A* chain (Fig. 2a): $[M_3(TO_4)_4\phi_6]$.

The *M*(4) octahedron links to two other *M*(4) octahedra *via* corner-sharing with *As*(1) and *As*(2) tetrahedra to form an $[M(TO_4)_2\phi_2]$ chain that occurs in minerals of the kröhnkite, talmessite and fairfieldite groups (Hawthorne 1985). This chain extends along [100] and is linked to its symmetrical equivalent along [001] *via* edge-sharing between two *M*(4) octahedra and the linking *M*(2) octahedra. The resulting heteropolyhedral ladder (Fig. 2b) is designated the *B* chain.

The *A* chain and the *B* chain link through the *M*(3) octahedron (Fig. 3) to form a heteropolyhedral sheet parallel to (010). The linking *M*(3) octahedron shares corners with the *M*(5) octahedron of the *A* chain and the *M*(4) octahedron of the *B* chain, and with both the *As*(1) and *As*(2) tetrahedra. Note that this linkage produces a local topology that is a fragment of one of the 7 Å $[M\phi_5]$ chains that are so common in phosphate and sulfate minerals (Moore 1970, Hawthorne 1990, 1998).

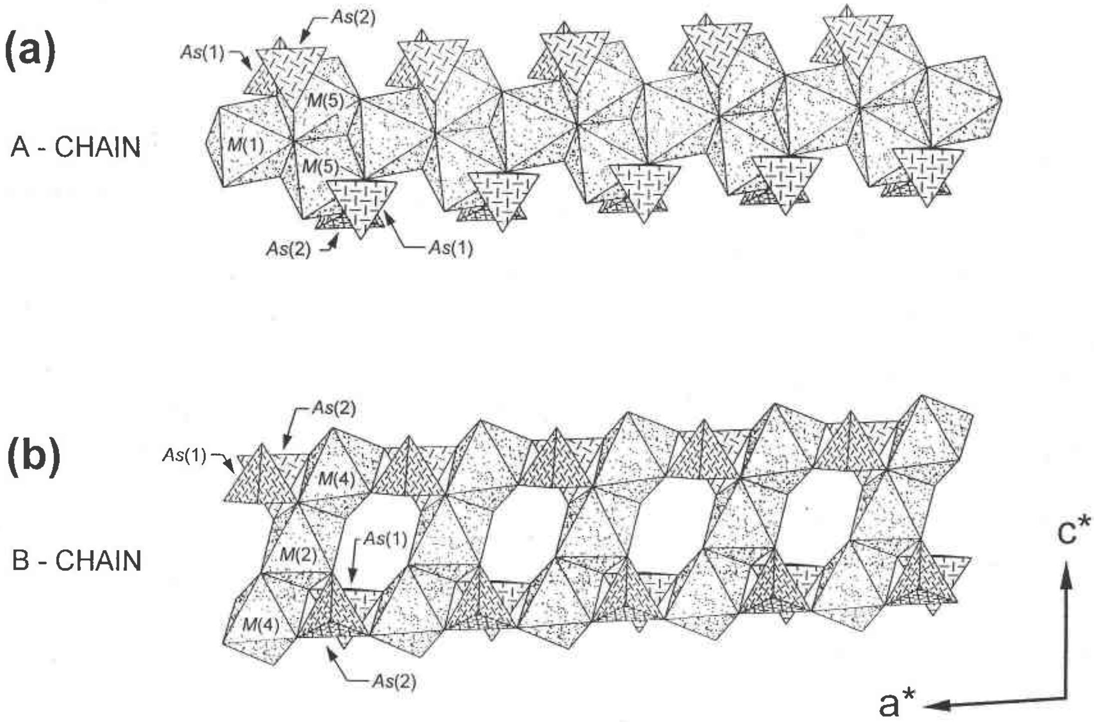

FIG. 2. Components of the structure of jamesite viewed down [010]; (a) the *A* chain; (b) the *B* chain. The *M* octahedra are shown by irregular dot-shading, and the *As*O$_4$ tetrahedra, by orthogonal broken-line shading.

These sheets link together along [010] to form a heteropolyhedral framework (Fig. 4). This linkage provides large cavities that accommodate the interstitial Pb^{2+} cations. Note that the *M*(3) octahedra that link the *A* and *B* chains together to form a sheet (Fig. 3) also link the sheets together to form the framework (Fig. 4).

HYDROGEN BONDING

The bond-valence table for jamesite, calculated with the parameters of Brown & Altermatt (1985), is shown in Table 6. Inspection of the bond-valence sums around the anions indicates that five of the anions [those designated as OH(1)–OH(5)] must be (OH) [or dominantly (OH)], as they have incident bond-valence sums of ~1 *vu* (valence units). A sensible H-bonding scheme can be assigned whereby the bond-valence sums incident at all anions in the structure are close to those expected from the valence-sum rule (Table 6), and the geometry of the bonds is reasonable (Table 3).

The one exception to this statement is the OH(5) anion: the OH(5)–OH(7) distance, 2.81(2) Å, is an edge of the *M*(4) octahedron. Hydrogen-bonding almost never occurs along the edge of an octahedron occupied by a divalent or trivalent cation. However, the O(7) anion has an incident bond-valence sum of 1.76 *vu* if no H-bond contributions are considered; it needs to be an acceptor of a H-bond. However, the only other possible H-bond donor is OH(1) at 3.34(1) Å, a distance that seems too long for a strong H-bond to occur.

THE CHEMICAL FORMULA OF JAMESITE

The results of the site-scattering refinement and the electron-microprobe analysis are in very close agreement, and the <*M*–O> bond-lengths indicate that all Fe is trivalent. Hence the cation part of the formula may be written as $Pb^{2+}_2\ Fe^{3+}_{4.8}\ Zn_{2.2}\ As^{5+}_4$, with a total charge of 42.8^+. The long-range (average) bond-valence table (Table 6) shows that O(1) to O(8) are O-atoms (*i.e.*, O^{2-}), that OH(1) to OH(4) are OH^-, and that OH(5) is both OH^- and O^{2-}. This leads to the following formula for jamesite:

$$Pb^{2+}_2\ (Fe^{3+}_{4.8}\ Zn_{2.2})\ (AsO_4)_4\ (OH)_8\ [(OH)_{1.2}O_{0.8}].$$

However, as three of the *M* sites are completely ordered [*M*(1) = Zn, *M*(2) = Fe^{3+}, *M*(3) = Fe^{3+}], we prefer to write the formula in the following way to more closely reflect the ordered features of the structure:

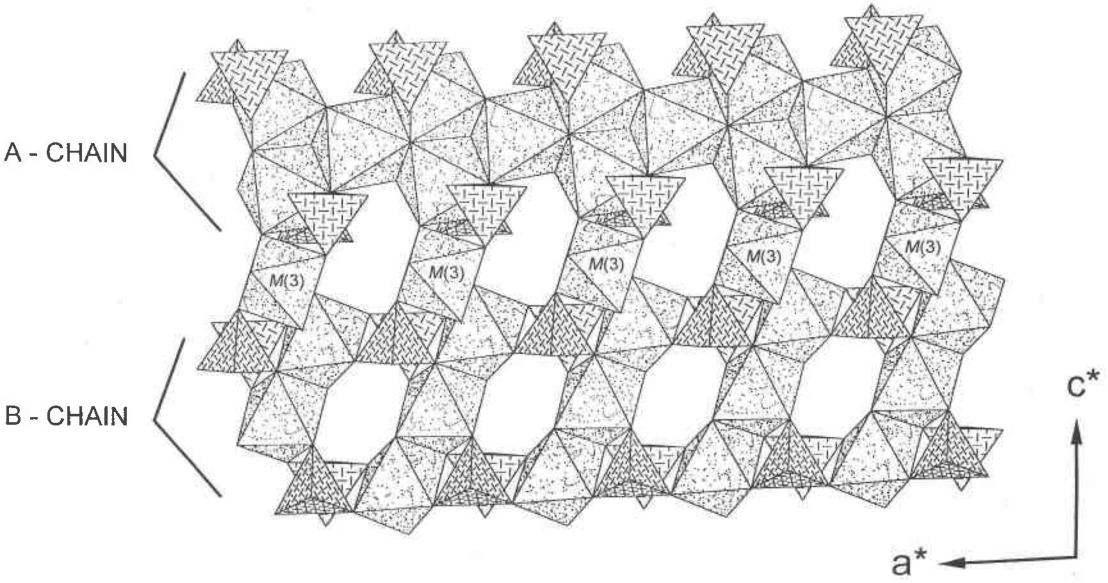

FIG. 3. The heteropolyhedral-sheet component of the structure of jamesite viewed down [010]; the *A* and *B* chains are indicated. The legend is as in Figure 2.

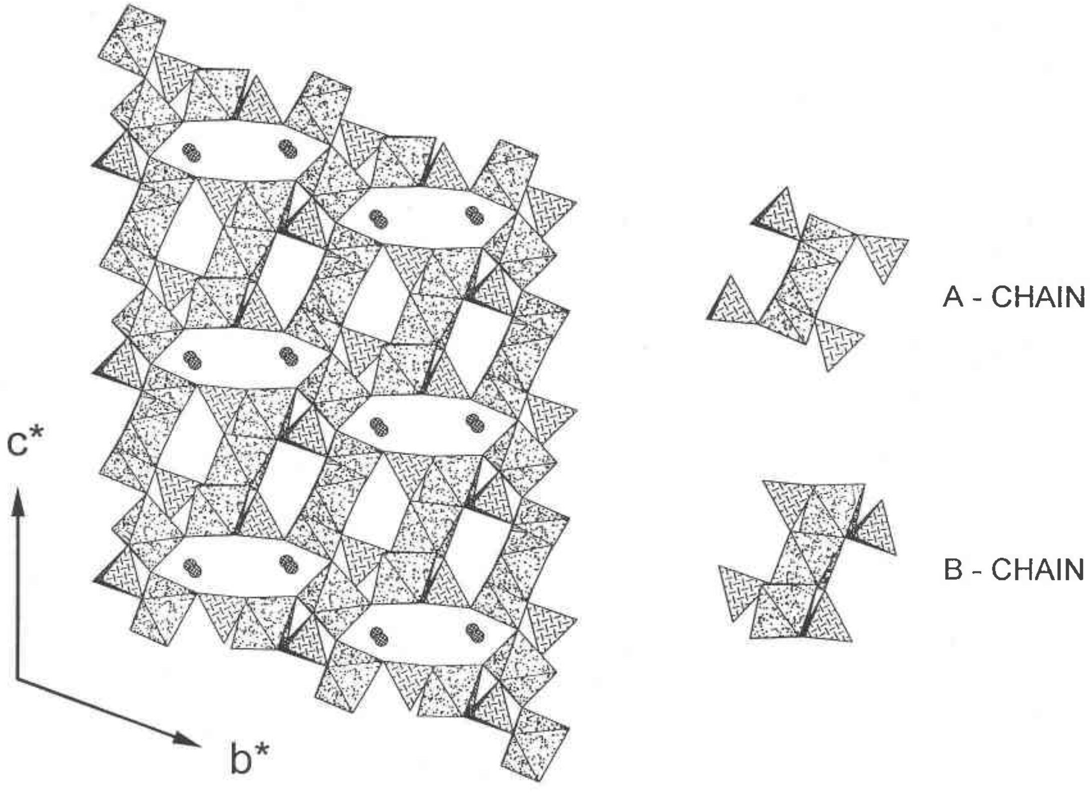

FIG. 4. The structure of jamesite viewed down [100], with legend as in Figures 1 and 2, with *Pb*–ϕ bonds omitted for clarity. The appearance of the *A* and *B* chains viewed from this direction is shown on the right of the figure.

TABLE 6. BOND–VALENCE* (*vu*) TABLE FOR JAMESITE

	Pb(1*a*)	*Pb*(1*b*)	*As*(1)	*As*(2)	*M*(1)	*M*(2)	*M*(3)	*M*(4)	*M*(5)	*H*(1)	*H*(2)	*H*(3)	*H*(4)	*H*(5)	Σ
O(1)			1.17			$0.46^{\times2}\downarrow$		0.32							1.95
O(2)	0.06		1.20		$0.28^{\times2}\downarrow$				0.37						1.91
O(3)			1.27					0.45			0.2				1.92
O(4)	0.18	0.04	1.27				$0.47^{\times2}\downarrow$								1.96
O(5)	0.23	0.04		1.17					0.50						1.94
O(6)	0.22	0.06		1.23				0.47							1.98
O(7)		0.03		1.27				0.47						0.12	1.89
O(8)				1.27		$0.49^{\times2}\downarrow$						0.2			1.96
OH(1)	0.10	0.10			$0.41^{\times2}\downarrow$				0.45	0.8			0.2		2.06
OH(2)	0.11	0.06					$0.46^{\times2}\downarrow$		0.50		0.8				1.93
OH(3)					$0.33^{\times2}\downarrow$				0.41 0.41			0.8			1.95
OH(4)						$0.55^{\times2}\downarrow$		0.45		0.2			0.8		2.00
OH(5)**	0.30	0.03					$0.55^{\times2}\downarrow$	0.52						0.48	1.88
	1.20	0.36	4.91	4.94	2.04	3.00	2.96	2.68	2.64	1.0	1.0	1.0	1.0	0.60	

* bond-valence curves from Brown & Altermatt (1985)
** OH(5) = 1.2 OH + 0.8 O

$Pb^{2+}_2\ Zn\ Fe^{3+}_2\ (Fe^{3+}_{2.8}\ Zn_{1.2})\ (AsO_4)_4\ (OH)_8\ [(OH)_{1.2}O_{0.8}]$.

This formula is very different from that given by Keller *et al.* (1981): $Pb_2\ Zn_2\ Fe^{3+}_5\ O_4\ (AsO_4)_5$. Comparison of the chemical compositions indicates close agreement for PbO, Fe_2O_3 and ZnO, but significant differences for As_2O_5 and H_2O. Keller *et al.* (1981) did not detect any H_2O by infrared spectroscopy and did not comment on the presence of OH, whereas the structure indicates an abundance of (OH) groups in the formula. However, the close agreement between the cell dimensions, the physical properties, and the observed powder pattern and that calculated from the refined structure indicates that these phases are the same.

SPLITTING OF THE Pb SITE

There are two Pb^{2+} atoms in the unit cell of jamesite, and these atoms ideally occupy a single site of equipoint rank 2. However, refinement shows that this site is actually split into two sites separated by ~0.6 Å. Only one of these two sites can be locally occupied, and site-scattering refinement shows the following occupancies: *Pb*(1*a*): 0.72 Pb^{2+} + 0.28 □; *Pb*(1*b*): 0.28 Pb^{2+} + 0.72 □. What is the driving force for this disorder? The key feature here is the occupancy of the OH(5) site by both (OH) and O^{2-}. Where OH(5) is occupied by (OH), the associated H-atom forms a H-bond to the O(7) anion (Table 6). Where the OH(5) site is occupied by O^{2-}, the O(7) anion does not receive any contribution from a H-bond, and hence would not seem to receive sufficient incident bond-valence. In order to compensate for this feature, the Pb atom occupies a different site, the *Pb*(1*b*) site, such that it forms a bond with the O(7) anion, essentially replacing the H-bond. Thus the disorder at the *Pb* site is driven by the (OH)–O^{2-} disorder at the OH(5) site, which is, in turn, controlled by the Fe^{3+}:Zn ratio at the *M*(4) [and *M*(5)] sites.

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REFERENCES

BROWN, I.D. & ALTERMATT, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.* **B41**, 244-247.

BURNS, P.C., COOPER, M.A. & HAWTHORNE, F.C. (1995): Parakhninite, $Cu^{2+}_3\ PbTe^{6+}O_6(OH)_2$: crystal structure and revision of chemical formula. *Can. Mineral.* **33**, 33-40.

COOPER, M.A. & HAWTHORNE, F.C. (1994a): The crystal structure of kombatite, $Pb_{14}(VO_4)_2O_9Cl_4$, a complex heteropolyhedral sheet mineral. *Am. Mineral.* **79**, 550-554.

________ & ________ (1994b): The crystal structure of wherryite, $Pb_7Cu_2(SO_4)_4(SiO_4)_2(OH)_2$, a mixed sulfate – silicate structure with $[^{[6]}M(TO_4)_2\phi]$ chains. *Can. Mineral.* **32**, 373-380.

________ & ________ (1995a): Diaboléite, $Pb_2Cu(OH)_4Cl_2$, a defect perovskite structure with stereoactive lone-pair behavior of Pb^{2+}. *Can. Mineral.* **33**, 1125-1129.

________ & ________ (1995b): The crystal structure of mottramite, and the nature of Cu $\rightleftharpoons$ Zn solid solution in the mottramite – descloizite series. *Can. Mineral.* **33**, 1119-1124.

________ & ________ (1996): The crystal structure of ludlockite, $PbFe^{3+}_4As^{3+}_{10}O_{22}$, the mineral with pentameric arsenite groups and orange hair. *Can. Mineral.* **34**, 79-89.

EFFENBERGER, H. & PERTLIK, F. (1984): Verfeinerung der Kristallstrukturen der Isotypen verbindungen $M_3(BO_3)_2$ mit M = Mg, Co, Ni (Strukturtyp: Kotoit). *Z. Kristallogr.* **166**, 129-140.

GRICE, J.D. & ROBERTS, A.C. (1995): Frankhawthorneite, a unique HCP framework structure of a cupric tellurate. *Can. Mineral.* **33**, 649-653.

HAWTHORNE, F.C. (1985): Towards a structural classification of minerals: the $^{VI}M^{IV}T_2\phi_n$ minerals. *Am. Mineral.* **70**, 455-473.

________ (1990): Structural hierarchy in $M^{[6]}T^{[6]}\phi_n$ minerals. *Z. Kristallogr.* **192**, 1-52.

________ (1998): Structure and chemistry of phosphate minerals. *Mineral. Mag.* **62**, 141-164.

________ & EBY, R.K. (1985): Refinement of the crystal structure of lindgrenite. *Neues Jahrb. Mineral. Monatsh.*, 234-240.

INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY (1992): Kluwer Academic Publishers, Dordrecht, The Netherlands.

KELLER, P., HESS, H. & DUNN, P.J. (1981): Jamesite, $Pb_2Zn_2Fe^{3+}{}_5O_4(AsO_4)_5$, ein neues Mineral von Tsumeb, Namibia. *Chem. Erde* **40**, 105-109.

LAM, A.E., GROAT, L.A., COOPER, M.A. & HAWTHORNE, F.C. (1994): The crystal structure of wickenburgite, $Pb_3CaAl[AlSi_{10}O_{27}](H_2O)_3$, a sheet structure. *Can. Mineral.* **32**, 525-532.

MOORE, P.B. (1970) Structural hierarchies among minerals containing octahedrally coordinating oxygen. I. Stereoisomerism among corner-sharing octahedral and tetrahedral chains. *Neues Jahrb. Mineral., Monatsh.*, 163-173.

POUCHOU, J.-L. & PICHOIR, F. (1985): "PAP" $\phi(\rho z)$ procedure for improved quantitative microanalysis. *Microbeam Anal.*, 104-106.

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