THE CRYSTAL STRUCTURE OF LUDLOCKITE, $PbFe_4^{3+}As_{10}^{3+}O_{22}$, THE MINERAL WITH PENTAMERIC ARSENITE GROUPS AND ORANGE HAIR

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ABSTRACT

The crystal structure of ludlockite, $PbFe_4^{3+}As_{10}^{3+}O_{22}$, a 10.426(4), b 12.074(5), c 18.349(8) Å, α 101.84(3), β 100.21(3), γ 90.60(3)°, V 2222(2) Å^3, $A\bar{1}$, $Z = 4$, has been solved by direct methods and refined to an R index of 4.7% for 3858 observed reflections measured with MoKα X-radiation. The chemical formula of ludlockite, originally given as $(Fe,Pb)As_2O_6$, has been revised, and the results of electron-microprobe analysis are in accord with the revised formula. The orientation of the unit cell has also been changed from P- to A-centered, such that the major structural features are easily related to the principal crystallographic axes. There is one unique Pb position surrounded by eight oxygen atoms in a triangular dodecahedral arrangement. There are four unique Fe positions, each surrounded by a distorted octahedral arrangement of oxygen atoms; the <Fe–O> distance of ~2.025 Å indicates that all Fe is in the trivalent state. There are ten unique As positions, each showing triangular pyramidal coordination with <As–ϕ> distances of ~1.79 Å, compatible with all As being in the trivalent state with a stereoactive lone-pair of electrons. The structural unit of ludlockite consists of a sheet of edge-sharing FeO_6 octahedra and PbO_8 triangular dodecahedra embraced by convoluted but topologically linear $[As_5O_{11}]$ groups. This sheet is parallel to (001), and adjacent sheets stack along [001]. There are no interstitial species, and interaction between adjacent sheets is very weak, accounting for the perfect cleavage of ludlockite.

Keywords: ludlockite, crystal structure, chemical formula, electron-microprobe analysis, arsenite, stereoactive lone-pair electrons.

SOMMAIRE

Nous avons résolu la structure cristalline de la ludlockite, $PbFe_4^{3+}As_{10}^{3+}O_{22}$, a 10.426(4), b 12.074(5), c 18.349(8) Å, α 101.84(3), β 100.21(3), γ 90.60(3)°, V 2222(2) Å^3, $A\bar{1}$, $Z = 4$, par méthodes directes jusqu'à un résidu R de 4.7% en utilisant 3858 réflexions observées avec rayonnement MoKα. La formule chimique de la ludlockite, considérée antérieurement comme $(Fe,Pb)As_2O_6$, a dû être modifiée, et les résultats des analyses à la microsonde électronique concordent avec la formule révisée. L'orientation de la maille élémentaire a aussi été changée de P à une maille centrée sur A, de sorte que les aspects importants de la structure sont plus facilement mis en relation avec les axes cristallographiques principaux. La structure contient une seule position occupée par le Pb, entourée de huit atomes d'oxygène dans un agencement dodécaédrique triangulaire. Il y a quatre positions uniques occupées par le Fe, chacune d'elles définissant un octaèdre difforme; la distance <Fe–O> d'environ 2.025 Å indique que dans chaque cas, le Fe est trivalent. Il y a dix positions uniques occupées par l'arsenic, chacun des atomes étant en coordination pyramidale triangulaire, avec une distance <As–O> d'environ 1.79 Å, ce qui est compatible avec l'attribution de chacun à l'état trivalent, avec une paire d'électrons isolés stéréoactifs. L'unité structurale est faite d'un feuillet d'octaèdres à arêtes partagées et de dodécaèdres triangulaires de PbO_8 entourés de groupes $[As_5O_{11}]$ topologiquement linéaires, mais fortement articulés. Ces feuillets, parallèles à (001), sont empilés le long de [001]. Il n'y a aucune espèce interstitielle, et l'interaction entre les feuillets est très faible, ce qui rend compte du clivage parfait de la ludlockite.

(Traduit par la Rédaction)

Mots-clés: ludlockite, structure cristalline, formule chimique, analyse à la microsonde électronique, arsenite, paire d'électrons isolés stéréoactifs.

INTRODUCTION

Ludlockite is a lead ferric-iron arsenite occurring in the "germanite section" of the mines at Tsumeb, Namibia. It was first described by Embrey *et al.* (1977) as $(Fe,Pb)As_2O_6$, and occurs as bundles of orange to orange-brown fibers associated with zincian siderite. As part of our general interest in oxide and oxysalt mineral structures (Hawthorne 1985a, 1986, 1990, 1994), we have solved the structure of ludlockite and present the results here.

EXPERIMENTAL

The crystals used in this study are from Tsumeb, Namibia, and were generously provided for study by

TABLE 1. MISCELLANEOUS STRUCTURAL AND REFINEMENT INFORMATION FOR LUDLOCKITE

Primitive Cell

a (Å)	10.426(4)	crystal size (mm)	0.250 x 0.030 x 0.011
b	11.972(5)		
c	9.894(4)	radiation/monochromator	MoKα/Gr
α (°)	113.76(3)		
β	99.83(3)	No. of intensities	6848
γ	82.50(3)		
V (Å³)	1111.0(8)	No. of |Fo| > 5σ	3858
Sp.Gr.	P1̄		
Z	2	min. transmission	0.271
Dc (g cm⁻³)	4.58	max. transmission	0.776
		mμ (mm⁻¹)	25.0

A–centered cell

a (Å)	10.426(4)	R(obs) %	4.7
b	12.074(5)	wR(obs) %	5.5
c	18.349(8)		
α (°)	101.84(3)	Cell contents: 4{PbFe₄³⁺(As₅³⁺O₁₁)₂}
β	100.21(3)		
γ	90.60(3)	$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$
V (Å³)	2222(2)		
Sp.Gr.	A1̄	$wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2]^{\frac{1}{2}}$
Z	4	$w = 1/\sigma^2 F + 0.001654\ F^2$

Mr. William Pinch. A flattened fiber was attached to a glass slide with epoxy and carbon-coated. It is impossible to polish ludlockite, as under the least stress, it disaggregates into a bundle of fibers. A chemical analysis of a crystal was obtained with a Cameca SX–50 according to the procedure described by Oberti *et al.* (1992); cobaltite (As), PbTe (Pb) and fayalite (Fe) were used as standards. A tip was gently cut from a fiber of ludlockite, and was mounted on a Nicolet *R3m* automated four-circle diffractometer. Thirty reflections over the range $5° < 2\theta < 30°$ were centered using graphite-monochromated MoKα X-radiation. The unit-cell dimensions (Table 1) were derived by least-squares techniques from the setting angles of the thirty automatically aligned reflections. After the structure was solved, we decided to re-orient the cell such that the major structural features are parallel to the crystallographic axes; this resulted in the *A*-centered cell given in Table 1. However, in the

TABLE 2. POSITIONAL AND DISPLACEMENT PARAMETERS FOR LUDLOCKITE

Site	x	y	z	*U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb	0.24520(6)	0.25922(5)	0.74729(4)	256(2)	357(3)	171(3)	219(3)	51(2)	–16(3)	–9(2)
Fe(1)	0.4840(2)	0.5230(1)	0.2627(1)	101(5)	44(8)	117(8)	138(9)	25(7)	2(7)	21(6)
Fe(2)	0.2503(2)	0.5827(1)	0.7475(1)	95(5)	55(7)	111(8)	118(9)	38(7)	–7(7)	11(6)
Fe(3)	0.0194(2)	0.5144(1)	0.2413(1)	104(5)	59(8)	103(8)	141(9)	27(7)	–9(7)	4(6)
Fe(4)	0.2521(2)	0.3460(1)	0.2532(1)	110(5)	60(8)	104(8)	154(9)	33(7)	–18(7)	4(6)
As(1)	0.1716(1)	0.6192(1)	0.92339(7)	116(4)	84(6)	132(6)	117(6)	15(5)	–7(5)	–2(4)
As(2)	0.2372(1)	0.4978(1)	0.12130(8)	122(4)	99(6)	144(6)	127(7)	43(5)	15(5)	–2(5)
As(3)	0.4370(1)	0.5037(1)	0.90356(8)	125(4)	77(6)	155(6)	143(7)	55(5)	–10(5)	31(5)
As(4)	0.4903(1)	0.2600(1)	0.13975(8)	110(4)	70(6)	106(6)	135(6)	6(5)	–9(5)	–10(4)
As(5)	0.0327(1)	0.3808(1)	0.90857(8)	151(4)	107(6)	175(6)	174(7)	81(5)	–21(5)	6(5)
As(6)	0.4586(1)	0.7718(1)	0.09138(8)	155(4)	104(6)	156(6)	165(7)	–10(5)	–34(5)	9(5)
As(7)	0.0551(1)	0.4156(1)	0.59003(8)	125(4)	71(6)	148(6)	131(7)	–5(5)	–6(5)	–2(4)
As(8)	0.3326(1)	0.5032(1)	0.57116(8)	130(4)	118(6)	151(6)	114(6)	35(5)	–7(5)	17(5)
As(9)	0.0032(1)	0.8215(1)	0.85918(7)	105(4)	68(5)	124(6)	113(6)	31(5)	–15(5)	21(4)
As(10)	0.2686(1)	0.5870(1)	0.38155(8)	130(4)	102(6)	165(6)	110(6)	10(5)	7(5)	32(5)
O(1)	0.1310(9)	0.5901(7)	0.8215(5)	140(27)	181(46)	136(41)	71(42)	–13(33)	–24(36)	–40(34)
O(2)	0.3493(8)	0.4862(7)	0.3212(5)	97(25)	24(36)	114(38)	117(43)	–31(32)	–14(32)	–17(29)
O(3)	0.1562(8)	0.1994(7)	0.1976(5)	108(26)	96(40)	89(38)	128(44)	19(32)	–2(34)	26(30)
O(4)	0.3676(8)	0.5415(7)	0.6720(5)	136(27)	71(39)	151(42)	154(47)	–17(35)	–4(35)	2(32)
O(5)	0.1162(8)	0.4554(7)	0.6911(5)	133(27)	101(41)	174(43)	111(44)	35(35)	–16(34)	–38(33)
O(6)	0.0905(8)	0.3885(7)	0.3038(5)	125(27)	89(40)	167(42)	133(45)	97(36)	–20(35)	39(32)
O(7)	0.4110(8)	0.3597(7)	0.2002(5)	116(26)	71(39)	82(37)	178(47)	–3(33)	16(35)	46(30)
O(8)	0.3470(8)	0.7297(7)	0.8059(5)	126(26)	121(41)	76(37)	143(45)	17(33)	–68(35)	30(31)
O(9)	0.3790(8)	0.4892(7)	0.8051(5)	138(27)	104(41)	180(43)	110(44)	57(35)	–67(34)	5(33)
O(10)	0.2067(8)	0.8945(7)	0.0602(5)	157(28)	57(40)	182(44)	178(49)	–51(37)	–15(36)	6(33)
O(11)	0.1468(8)	0.6236(7)	0.3122(6)	149(28)	32(38)	133(41)	256(53)	52(37)	–51(36)	–11(31)
O(12)	0.4408(9)	0.3279(8)	0.6851(5)	186(30)	249(51)	193(45)	84(45)	–14(36)	2(39)	–33(38)
O(13)	0.2867(8)	0.5113(8)	0.9351(6)	173(30)	89(42)	249(48)	217(54)	78(41)	87(39)	95(36)
O(14)	0.3631(9)	0.2171(8)	0.8860(6)	215(31)	47(40)	195(47)	318(60)	–42(41)	–80(39)	–24(34)
O(15)	0.0439(9)	0.3668(8)	0.8123(6)	231(34)	275(54)	212(49)	237(57)	131(42)	29(45)	83(40)
O(16)	0.0419(9)	0.5346(8)	0.9390(5)	165(29)	150(46)	218(46)	127(47)	65(37)	–2(37)	–22(36)
O(17)	0.4511(6)	0.9014(8)	0.0538(6)	167(29)	123(43)	184(44)	209(53)	13(38)	99(39)	74(34)
O(18)	0.4783(9)	0.6521(8)	0.9242(6)	175(30)	177(46)	168(44)	211(52)	114(39)	37(39)	–44(35)
O(19)	0.1546(8)	0.4398(7)	0.1854(5)	125(27)	77(40)	183(43)	101(44)	26(34)	–15(34)	18(32)
O(20)	0.1440(9)	0.6248(8)	0.1108(6)	204(32)	87(42)	259(50)	309(59)	197(44)	–7(40)	9(36)
O(21)	0.3577(8)	0.5858(7)	0.1911(5)	136(27)	67(39)	163(42)	181(48)	70(36)	–8(35)	–36(32)
O(22)	0.0326(9)	0.5554(8)	0.5752(5)	187(31)	254(52)	191(46)	129(48)	54(38)	46(40)	19(38)

* *U* values x 10^4

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN LUDLOCKITE

Pb–O(5)	3.010(9)	As(1)–O(1)	1.802(9)
Pb–O(9)	2.995(8)	As(1)–O(13)	1.800(9)
Pb–O(11)e	2.520(10)	As(1)–O(16)	1.784(10)
Pb–O(12)	2.707(11)	<As(1)–O>	1.795
Pb–O(14)	2.772(11)		
Pb–O(15)	2.797(11)	As(2)–O(19)	1.817(10)
Pb–O(20)e	2.716(9)	As(2)–O(20)	1.849(10)
Pb–O(21)e	2.534(9)	As(2)–O(21)	1.786(8)
<Pb–O>	2.756	<As(2)–O>	1.817
Fe(1)–O(2)	2.009(9)	As(3)–O(9)	1.772(9)
Fe(1)–O(4)c	2.046(9)	As(3)–O(13)	1.761(10)
Fe(1)–O(7)	2.125(8)	As(3)–O(18)	1.785(9)
Fe(1)–O(9)c	2.043(10)	<As(3)–O>	1.773
Fe(1)–O(12)c	1.942(9)		
Fe(1)–O(21)	1.962(9)	As(4)–O(7)	1.778(9)
<Fe(1)–O>	2.021	As(4)–O(8)c	1.798(8)
Δ	0.89	As(4)–O(18)c	1.803(11)
		<As(4)–O>	1.793
Fe(2)–O(1)	1.987(10)		
Fe(2)–O(3)b	2.006(9)	As(5)–O(15)	1.765(11)
Fe(2)–O(4)	1.998(10)	As(5)–O(16)	1.823(9)
Fe(2)–O(5)	2.045(8)	As(5)–O(20)a	1.811(9)
Fe(2)–O(8)	2.028(8)	<As(5)–O>	1.800
Fe(2)–O(9)	2.052(9)		
<Fe(2)–O>	2.019	As(6)–O(12)f	1.756(10)
Δ	0.14	As(6)–O(14)c	1.828(9)
		As(6)–O(17)	1.833(10)
Fe(3)–O(1)a	2.025(8)	<As(6)–O>	1.806
Fe(3)–O(5)a	2.030(8)		
Fe(3)–O(6)	2.149(10)	As(7)–O(5)	1.812(9)
Fe(3)–O(11)	1.961(8)	As(7)–O(10)e	1.766(9)
Fe(3)–O(15)a	1.956(11)	As(7)–O(22)	1.776(10)
Fe(3)–O(19)	2.003(9)	<As(7)–O>	1.785
<Fe(3)–O>	2.021		
Δ	1.01	As(8)–O(4)	1.783(9)
		As(8)–O(10)e	1.802(9)
		As(8)–O(17)e	1.775(9)
		<As(8)–O>	1.787

TABLE 3. continued

Fe(4)–O(2)	2.024(7)	As(9)–O(3)a	1.783(8)
Fe(4)–O(3)	2.008(8)	As(9)–O(6)b	1.779(10)
Fe(4)–O(6)	2.083(9)	As(9)–O(22)g	1.798(9)
Fe(4)–O(7)	2.086(10)	<As(9)–O>	1.787
Fe(4)–O(8)d	2.032(9)		
Fe(4)–O(19)	2.005(9)	As(10)–O(2)	1.793(8)
<Fe(4)–O>	2.040	As(10)–O(11)	1.760(9)
Δ	0.26	As(10)–O(14)f	1.825(10)
		<As(10)–O>	1.793

Long As–O distances < 4.0 Å between slabs

As(1)–O(10)h	3.703(8)	As(5)–O(16)l	3.014(10)
As(1)–O(20)h	3.489(12)		
		As(6)–O(13)i	3.961(8)
As(2)–O(13)i	3.581(11)	As(6)–O(18)i	3.154(10)
As(2)–O(16)i	3.707(9)		
		As(7)–O(22)a	3.099(10)
As(3)–O(13)j	3.782(9)		
As(3)–O(18)j	3.974(11)	As(8)–O(17)m	3.812(11)
As(4)–O(17)k	3.839(10)	As(9)–O(10)h	3.839(9)

a: x̄, ȳ+1, z̄+1; b: x, y+½, z+½; c: x̄+1, ȳ+1, z̄+1; d: x, y–½, z–½; e: x, y–½, z+½; f: x, y+½, z–½; g: x̄, ȳ+1½, z̄+1½; h: x, y, z+1; i: x, y, z–1; j: x̄+1, ȳ+1, z̄+2; k: x̄+1, ȳ+1, z̄; l: x̄, ȳ+1, z̄+2; m: x̄+1, ȳ+1½, z̄+½

absorption correction was done; minimum and maximum transmission values were 0.271 and 0.776. The data were then corrected for Lorentz, polarization and background effects, and reduced to structure factors. Of the 6848 reflections, 3858 were considered as observed [|F| > 5σF].

This rather abbreviated account does not truly represent an effort that extended over eleven years; we examined numerous crystals from twenty-five different samples by rotation or precession photography. It was extremely difficult to prepare and mount a crystal for diffraction without damaging it, and fiber cross-sections were invariably too small. Mr. William Pinch allowed us to pick crystals from the best specimen of ludlockite in existence, and we were fortunate to find and mount one small crystal. We wish to emphasize the importance of access to good material when dealing with "difficult" crystals, and recognize the major role that collectors play in finding the best material and making it available for scientific work.

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, with anomalous dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. 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 throughout this study.

experimental section, we refer everything to the primitive cell, as this was used for the experimental part of the work.

Intensity data were collected using θ–2θ scans with a scan range of 2.4°. A variable scan-rate inversely proportional to the peak intensity was used, with maximum and minimum scan-rates of 14.65°2θ/min and 2.02°2θ/min, respectively. A total of 6848 reflections were measured over the range 4° ≤ 2θ ≤ 60°, with index ranges –15 ≤ h ≤ 15, –17 ≤ k ≤ 17, –14 ≤ l ≤ 0. Two standard reflections were measured every fifty-eight reflections; there were no significant changes in their intensities during data collection. The crystal was a flat fiber, 250 μm long and 11 × 30 μm in cross-section. The faces of the crystal were indexed, and an analytical

TABLE 4. SELECTED INTERATOMIC ANGLES (°) IN LUDLOCKITE

As(1) group		As(2) group	
O(1)–As(1)–O(13)	99.3(4)	O(19)–As(2)–O(20)	101.7(4)
O(1)–As(1)–O(16)	97.4(4)	O(19)–As(2)–O(21)	97.8(4)
O(13)–As(1)–O(16)	92.2(4)	O(20)–As(2)–O(21)	89.1(4)
<O–As(1)–O>	96.3	<O–As(2)–O>	96.2
As(3) group		**As(4) group**	
O(9)–As(3)–O(13)	99.2(4)	O(7)–As(4)–O(8)c	101.3(4)
O(9)–As(3)–O(18)	97.1(4)	O(7)–As(4)–O(18)c	98.6(4)
O(13)–As(3)–O(18)	97.7(4)	O(8)c–As(4)–O(18)c	97.0(4)
<O–As(3)–O>	98.0	<O–As(4)–O>	99.0
As(5) group		**As(6) group**	
O(15)–As(5)–O(16)	100.4(5)	O(12)f–As(6)–O(14)c	93.8(5)
O(15)–As(5)–O(20)a	93.3(5)	O(12)f–As(6)–O(17)	100.1(4)
O(16)–As(5)–O(20)a	92.3(4)	O(14)c–As(6)–O(17)	92.3(4)
<O–As(5)–O>	95.3	<O–As(6)–O>	95.4
As(7) group		**As(8) group**	
O(5)–As(7)–O(10)e	97.9(4)	O(4)–As(8)–O(10)e	98.7(4)
O(5)–As(7)–O(22)	96.4(4)	O(4)–As(8)–O(17)e	100.9(4)
O(10)e–As(7)–O(22)	98.2(5)	O(10)e–As(8)–O(17)e	92.0(4)
<O–As(7)–O>	97.5	<O–As(8)–O>	97.2
As(9) group		**As(10) group**	
O(3)a–As(9)–O(6)b	101.9(4)	O(2)–As(10)–O(11)	98.0(4)
O(3)a–As(9)–O(22)g	95.7(4)	O(2)–As(10)–O(14)f	100.9(4)
O(6)b–As(9)–O(22)g	99.4(4)	O(11)–As(10)–O(14)f	90.0(4)
<O–As(9)–O>	99.0	<O–As(10)–O>	96.6
Fe(1) octahedron		**Fe(2) octahedron**	
O(4)c–Fe(1)–O(9)c	80.0(4)	O(1)–Fe(2)–O(5)	79.6(4)
O(4)c–Fe(1)–O(12)c	86.9(4)	O(1)–Fe(2)–O(9)	92.0(4)
O(4)c–Fe(1)–O(2)	93.7(4)	O(1)–Fe(2)–O(8)	92.0(4)
O(4)c–Fe(1)–O(7)	92.8(3)	O(1)–Fe(2)–O(3)b	93.2(4)
O(21)–Fe(1)–O(9)c	92.5(4)	O(4)–Fe(2)–O(5)	92.2(4)
O(21)–Fe(1)–O(12)c	92.5(4)	O(4)–Fe(2)–O(9)	80.9(4)
O(21)–Fe(1)–O(2)	93.7(4)	O(4)–Fe(2)–O(8)	97.4(4)
O(21)–Fe(1)–O(7)	87.3(3)	O(4)–Fe(2)–O(3)b	95.6(4)
O(9)c–Fe(1)–O(12)c	89.2(4)	O(5)–Fe(2)–O(9)	98.6(4)
O(12)c–Fe(1)–O(2)	105.8(4)	O(9)–Fe(2)–O(8)	91.5(3)
O(2)–Fe(1)–O(7)	78.2(3)	O(8)–Fe(2)–O(3)b	77.1(3)
O(7)–Fe(1)–O(9)c	86.8(4)	O(3)b–Fe(2)–O(5)	93.3(3)
<O–Fe(1)–O>	90.0	<O–Fe(2)–O>	90.3
σ	51.3	σ	50.3
Fe(3) octahedron		**Fe(4) octahedron**	
O(1)a–Fe(3)–O(6)	92.3(3)	O(7)–Fe(4)–O(2)	78.8(3)
O(1)a–Fe(3)–O(19)	95.2(3)	O(7)–Fe(4)–O(19)	87.9(4)
O(1)a–Fe(3)–O(15)a	89.3(4)	O(7)–Fe(4)–O(3)	105.4(3)
O(1)a–Fe(3)–O(5)a	79.1(4)	O(7)–Fe(4)–O(8)d	89.1(4)
O(11)–Fe(3)–O(6)	88.1(4)	O(6)–Fe(4)–O(2)	88.7(3)
O(11)–Fe(3)–O(19)	93.3(4)	O(6)–Fe(4)–O(19)	77.9(4)
O(11)–Fe(3)–O(15)a	90.1(4)	O(6)–Fe(4)–O(3)	88.6(3)
O(11)–Fe(3)–O(5)a	92.4(4)	O(6)–Fe(4)–O(8)d	106.9(4)
O(6)–Fe(3)–O(19)	76.4(4)	O(2)–Fe(4)–O(19)	91.0(3)
O(19)–Fe(3)–O(15)a	104.8(4)	O(19)–Fe(4)–O(3)	94.9(3)
O(15)a–Fe(3)–O(5)a	91.9(4)	O(3)–Fe(4)–O(8)d	77.0(3)
O(5)a–Fe(3)–O(6)	87.1(4)	O(8)d–Fe(4)–O(2)	97.6(3)
<O–Fe(3)–O>	90.0	<O–Fe(4)–O>	90.3
σ	53.5	σ	95.8

The E-statistics indicate a center of symmetry, and the direct methods solution with the highest figure of merit gave the positions of many of the cations. Subsequent cycles of least-squares refinement and

difference-Fourier synthesis resulted in the complete structure. Full-matrix least-squares refinement of all variables for an anisotropic displacement model converged to R and wR indices of 4.7% and 5.5%, respectively. Positional and anisotropic displacement parameters are given in Table 2, selected interatomic distances and angles in Tables 3 and 4, and a bond-valence analysis in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

DESCRIPTION OF THE STRUCTURE: COORDINATION OF THE CATIONS

Pb coordination

There is one unique Pb position surrounded by eight oxygen anions between 2.52 and 3.01 Å. Six of these oxygen atoms lie within the range 2.52–2.80 Å and form a very distorted octahedral arrangement. However, the bond-valence sum around the central Pb atom indicates that the more distant anions do have a significant interaction with the Pb, and the eight atoms of oxygen form a triangular dodecahedron. However, the bond-valence sum around the Pb is only 1.56 vu, far smaller than the ideal value of 2.0 vu. The closest oxygen atoms beyond 3.01 Å are at 3.26 and 3.54 Å, too far to be considered as forming significant bonds to the Pb atom. To exclude possible substitution of a mystery cation for Pb, we refined the site scattering at the Pb site, but it remained obstinately at 82 e, indicating complete occupancy by Pb. As discussed below, electron-microprobe analysis also indicates complete occupancy of this site by Pb (Table 6). The isotropic displacement parameter of Pb is by far the largest in the structure (Table 2). Although this is to be expected, as Pb is by far the largest cation, this value may also contain a component of static or dynamic positional disorder. Such disorder would lower the bond-valence sum at the cation site while maintaining the effective scattering at that site (as modified by the high equivalent isotropic displacement parameter). Such positional disorder is in accord with the high degree of strain (polyhedral distortion) in the structure, and suggests the occurrence of a phase transition above room temperature by which the structure attains a much less strained arrangement.

Fe coordination

There are four distinct Fe sites, each surrounded by six atoms of oxygen in distorted arrangements. The Fe–O distances span the range 1.94–2.15 Å, with <Fe–O> distances of 2.021, 2.019, 2.021 and 2.040 Å, respectively; these values are typical mean bond-lengths for octahedrally coordinated Fe^{3+}. The sum of the empirical radii is 0.645 + 1.363 = 2.008 Å, in

TABLE 5. BOND-VALENCE* TABLE FOR LUDLOCKITE

	Pb	Fe(1)	Fe(2)	Fe(3)	Fe(4)	As(1)	As(2)	As(3)	As(4)	As(5)	As(6)	As(7)	As(8)	As(9)	As(10)		Σ
O(1)			0.54	0.49		0.97										O(1)	2.00
O(2)		0.51			0.49										0.99	O(2)	1.99
O(3)			0.51		0.51								1.02			O(3)	2.04
O(4)		0.46	0.52											1.02		O(4)	2.00
O(5)	0.09		0.46	0.48						0.94						O(5)	1.97
O(6)				0.35	0.42									1.03		O(6)	1.80
O(7)		0.37			0.41				1.03							O(7)	1.81
O(8)			0.48		0.48				0.98							O(8)	1.94
O(9)	0.09	0.46	0.45					1.05								O(9)	2.05
O(10)												1.06	0.97			O(10)	2.03
O(11)	0.33			0.58											1.08	O(11)	1.99
O(12)	0.20	0.61									1.09					O(12)	1.90
O(13)						0.97		1.08								O(13)	2.05
O(14)	0.17										0.90				0.91	O(14)	1.98
O(15)	0.16			0.59						1.07						O(15)	1.82
O(16)								1.01		0.91						O(16)	1.92
O(17)											0.89	1.04				O(17)	1.93
O(18)							1.01		0.96							O(18)	1.97
O(19)				0.52	0.51		0.93									O(19)	1.96
O(20)	0.20						0.85					0.94				O(20)	1.99
O(21)	0.32	0.58				1.01										O(21)	1.91
O(22)													1.04	0.98		O(22)	2.02
Σ	1.56	2.99	2.96	3.01	2.82	2.95	2.79	3.14	2.97	2.92	2.88	3.04	3.03	3.03	2.98		

* bond-valence curves from Brown & Altermatt (1985)

reasonable accord with three of the four mean octahedron bond-lengths and slightly smaller than the fourth value, 2.040 Å; this latter difference is within the dispersion of mean bond-lengths caused by inductive structural effects. The FeO_6 octahedra are quite distorted, particularly with respect to the observed bond-angles (Table 4), which span the range 76.4–106.9°; this is a much larger range than is generally observed in inorganic structures. The distortion parameters $\Delta\ [= \sum (\langle l \rangle - l)^2/\langle l \rangle^2 \cdot n]$ and σ $[= \sum_n (\langle \theta \rangle - \theta)^2/ (n - 1)]$ are also given in Tables 3 and 4; note that there is no correspondence between Δ and σ. As with the low bond-valence sum around the Pb cation, these large distortions reflect the very strained nature of the structure.

TABLE 6. CHEMICAL COMPOSITION*
AND UNIT FORMULA OF LUDLOCKITE

As_2O_3	60.67	wt%	As^{3+}	9.93
Fe_2O_3	19.96		Fe^{3+}	4.04
PbO	14.41		Pb	1.04
Sum	95.04			

* Ca and Sb detected at the 0.x wt% level

As coordination

There are 10 crystallographically distinct As positions. Each As atom is strongly bonded to three atoms of oxygen arranged in a triangle, and the As atom lies out of the plane of the anions such that the four atoms lie at the vertices of a triangular pyramid. The As–O distances lie in the range 1.76–1.85 Å, with mean values in the range 1.77–1.82 Å. Both the As–O distances and the geometry of the coordinations are characteristic of As^{3+} (Hawthorne 1985b); thus ludlockite is an arsenite. This type of one-sided coordination is typical of stereoactive lone-pair cations, and As^{3+} is in this category, although no electron density was observed in the positions corresponding to the lone pairs. The O–As–O angles lie in the range 89–102°, with mean values in the range 95–99°; the <O–As–O> values provide an indirect measure of the pyramidal character, a value of 120° being characteristic of planar triangular coordination.

STRUCTURE TOPOLOGY

Nature has really outdone herself with the structure of ludlockite, as the initially simple formula concealed a structure of considerable elegance and complexity. An important element of the structure is shown in Figure 1. FeO_6 octahedra share edges to form α–PbO_2-like $[M\phi_4]$ chains that extend along [100] (ϕ: unspeci-
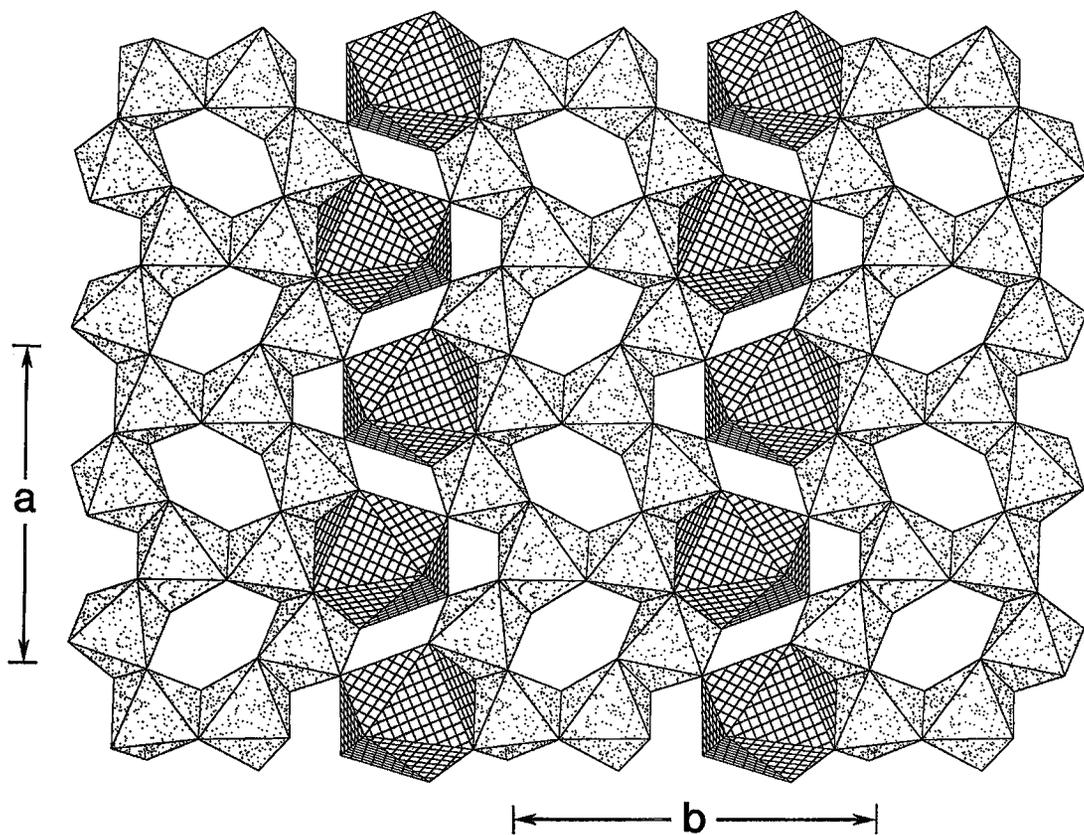
FIG. 1. Part of the crystal structure of ludlockite projected onto (001); FeO$_6$ octahedra are random dot-shaded, PbO$_8$ polyhedra are 4^4-lattice shaded. Adjacent α-PbO$_2$-like chains of octahedra connect *via* the common O(3)–O(8) edge of the Fe(2)O$_6$ and Fe(4)O$_6$ octahedra.

fied anion). Pairs of these chains fuse along [010] by sharing edges to form a strip of octahedra that resembles a slice of the dioctahedral sheet in gibbsite. These strips extend along [100] and are cross-linked in the [010] direction by PbO$_8$ triangular dodecahedra to form the sheet illustrated in Figure 1. We can consider this sheet as a modified sheet of edge-sharing octahedra extracted from an array of close-packed anions. As shown in Figure 2, the prototype sheet is an array of edge-sharing octahedra in which half the octahedra are occupied by cations. In one row of octahedra (parallel to [010]), alternate octahedra are occupied, whereas in the other row of octahedra (parallel to [010]), alternate pairs of octahedra are occupied; these two types of rows alternate along [100] to form the sheet (Fig. 2). The sheet in Figure 1 is formed from the sheet in Figure 2 by omitting the central two anions (A and B in Fig. 2) of the vacant pair of octahedra in each alternate row and replacing them by a Pb atom, as shown conceptually in Figure 2.

The arsenite groups link by sharing corners to form rather convoluted topologically linear groups of the form [As$_5$O$_{11}$]. There are two crystallographically distinct groups of this form, but as is apparent from Figure 3, the two are almost identical in their geometrical characteristics, suggesting very strong pseudosymmetry in this structure. The relative arrangement of these groups is shown in Figure 4, in which the groups above the sheet of octahedra are shown with shaded bonds, and the groups below the sheet of octahedra are shown with unshaded bonds. As is apparent from the positions of the Pb atoms, the groups are arranged in rows above and below the octahedra of the sheet shown in Figure 1; note that Figure 4 effectively displays the convoluted nature of the [As$_5$O$_{11}$] groups.

Figure 5 shows the structural unit of ludlockite with the lower [As$_5$O$_{11}$] groups omitted for clarity. The [As$_5$O$_{11}$] groups embrace the chains of octahedra like geometrical spiders consuming their prey. In each
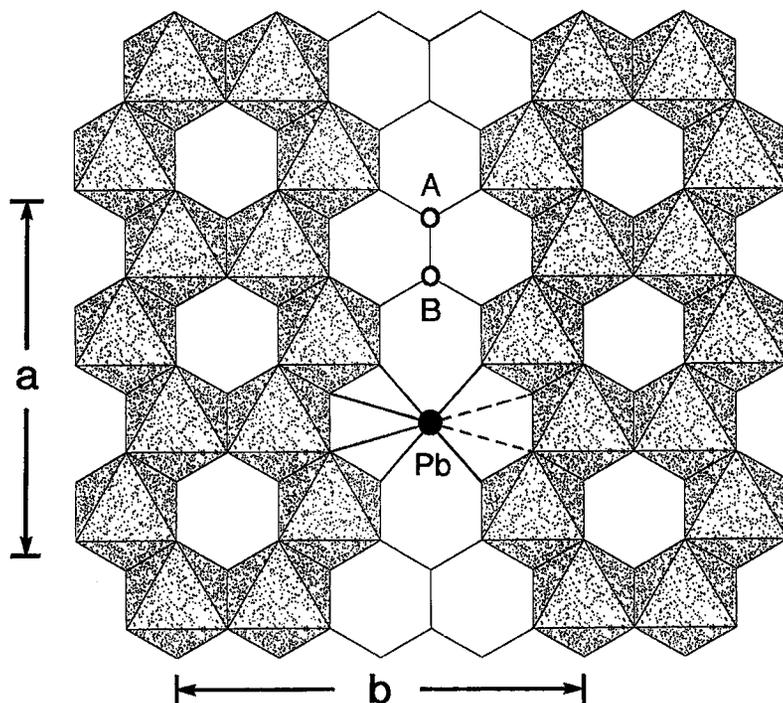
FIG. 2. Idealized sheet of octahedra showing the pattern of occupied and unoccupied octahedra and the omission of two anions (A and B), each adjacent to three vacant octahedra, to form the cavity that is occupied by the Pb cation; random dot-shaded octahedra: Fe; large solid circle: Pb; the orientation of this idealized sheet is the same as that of the observed sheet (Fig. 1) in ludlockite.
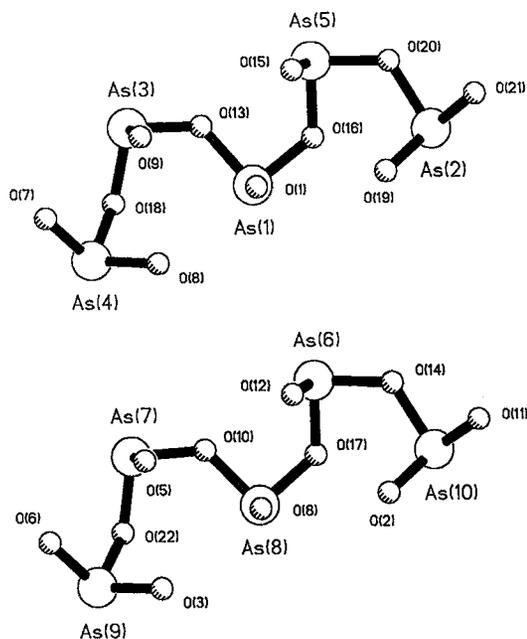

FIG. 3. The two symmetrically distinct [As$_5$O$_{11}$] groups projected onto (001); large circles are As^{3+}, small shaded circles are oxygen atoms, and the heavy black lines are chemical bonds. Note that the two groups are topologically (and, geometrically, virtually) identical, although they are crystallographically distinct.

[As$_5$O$_{11}$] group, terminal AsO$_3$ pyramids share two anions with the octahedra, whereas the three central AsO$_3$ groups share only one anion with the octahedra, the others bridging between neighboring AsO$_3$ groups. In each [As$_5$O$_{11}$] group, one bridging anion also is bonded to Pb, and each of the terminal AsO$_3$ groups shares an edge with a PbO$_8$ triangular dodecahedron. The formula of the structural unit is the formula of ludlockite, as there are no interstitial species present.

The attitude of adjacent sheets is shown in Figure 6. There is significant separation between the sheets. All As^{3+} atoms of one sheet are beyond 3 Å from the anions of the adjacent sheet (Table 3), and the mode of interaction between the sheets is not clear. In some cases, it is considered that there is a weak but significant interaction between As^{3+} and the anions that lie beyond the stereoactive lone-pair of electrons. However, this is somewhat difficult to establish with any certainty. Is there some unusual interaction between opposing lone-pairs of electrons across the interstitial space? Is the interaction solely a Van der Waals attraction? Whatever the mechanism, it is certain that the interunit interaction is very weak, in accord with the perfect cleavage observed parallel to the sheets.
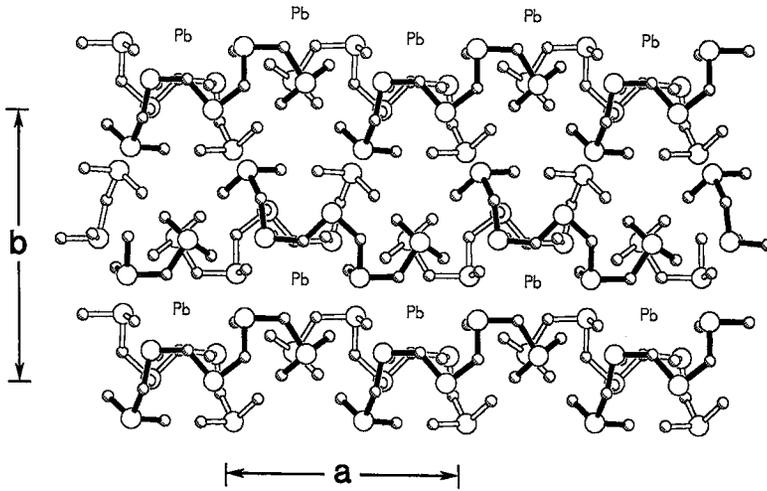
FIG. 4. The assemblage of [As$_5$O$_{11}$] groups projected onto (001); legend as in Fig. 3, except groups above the sheet of octahedra (not shown) have their bonds shaded in black, whereas groups below the sheet of octahedra have their bonds unshaded, and the Pb positions are indicated by the symbol Pb. The [As$_5$O$_{11}$] groups form rather convoluted strips that lie to either side of the rows of Pb atoms.
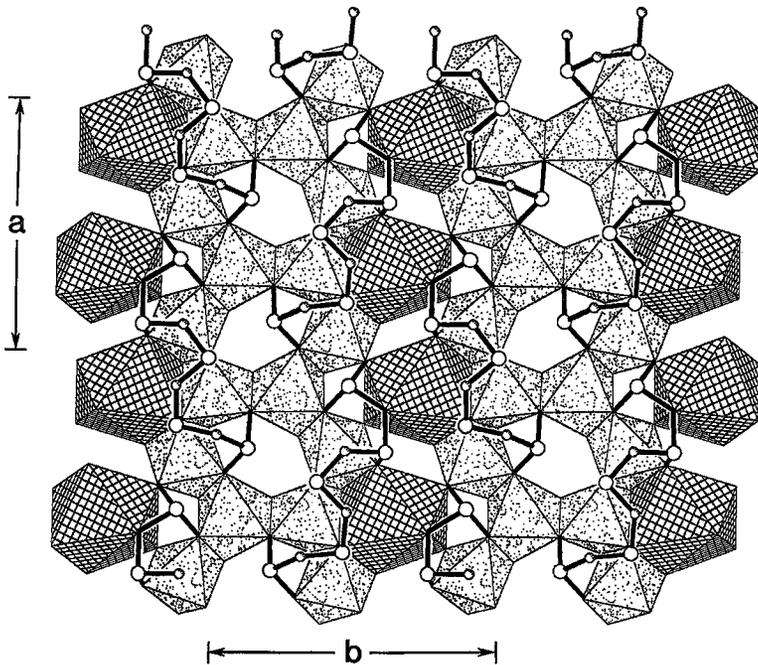

FIG. 5. The crystal structure of ludlockite projected onto (001), showing the structural unit; legend as in Figs. 1 and 3. Although the polymerized arsenite groups seem to wrap themselves around the strips of octahedra, this is somewhat illusory, as they only form finite groups rather than infinite chains.
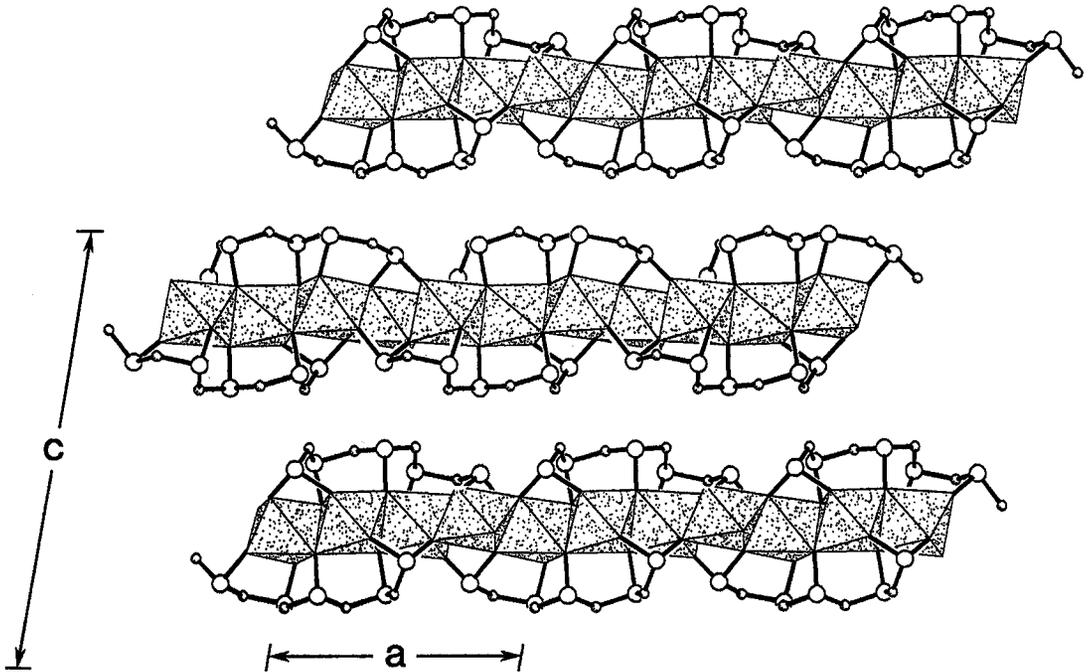
FIG. 6. The crystal structure of ludlockite projected onto (010), showing adjacent structural units stacked along (001); legend as in Figs. 1 and 3.

THE CHEMICAL FORMULA OF LUDLOCKITE

Counting the atoms in the unit cell of ludlockite leads to the chemical formula $PbFe_4^{3+}As_{10}^{3+}O_{22}$, different from the current formula $(Fe,Pb)As_2O_6$ in which (most of) the As is assumed to be pentavalent. The <Fe–O> bond-lengths, 2.02–2.04 Å, show Fe to be entirely in the trivalent state, in accord with the Mössbauer results quoted by Embrey *et al.* (1977). Possibly, the slightly longer value, 2.04 Å, for the Fe(4) site, compared with 2.03 Å for the Fe(1), Fe(2) and Fe(3) sites, could be due to a small amount of Fe^{2+} (~4% of the total Fe); conversely, the slightly longer <Fe(4)–O> distance could result from some minor inductive (structural) effect. All 10 of the As positions show triangular pyramidal coordination, with $<^{[3]}As–O>$ distances (1.77–1.82 Å) and $<O–^{[3]}As–O>$ angles (95.3–99.0°) completely characteristic of As^{3+} (with a stereoactive lone-pair of electrons). There is no indication of As^{5+}, which is generally tetrahedrally coordinated with a $<^{[4]}As^{5+}–O>$ distance of ~1.79 Å. Furthermore, site-scattering refinement at the Pb site shows it to be completely occupied by Pb. The resulting formula, $PbFe_4^{3+}As_{10}^{3+}O_{22}$, is neutral.

The results of electron-microprobe analysis (Table 6) are in accord with this formula: the unit formula, calculated on the basis of 22 oxygen atoms, is $Pb_{1.04}Fe_{4.04}^{3+}As_{9.93}^{3+}O_{22}$, using the valence states of the cations determined from the stereochemistry of their structural environment. The analytical total (Table 6) is low at ~95 wt%. This could result from problems producing a flat surface to analyze, combined with possible charging effects due to the difficulty of forming a continuous coat of carbon on a rough surface that also may tend to exfoliate when in vacuum. Nevertheless, the analytical results are completely in accord with the formula determined from structure solution and refinement.

Pseudosymmetry in ludlockite

There is a significant degree of pseudosymmetry in the ludlockite structure. Inspection of the structural unit in Figure 5 shows the presence of pseudo-*a*-glide planes at $y \approx \pm\frac{1}{4}$, pseudo-diad axes parallel to [010] at $x \approx \frac{1}{4}$ and $\frac{3}{4}$, and a pseudo-center of symmetry at $x \approx 0$, $y \approx \frac{1}{4}$. The *structural unit* thus has pseudo-symmetry *P2/a* in the (conventional) monoclinic second setting, with the origin of the pseudo-unit-cell lying at the center of the single vacant octahedron of the sheet (Figs. 2, 5). The pseudosymmetry within the structural unit is particularly notable in regard to the two distinct $[As_5O_{11}]$ groups (Fig. 3). Despite the fact that they are symmetrically distinct, they are topologically identical and geometrically extremely similar.

The true symmetry of ludlockite is triclinic $A\bar{1}$, and the interaxial angles differ markedly from those required by monoclinic symmetry: specifically, $\alpha = 101.84$ and $\gamma = 90.60°$. Thus γ is close to the monoclinic requirement that $\alpha = \gamma = 90°$, but α deviates considerably from this condition. Furthermore, the true center of symmetry in ludlockite occurs at the boundary between the structural unit and the interstitial space (Fig. 6), rather than within the sheet of octahedra. However, if the adjacent sheets are shifted in the (001) plane such that $\alpha = \gamma = 90°$, the symmetry of the structure can become monoclinic $A2/a$ with the origin of the unit cell at the center of the empty octahedron in the sheet. This suggests the presence of a very interesting phase transition in ludlockite, whereby the structure has $A2/a$ geometry at high temperature and inverts to $A\bar{1}$ symmetry on cooling, the change involving a drastic rearrangement of the interactions between adjacent sheets. It is not beyond the realms of possibility that ludlockite crystallized as a close-packed structure with octahedrally coordinated As^{3+} with non-stereoactive lone-pairs of electrons, and the transition involved non-stereoactive $\rightarrow$ stereoactive

behavior of the lone-pair electrons of As^{3+}, inducing a radical change in structure from a close-packed arrangement of octahedra to the currently observed sheet-structure arrangement. This possibility is currently under investigation.

Relation to other structures

The most common occurrence of (AsO_3) triangular pyramids in minerals (Hawthorne 1985b, 1986) is as a discrete (AsO_3) group. However, several minerals with polymerized (AsO_3) groups are known, and ludlockite occupies an interesting position in the range of known (AsO_3) polymerizations. Corner-sharing dimers of $[As_2O_5]$ occur in the structures of paulmooreite, $Pb_2[As_2O_5]$ (Araki et al. 1980), schneiderhöhnite, $Fe^{2+}Fe^{3+}_3(AsO_3)[As_2O_5]_2$ (Hawthorne 1985b) and fetiasite, $(Fe^{2+},Fe^{3+},Ti)_3$ $O_2[As_2O_5]$ (Graeser et al. 1994). Stenhuggarite, $CaFeSbAs_2O_7$ (Coda et al. 1977), has an (AsO_3) monomer and an $[As_4O_8]$ ring, and had the largest known finite arsenite cluster in a mineral structure. This $[As_4O_8]$ ring has now been surpassed in size by
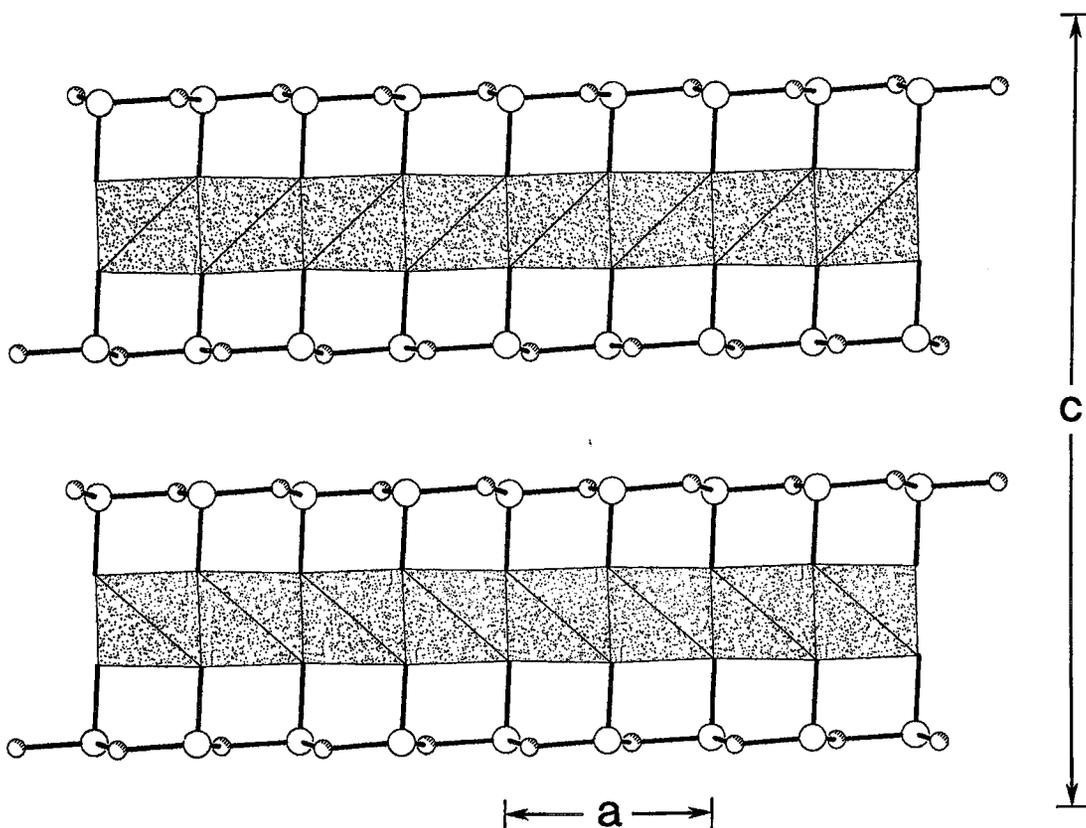

FIG. 7. The crystal structure of leitite projected onto (010), showing the sheet-like structural units stacked along [001]. ZnO_4 tetrahedra are random-dot shaded, large circles are As^{3+}, and small shaded circles are oxygen atoms.

the $[As_5O_{11}]$ clusters in ludlockite. There is then a gap in size of the polymerized clusters until the $[As_2O_4]$ infinite chains in trippkeite, $Cu[As_2O_4]$ (Pertlik 1975), and leiteite, $Zn[As_2O_4]$ (Ghose *et al.* 1987). This behavior is similar to that exhibited by the silicate structures, in which chain fragments occur from two to five silicate groups long, followed by a gap until the infinite $[SiO_3]$ chain is stable (Hawthorne 1984).

Most oxy-arsenite minerals have framework structures. Ludlockite is the one exception for arsenite minerals with octahedrally coordinated cations. However, leiteite (Ghose *et al.* 1987) also is a sheet structure (Fig. 7), consisting of corner-linked sheets of ZnO_4 tetrahedra decorated by $[AsO_2]$ chains. As with ludlockite, the intersheet linkage occurs *via* very long As–O bonds, resulting in a perfect {001} cleavage.

REFERENCES

ARAKI, T., MOORE, P.B. & BRUNTON, G.D. (1980): The crystal structure of paulmooreite, $Pb_2[As_2O_5]$: dimeric arsenite groups. *Am. Mineral.* **65**, 340-345.

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.

CODA, A., DAL NEGRO, A., SABELLI, C. & TAZZOLI, V. (1977): The crystal structure of stenhuggerite. *Acta Crystallogr.* **B33**, 1807-1811.

CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* **53**, 1891-1898.

———— & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree–Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.

EMBREY, P.G., HEY, M.H. & DAVIS, R.J. (1977): Ludlockite: a new mineral from Tsumeb. *Mineral. Rec.* **8**, 91-94.

GHOSE, S., SEN GUPTA, P.K. & SCHLEMPER, E.O. (1987): Leiteite, $ZnAs_2O_4$: a novel type of tetrahedral layer structure with arsenite chains. *Am. Mineral.* **72**, 629-632.

GRAESER, S., SCHWANDER, H., DEMARTIN, F., GRAMACCIOLI, C.M., PILATI, T. & REUSSER, E. (1994): Fetiasite $(Fe^{2+},Fe^{3+},Ti)_3O_2[As_2O_5]$, a new arsenite mineral: its description and structure determination. *Am. Mineral.* **79**, 996-1002.

HAWTHORNE, F.C. (1984): The crystal structure of ruizite, a sorosilicate with an $[Si_4O_{13}]$ cluster. *Tschermaks Mineral. Petrogr. Mitt.* **33**, 135-146.

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

———— (1985b): Schneiderhöhnite $Fe^{2+}Fe_3^{3+}As_5^{3+}O_{13}$, a densely packed arsenite structure. *Can. Mineral.* **23**, 675-679.

———— (1986): Structural hierarchy in $^{IV}M_x^{III}T_y\phi_z$ minerals. *Can. Mineral.* **24**, 625-642.

———— (1990): Structural hierarchy in $M^{[6]}T^{[4]}\phi_n$ minerals. *Z. Kristallogr.* **192**, 1-52.

———— (1994): Structural aspects of oxide and oxysalt crystals. *Acta Crystallogr.* **B50**, 481-510.

OBERTI, R., UNGARETTI, L., CANNILLO, E. & HAWTHORNE, F.C. (1992): The behavior of Ti in amphiboles. I. Four- and six-coordinate Ti in richterite. *Eur. J. Mineral.* **4**, 425-439.

PERTLIK, F. (1975): Verfeinerung der Kristallstruktur von synthetischem Trippkeit, $CuAs_2O_4$. *Tschermaks Mineral. Petrogr. Mitt.* **22**, 211-217.