

THE CRYSTAL STRUCTURE OF PLUMBOJAROSITE $\text{Pb}[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]_2$

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ABSTRACT

The crystal structure of plumbojarosite, $\text{Pb}[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]_2$, has been refined to a residual $R = 1.60\%$ from 1274 unique reflections (1199 observed) obtained by averaging five segments of absorption-corrected X-ray-intensity data, collected with graphite-monochromated $\text{MoK}\alpha$ radiation. The structure is rhombohedral, space group $R\bar{3}m$, with (hexagonal) cell dimensions $a = 7.3055(7)$, $c = 33.675(2)$ Å. The prediction of Hendricks (1937) that plumbojarosite has a two-tiered jarosite structure with the K sites along z being alternately vacant and filled with Pb, is confirmed in essence. The actual occupancies of these sites are 0.039 and 0.961(2). The two sulfate ions, each located on the threefold axis, have comparable bond-lengths and angles, and these differ markedly from those found in jarosite (Kato & Miura 1977). The unique independent Fe atom is co-ordinated in an irregular octahedron by four (equatorial) hydroxyl groups and two (axial) oxygen atoms, whose bond lengths range from 1.953(1) to 2.093(1) Å. Layers of $\text{Fe}(\text{OH})_4\text{O}_2$ octahedra are stacked parallel to the (0001) plane at $z = (2n + 1)/12$. Within these octahedra, two opposite triangular faces, each composed of the axial oxygen atom and two hydroxyl groups, form part of the co-ordination icosahedron around each of the Pb atoms. The $\text{Fe}(\text{OH})_4\text{O}_2$ octahedra thus form a bridge between the icosahedra. The hydrogen atoms of the hydroxyls were observed and refined with isotropic thermal parameters; the two O-H bonds are of equal length.

Keywords: plumbojarosite, stoichiometric lead jarosite, two-tiered jarosite structure, alternate near-vacant cation sites, structure refinement to $R = 1.60\%$.

SOMMAIRE

La structure cristalline de la plumbojarosite, $\text{Pb}[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]_2$, a été affinée jusqu'au résidu $R = 1.60\%$ sur 1274 réflexions indépendantes (dont 1199 observées), obtenues en faisant la moyenne de cinq ensembles uniques de données d'intensité de rayons X, mesurées en rayonnement $\text{MoK}\alpha$ monochromatisé sur graphite, et corrigées pour l'absorption. La structure est rhomboédrique, le groupe spatial $R\bar{3}m$; les dimensions de la maille hexagonale sont $a = 7.3055(7)$, $c = 33.675(2)$ Å. La prédiction d'Hendricks (1937), suivant laquelle la structure de la plumbojarosite serait celle d'une jarosite dont les sites de K le long de z seraient alternativement vacants et occupés par le Pb, est essentiellement confirmée. L'occupation affinée de ces sites est 0.039 et 0.961(2). Les deux ions sulfates, situés chacun sur l'axe d'ordre trois, ont des angles et distances de liaison comparables, mais nettement différents de ceux

qu'on observe dans la jarosite (Kato & Miura 1977). La coordination de l'atome de Fe indépendant est un octaèdre difforme, avec quatre hydroxyles équatoriaux et deux atomes d'oxygène axiaux. La longueur des liaisons au Fe varie entre 1.953(1) et 2.093(1) Å. Les couches d'octaèdres $\text{Fe}(\text{OH})_4\text{O}_2$, parallèles au plan (0001), sont aux cotes $z = (2n + 1)/12$. Deux faces opposées de ces octaèdres, chacune composée d'un atome axial d'oxygène et de deux hydroxyles, font partie de l'icosaèdre de coordination entourant chacun des atomes Pb. Ces octaèdres forment ainsi un pont entre les icosahèdres. Les atomes d'hydrogène des hydroxyles ont été observés et affinés avec paramètres thermiques isotropes; les deux liaisons O-H sont d'égale longueur.

Mots-clés: plumbojarosite, jarosite plombifère stoechiométrique, structure de type jarosite ordonnée, sites cationiques alternés quasi-vacants, affinement jusqu'à $R = 1.60\%$.

INTRODUCTION

Plumbojarosite, $\text{Pb}[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]_2$, is a member of the alunite group (Palache *et al.* 1951, Fleischer 1983), which includes alunite itself, jarosite, and various minerals with alkali cations substituting for K in these two. It occurs widely in the oxidized part of sulfide deposits, and commonly incorporates significant amounts of Ag that was present in the original sulfide ore. Occasionally, the quantity of plumbojarosite has been large enough to permit its being processed for its Pb and Ag values (Dutrizac & Jambor 1984). Synthetic plumbojarosite, commonly referred to as lead jarosite in metallurgical-chemical publications, is often produced during the hydrometallurgical processing of Pb-bearing concentrates and especially during the pressure leaching of Zn-Pb concentrates. The formation of synthetic plumbojarosite is usually undesirable as this phase collects much of the Ag in the feed (Dutrizac & Chen 1984). Although a plumbojarosite concentrate can be recuperated, this is not a particularly desirable feed for further processing as it has a relatively low Pb-Ag content and requires considerable heat for its decomposition.

The plumbojarosite formed during hydrometallurgical processing commonly incorporates significant amounts of Ag, Cu, H_3O and Na. Efforts have been made to avoid the losses of Pb and Ag into the jarosite and natrojarosite by causing alkali ions to substitute for Pb or Ag (or both), and indeed, con-

siderable work is being done to avoid jarosite formation altogether. Such studies require a detailed knowledge of the crystal structures of the alunite family and, in particular, a knowledge of which crystal sites are occupied, and which elements substitute in specific sites. Although such information is available for stoichiometric end-member jarosite, natrojarosite and alunite, the data for plumbojarosite are considerably sparser. This paper describes a study of stoichiometric plumbojarosite to define the crystal structure and its relationship to that of the other members of the alunite family.

EXPERIMENTAL

Crystals of plumbojarosite from the Tintic Standard mine, Dividend, U.S.A., obtained from the U.S. National Museum (Catalogue #104271), were examined extensively with precession photography. The majority of the crystals show minor splitting of spots, principally a minor rotation of the twin components about the hexagonal [0001] direction, and clearly visible in the $hki0$ reflections. No evidence of twinning was seen in the $000l$ reflections. Several apparently excellent specimens were finally found, and one was selected for the structure determination. Throughout this paper, the *hexagonal* system of indexing will be used, rather the *rhombohedral*. The crystal forms observed are the pinacoid {0001} and the trigonal antiprism {10 $\bar{1}$ 4}, with the following distances (in mm) between the crystal faces: 0.036 for (0001), (000 $\bar{1}$); 0.186 for (10 $\bar{1}$ 4), ($\bar{1}$ 014); 0.200 for ($\bar{1}$ 104), (1 $\bar{1}$ 04); 0.181 for (0 $\bar{1}$ 14), (01 $\bar{1}$ 4). Prior to data collection, reflection profiles were examined in various regions of reciprocal space, and no untoward reflections or splitting of reflections were observed. The cell dimensions were refined by least squares (Busing 1970) for the observed 2θ , χ , ϕ and ω values of 72 reflections in the range $51 < 2\theta < 67^\circ$ for $\lambda(\text{MoK}\alpha_1) = 0.70930 \text{ \AA}$, and are given in Table 1.

Intensity data were collected using graphite-monochromated MoK α radiation, in a θ - 2θ scan mode at a rate of $2^\circ (2\theta)/\text{min.}$, and a scan range of

$1.6^\circ (2\theta)$ increasing with K α dispersion. Background counts were measured for 20 seconds on either side of the reflection. The unique segment of reciprocal space was defined as h, k, i, l for $h, k, l \geq 0$, and in terms of these indices, the data were collected to $2\theta = 80^\circ$ for the following five segments: $h, k, l; i, h, l; -h, -i, l; -h, -k, -l; h, i, -l$. The first three are equivalent in space groups $R\bar{3}m$ and $R3m$. The latter two differ from the first three by virtue of the anomalous scattering component of the structure factor in the event of the space group being $R\bar{3}m$ (noncentrosymmetric). The problem of measurement of the intensity of the low-angle ($2\theta = 3.63^\circ$) 0003 and 000 $\bar{3}$ reflections, where scatter from the collimators overlaps the low- 2θ background and reflection positions, was resolved as follows: a 48-point step-scan was collected six times through the peak and averaged, and compared with an averaged step-scan of identical 2θ range, but with the crystal offset from the scattering vector by 3° . The latter profile was considered as background, and was subtracted from the former profile to give the net intensity. Absorption corrections were applied to the data using a Gaussian integration procedure (Gabe & O'Byrne 1970) using a grid of $10 \times 10 \times 10$ points and $\mu = 127.5 \text{ cm}^{-1}$. The absorption-correction factors varied between 1.48 and 10.65. A total of 1274 independent reflections was collected in each segment, and a detailed comparison was carried out to see whether the first three segments differ significantly from the last two. No difference was found as a result of this comparison, and the factor of overall agreement $[\sum |I - \bar{I}| / \sum I]$ between the five absorption-corrected segments is 1.89%. Of the 1274 unique reflections, 1199 are considered observed on the criterion that $I_{\text{obs}} > 1.65\sigma(I)$.

STRUCTURE DETERMINATION

The structure was solved by Patterson and Fourier methods, using as a model the known structures of alunite and jarosite [Menchetti & Sabelli (1976) and especially the model proposed by Hendricks (1937) for plumbojarosite]. The structure refinement was nearly complete when the author obtained the bond lengths (but *not* the structure parameters) for plumbojarosite from a previous analysis by Prof. Toshio Kato (Kato 1979 and priv. comm.). As the latter determination had resulted in an agreement factor R of 5.8%, and as the present refinement was already well below this, the present work was continued and resulted in a model with significantly different bond-lengths from those given by Kato (see Discussion). The refinement was carried out using the neutral scattering form-factors for Pb, Fe, S and O from Cromer & Mann (1968), and the hydrogen curve of Stewart *et al.* (1965). The components for the anomalous scattering were taken from Cromer & Liberman (1970). In all the calculations for the

TABLE 1. CRYSTAL DATA

Plumbojarosite, $\text{Pb}[\text{Fe}_2(\text{SO}_4)_2(\text{OH})_6]_2$
Formula Weight: 1130.60
Source: Tintic Standard mine, Dividend, Utah, U.S.A., obtained from U.S. National Museum, Reference # 104271.
Microprobe analysis: $\text{Pb}_{0.99}\text{Fe}_{5.85}\text{S}_{4.06}$, (based on O=28)
Crystal System: Rhombohedral, (hexagonal axes), $a = 7.3055(7)$, $c = 33.675(2) \text{ \AA}$.
Systematic absences: $hkiZ, -h + k + l + 3n$
Space group: $R\bar{3}m, (\#166)$.
Density: $D_{\text{calc}} = 3.618 \text{ g cm}^{-3}$; D_{obs} not measured.
Linear absorption coefficient: $\mu(\text{MoK}\alpha) = 127.5 \text{ cm}^{-1}$.
X-ray data: 5 equivalent segments collected to $2\theta=80^\circ$, absorption-corrected and averaged to give 1274 independent reflections, [1199 with $I > 1.65\sigma(I)$]. Refined to $R = 1.60\%$.

TABLE 2. POSITIONAL AND THERMAL ($\times 100$) PARAMETERS WITH STANDARD DEVIATIONS

Atom site*	site symmetry	x	y	z	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	
Pb(1)	3b	$\bar{3}m$.0	.0	.0	$2xU_{12}$	$2xU_{12}$	2.38(27)	1.93(12)	.0	.0
S(1)	6c	$3m$.0	.0	.15605(2)	$2xU_{12}$	$2xU_{12}$	0.714(23)	0.336(8)	.0	.0
O(1)	6c	$3m$.0	.0	.19934(7)	$2xU_{12}$	$2xU_{12}$	0.75(8)	0.67(3)	.0	.0
O(2)	18h	m	.22315(11)	2x	.02688(4)	1.75(5)	$2xU_{12}$	1.16(5)	0.41(2)	0.05(2)	$2xU_{13}$
O(3)	18h	m	.13053(12)	2x	-.06940(4)	0.79(3)	$2xU_{12}$	1.59(5)	0.59(3)	-.24(2)	$2xU_{13}$
H(3)	18h	m	.1700(40)	2x	-.0520(12)	5.6(1.4)	—	—	—	—	—
Pb(2)	3a	$\bar{3}m$.0	.0	.5	$2xU_{12}$	$2xU_{12}$	1.247(8)	1.056(4)	.0	.0
S(2)	6c	$3m$.0	.0	.65456(2)	$2xU_{12}$	$2xU_{12}$	0.721(24)	0.416(8)	.0	.0
O(4)	6c	$3m$.0	.0	.69971(7)	$2xU_{12}$	$2xU_{12}$	0.70(8)	0.82(3)	.0	.0
O(5)	18h	m	.22315(11)	2x	.52569(4)	1.42(4)	$2xU_{12}$	1.13(3)	0.38(2)	0.07(2)	$2xU_{13}$
O(6)	18h	m	.12303(11)	2x	.43485(4)	0.67(3)	$2xU_{12}$	1.42(5)	0.39(2)	-.09(2)	$2xU_{13}$
H(6)	18h	m	.1803(41)	2x	.4430(13)	6.0(1.5)	—	—	—	—	—
Fe	18h	m	.16457(02)	2x	.08228(1)	0.660(7)	$2xU_{12}$	1.064(10)	0.248(5)	0.010(4)	$2xU_{13}$

The occupancies of Pb(1) [0,0,0] and Pb(2) [0,0, $\frac{1}{2}$] are 0.039 and 0.961(2) respectively. *The "site" column is a combination of the multiplicity and the Wyckoff letter (International Tables, A, 1983). The anisotropic temperature-factors are expressed as follows: $T = \exp[-2\pi^2(U_{11}a^2h^2 + 2U_{12}ab*hk + \dots)]$. The two groups of atoms above are related to each other by a translation of approximately $a/2$.

structure determination and refinement, the XRAY-76 system of crystallographic computer-programs was used (Stewart *et al.* 1976). Anisotropic thermal refinement was used for all atoms heavier than hydrogen. Because results of microprobe analyses of a number of plumbojarosite crystals in the specimen examined indicated stoichiometry, the occupancy parameters of the two Pb atom sites were refined as α and reset as $1-\alpha$, respectively. When refinement had converged for the heavier atoms, the two hydrogen atoms were located from a difference map, and their positions and isotropic thermal parameters were included in the final cycles of refinement. The final agreement-factor R was 1.60%, and the maximum relative shift $[\Delta\rho/\sigma(\rho)]$ was less than 0.004. Attempts to refine the structure using ionized-species form-factors resulted in the same parameters within 1.5σ , but gave a higher agreement factor R of 1.72%, and consequently this model is rejected. The final positional, thermal and occupancy parameters, with their standard deviations, are listed in Table 2. The final difference-map, calculated after the last least-squares cycle, was completely featureless. The observed and calculated structure-factors are given in Table 3, and are available at nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DESCRIPTION OF THE STRUCTURE

The basic elements of a jarosite structure (Menchetti & Sabelli 1976, Kato & Miura 1977) can be described as follows: three corner-sharing $\text{Fe}(\text{OH})_4\text{O}_2$ octahedra, centred at $z = 1/6, 3/6, 5/6$, are located around the threefold axis with the three

apical Fe-O bonds tilted toward the axis. These three oxygen atoms form the base of the sulfate tetrahedron, which is on the threefold axis. The sulfate tetrahedra form layers close to $z = 0, 1/3, 2/3$, and are not joined to each other. The centres of symmetry (e.g., at the origin) give rise to a second trio of sulfate tetrahedra, pointing in the opposite sense along z , which form part of the same layer. At these centres of symmetry, the alkali cations are found inside oxygen and hydroxyl icosahedra. The structure is thus made up of layers of tilted $\text{Fe}(\text{OH})_4\text{O}_2$ octahedra joining layers of combined sulfate tetrahedra and alkali co-ordination icosahedra.

The present structure is noteworthy in that the presence of the divalent cation Pb results in a doubling of the c axis of the hexagonal cell when compared with jarosite, with a remarkable degree of ordering in the "vacant" [occupancy = 0.039] and "occupied" [occupancy = 0.961(2)] Pb positions. These are the $3a$ (0,0,0) and $3b$ (0,0,1/2) space-group sites (see Table 3). Hendricks (1937) had correctly predicted the reason for the doubling of the hexagonal cell when a divalent cation, in this case Pb, replaces K in the jarosite structure, except that he had presumed there would be fully occupied sites alternating with vacant sites, *i.e.*, partial occupancy was not considered. The doubling of the c axis results in two crystallographically different cation positions and co-ordination icosahedra and two different sulfate tetrahedra. The layers of sulfate tetrahedra are stacked in twelfths at $z = 0, 4, 8$ and $2, 6, 10$, respectively, with the $\text{Fe}(\text{OH})_4\text{O}_2$ octahedra, which join the above layers, being centred on $z = 1, 3, 5, 7, 9, 11$ twelfths.

The bond lengths and angles of the co-ordination polyhedra around the Pb atoms are given in Table

TABLE 4. BOND LENGTHS AND INTERBOND ANGLES WITH STANDARD DEVIATIONS

1. Co-ordination of Pb(1), [Occupancy = 0.039]. Table of angles, (°).											Superscripts refer to the following equivalent positions:				
Bond lengths: 6x Pb-O(2)=2.965(1), 6x Pb-O(3)=2.862(1)Å. E.s.d. of angles = 0.03° or less.											1.	-w.	-y.	1-s	
Atom	O(2) ²	O(2) ⁴	O(2) ⁸	O(2) ¹⁰	O(2) ¹⁴	O(3)	O(3) ²	O(3) ⁴	O(3) ⁸	O(3) ¹⁰	O(3) ¹⁴	2.	-w.	-y.	-s
O(2)	180.	111.11	68.89	111.11	68.89	72.52	107.48	121.61	58.39	121.61	58.39	3.	1/3-w.	2/3-y.	2/3-s
O(2) ²	-	68.89	111.11	68.89	111.11	107.48	72.52	58.39	121.61	58.39	121.61	4.	-y.	w-y.	s
O(2) ⁴	-	-	180.	111.11	68.89	121.61	58.39	72.52	107.48	121.61	58.39	5.	1/3-y.	2/3+w-y.	-1/3+s
O(2) ⁸	-	-	-	68.89	111.11	58.39	121.61	107.48	72.52	58.39	121.61	6.	2/3-y.	1/3+w-y.	1/3+s
O(2) ¹⁰	-	-	-	-	180.	121.61	58.39	121.61	58.39	72.52	107.48	7.	-y.	y-w.	1-s
O(2) ¹⁴	-	-	-	-	-	58.39	121.61	58.39	121.61	107.48	72.52	8.	-y.	y-w.	-s
O(3)	-	-	-	-	-	-	180.	120.02	59.98	120.02	59.98	9.	-2/3+y.	-1/3+y-w.	2/3-s
O(3) ²	-	-	-	-	-	-	-	120.02	59.98	120.02	59.98	10.	-y-w.	-w.	s
O(3) ⁴	-	-	-	-	-	-	-	-	180.	59.98	120.02	11.	1/3+y-w.	2/3-w.	-1/3+s
O(3) ⁸	-	-	-	-	-	-	-	-	-	120.02	59.98	12.	-1/3+y-w.	1/3-w.	1/3+s
O(3) ¹⁰	-	-	-	-	-	-	-	-	-	-	180.	13.	w-y.	w.	1-s
O(3) ¹⁴	-	-	-	-	-	-	-	-	-	-	-	14.	w-y.	w.	-s
												15.	1/3+w-y.	-1/3+w.	2/3-s
2. Co-ordination of Pb(2), [Occupancy = 0.961(2)]. Table of angles, (°).															
Bond lengths: 6x Pb-O(5)=2.953(1), 6x Pb-O(6)=2.690(1)Å. E.s.d. of angles = 0.03° or less.															
Atom	O(5) ¹	O(5) ⁴	O(5) ⁷	O(5) ¹⁰	O(5) ¹³	O(6)	O(6) ¹	O(6) ⁷	O(6) ¹⁰	O(6) ¹³					
O(5)	180.	111.80	68.20	111.80	68.20	71.68	108.33	121.03	58.97	121.03	58.97				
O(5) ¹	-	68.20	111.80	68.20	111.80	108.33	71.68	58.97	121.03	58.97	121.03				
O(5) ⁴	-	-	180.	111.80	68.20	121.03	58.97	71.68	108.33	121.03	58.97				
O(5) ⁷	-	-	-	68.20	111.80	58.97	121.03	108.33	71.68	58.97	121.03				
O(5) ¹⁰	-	-	-	-	180.	121.03	58.97	121.03	58.97	71.68	108.33				
O(5) ¹³	-	-	-	-	-	58.97	121.03	58.97	121.03	108.33	71.68				
O(6)	-	-	-	-	-	-	180.	60.15	119.85	60.15	119.85				
O(6) ¹	-	-	-	-	-	-	-	119.85	60.15	119.85	60.15				
O(6) ⁷	-	-	-	-	-	-	-	-	180.	60.15	119.85				
O(6) ¹⁰	-	-	-	-	-	-	-	-	-	119.85	60.15				
O(6) ¹³	-	-	-	-	-	-	-	-	-	-	180.				
3. Co-ordination of Fe:											Non-bonded O...O distances (Å), (edges of octahedron).				
Atom	d(Å)	O(5) ⁸	O(6) ⁵	O(3) ⁸	O(6) ¹³	O(3) ¹⁴									
O(2)	2.007(1)	177.53(2)°	92.87(4)°	91.79(5)°	92.87(4)°	91.79(5)°	O(2) ... O(3) ⁸	2.844(1)	O(2) ... O(3) ¹⁴	2.844(1)					
O(5) ⁸	2.093(1)	-	85.30(4)	89.90(4)	85.30(4)	89.90(4)	O(2) ... O(6) ¹¹	2.918(2)	O(2) ... O(6) ⁵	2.918(2)					
O(6) ⁵	2.020(1)	-	-	173.04(5)	83.76(3)	90.84(3)	O(5) ... O(3) ⁸	2.860(2)	O(5) ... O(3) ¹⁴	2.860(2)					
O(3) ⁸	1.953(1)	-	-	-	90.84(3)	94.19(3)	O(5) ... O(6) ⁵	2.787(1)	O(5) ... O(6) ¹¹	2.787(1)					
O(3) ¹¹	2.020(1)	-	-	-	-	173.04(5)	O(3) ⁸ ... O(6) ¹¹	2.830(1)	O(6) ⁵ ... O(3) ¹⁴	2.830(1)					
O(3) ¹⁴	1.953(1)	-	-	-	-	-	O(3) ⁵ ... O(3) ¹⁴	2.861(1)	O(6) ⁵ ... O(6) ¹¹	2.696(1)					
4. Co-ordination of S(1):											5. Co-ordination of S(2):				
Atom	d(Å)	Angles (°).				Atom	d(Å)	Angles (°).							
O(1)	1.458(2)	O(1) - S(1) - O(5) = 3x 110.00(5)				O(4)	1.453(2)	O(4) - S(2) - O(2) = 3x 109.64(6)							
O(5) ⁸	1.484(1)	O(5) - S(1) - O(5) = 3x 108.93(6)				O(2) ⁸	1.480(1)	O(2) - S(2) - O(2) = 3x 109.30(6)							
O(5) ⁹	1.484(1)	-				O(2) ⁹	1.480(1)	-							
O(5) ¹³	1.484(1)	distance O(1)...O(5) = 2.410(2)Å				O(2) ¹⁵	1.480(1)	distance O(4)...O(2) = 2.398(1)Å							
		distance O(5)...O(5) = 2.415(1)Å						distance O(2)...O(2) = 2.415(1)Å							
6. Bonding to oxygens, including hydrogen-bonding.															
O(1) - S(1)	1.458(2)Å	S(1) - O(1)...H(6) = 3x 113(1)°				O(4) - S(2)	1.453(2)Å	S(2) - O(4)...H(3) = 3x 109(1)°							
O(1)...H(6) ⁸	2.102(17)	H(6)...O(1)...H(6) = 3x 106(1)				O(4)...H(3) ⁸	2.183(13)	H(3)...O(4)...H(3) = 3x 110(1)							
O(1)...H(6) ⁹	2.102(17)	-				O(4)...H(3) ¹⁵	2.183(13)	-							
O(1)...H(6) ¹³	2.102(17)	-				O(4)...H(3) ¹⁵	2.183(13)	-							
O(2) - Pb(1)	2.965(1)Å	Fe - O(2) - Pb(1) = 86.11(1)°				O(5) - Pb(2)	2.953(1)Å	Fe ⁸ - O(5) - Pb(2) = 87.84(1)°							
O(2) - Fe	2.007(1)	Fe - O(2) - S(2) ⁸ = 131.31(7)				O(5) - Fe ⁸	2.093(1)	Fe ⁸ - O(5) - S(1) ⁸ = 129.20(6)							
O(2) - S(2) ⁸	1.480(1)	Pb(1) - O(2) - S(2) ⁸ = 142.59(8)				O(5) - S(1) ⁸	1.484(1)	S(1) ⁸ - O(5) - Pb(2) = 142.96(8)							
O(3) - Pb(1)	2.862(1)	H(3) Fe ⁸ Fe ¹⁰				O(6) - Pb(2)	2.690(1)	H(3) Fe ⁸ Fe ¹²							
O(3) - H(3)	0.771(31)	76(2)° 90.06(3)° 90.06(3)°				O(6) - H(6)	0.775(15)	105(3)° 96.98(3)° 96.98(3)°							
O(3) - Fe ⁸	1.953(1)	- 112(2) 112(2)				O(6) - Fe ⁸	2.020(1)	- 110(2) 110(2)							
O(3) - Fe ¹⁰	1.953(1)	- - 134.90(5)				O(6) - Fe ¹²	2.020(1)	- - 132.61(6)							
7. Bonding to hydrogen.															
H(3) - O(3)	0.771(31)Å	O(3) - H(3)...O(4) ⁸ = 149(3)°				H(6) - O(6)	0.775(15)Å	O(6) - H(6)...O(1) ⁸ = 178(4)°							
H(3)...O(4) ⁸	2.183(13)	-				H(6)...O(1) ⁸	2.102(16)	-							

4, and are illustrated in Figures 1a and 1b. An icosahedron of twelve oxygen atoms around Pb(2) (nearly full occupancy) is made up according to the following factors; there is a trio of hydroxyl oxygen atoms [Pb(2)-O(6) = 2.690 Å] in a plane, $\Delta z = 2.194$ Å above Pb(2) and a trio of oxygen atoms in a second plane $\Delta z = 0.865$ Å at a distance Pb(2)-O(5) = 2.953(1) Å. This second trio is rotated 60° when viewed down the *c* axis. These six oxygen atoms

are related to six more by the centre of symmetry at the Pb(2) position. For the Pb(1) icosahedron, the distances are as follows: there is a trio of hydroxyl oxygen atoms at Pb(1)-O(2) = 2.682(1) Å, with $\Delta z = 2.337$ Å, and the second trio of oxygen atoms at Pb(1)-O(2) = 2.965(1) Å and $\Delta z = 0.905$ Å. As with Pb(2) above, the six atoms that bond to Pb(1) are related to six more by the centre of symmetry at Pb(1). Other than the longer metal-oxygen dis-

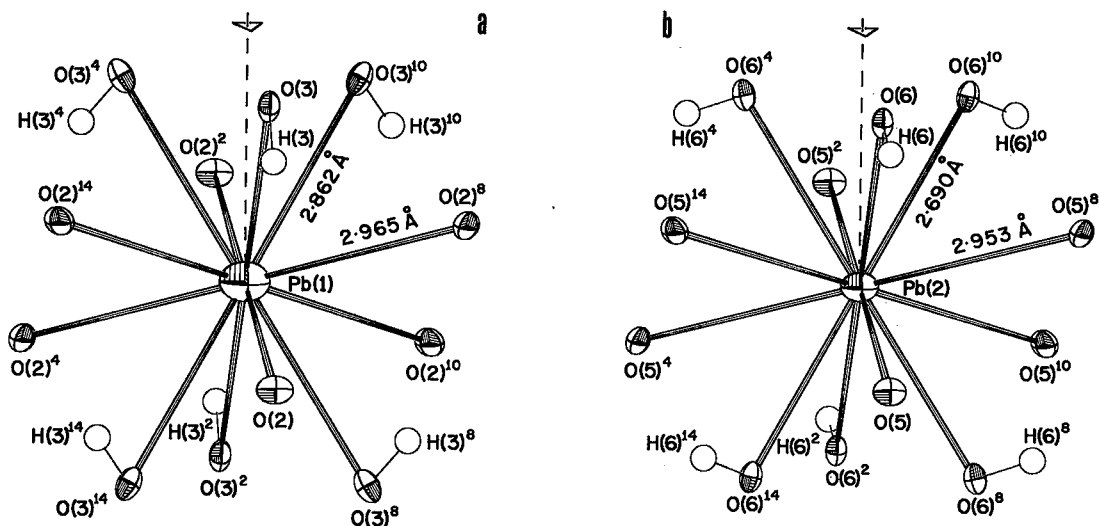


FIG. 1. In a, co-ordination polyhedron of Pb(1) [occupancy 0.039], and in b, co-ordination polyhedron of Pb(2) [occupancy 0.961(2)]. In both cases, the Pb atom is at a centre of symmetry on the threefold axis. The equivalent positions are explained in Table 4. The thermal ellipsoids are drawn at 50% probability using the program ORTEP-II (Johnson 1965).

tances in the Pb(1) icosahedron [as expected in a near-vacant site (Shannon 1976)], the most significant difference between the icosahedra is in the position of the hydrogen atoms of the hydroxyls: these are clearly shifted toward the vacant site [Pb(1) . . . H(3) = 2.77(3) Å], and are in fact closer to Pb(1) than are the hydroxyl oxygen atoms, so that the angle Pb(1)–O(3)–H(3) is 76(2)°, whereas the angle Pb(2)–O(6)–H(6) is 105(3)°. This difference is readily visible in Figures 1a and 1b.

The unique Fe atom in the structure is co-ordinated in a distorted octahedron by four hydroxyl groups in the equatorial plane and two oxygen atoms in the axial positions (see Fig. 2). The O(2)–O(5) axis of the octahedron is inclined at about 20° to the *c* axis. Diagonally opposite faces of this octahedron, each face composed of one axial oxygen atom and two hydroxyl groups, form part of the co-ordination icosahedron around Pb(1) and Pb(2), and thus form a bridge between the two different sulfate-and-cation layers. The *c/2* subcell relationship is indicated in Table 2, where all atoms except Fe are grouped in two sets with approximately *c/2* between corresponding atoms. The Fe–O bond lengths are $2 \times 1.953(1)$, $2 \times 2.020(1)$ Å (equatorial hydroxyl oxygen atoms) and 2.007(1) and 2.093(1) Å (axial oxygen atoms). Details of nonbonded O . . . O distances (edges of octahedron) are given in Table 4.

The two sulfate ions are illustrated in Figures 3a and 3b. The first sulfate shows three O(5) oxygen atoms at 1.484(1) Å and the fourth, O(1), at 1.458(1) Å, with the angles O(5)–S(1)–O(5) being 108.93(6)°

and O(1)–S(1)–O(5) being 110.00(5)°. The second sulfate has three O(2) oxygen atoms at 1.480(1) Å and a fourth, O(4), at 1.453(1) Å. The corresponding angles are O(2)–S(2)–O(2) = 109.30(6)° and O(2)–S(2)–O(4) = 109.64(6)°. The differences between these sulfate groups are statistically significant but not noteworthy. The nonbonded O . . . O distances in the sulfate groups (edges of tetrahedra) are virtually the same: 2.410(2), 2.398(2) Å for the apical to basal oxygen atom (defined in terms of the crystallographic threefold axis), and 2.415(1), 2.415(1) Å for the basal to basal oxygen atom for the first and second sulfate groups, respectively (Table 4).

NONHOMOGENEITY OF CRYSTAL SPECIMEN

After structural refinement was complete, the crystal on which the X-ray data had been collected was mounted in a polished section and analyzed by electron microprobe. The bulk of the crystal had virtually the stoichiometric plumbojarosite composition, thus justifying the restrictions placed on the occupancies of the two Pb sites during refinement. It was found, however, that the core of this crystal consists of a small lath of jarosite containing some Pb (Fig. 4, Table 5).

Figure 4 shows the (0001) plane of the crystal mounted at about 20° to the polished face. Generally, it has been observed that the shape of the surrounding crystal closely follows the shape of the included core. The relative area of the jarosite core

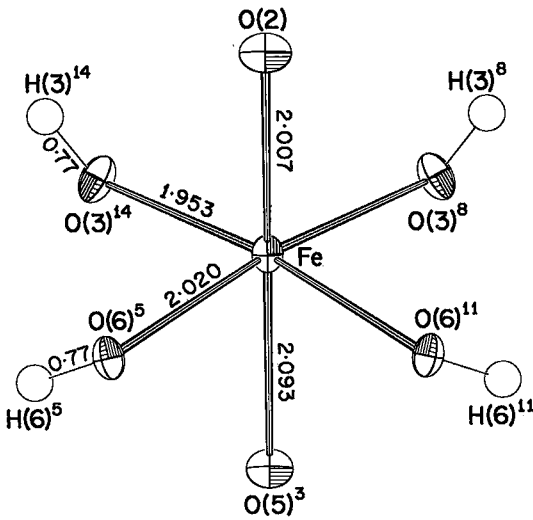


FIG. 2. Co-ordination polyhedron of Fe. Atoms O(5), Fe, O(2) lie on the crystallographic mirror-plane, which relates the pairs of O(3)-H(3) and O(6)-H(6) atoms.

in the (0001) plane (22%) can be calculated from the square of the ratio of the length of the core lath to that of the crystal. The fraction of the core relative to the crystal at right angles to this (1/10) represents the relative thickness of the core. The volume of the core is thus about 2.2%, and if all possible sources of error are considered, the core size is no more than twice this value. In order to confirm this estimate, an attempt was made to remount the crystal in another polished section at right angles to that shown in Figure 4. However, this was unsuccessful, and the crystal was lost during the procedure.

The small jarosite core is at the centre of a crystal with a high absorption-coefficient [$\mu(\text{MoK}\alpha) = 127.5 \text{ cm}^{-1}$], and is not likely to contribute to any significant extent to the diffraction intensities. Certainly it was not in evidence when the profiles of 000/ reflections were examined on the diffractometer or when long-exposure precession photographs were taken of the $hk0$ zone. The difference in the cell dimensions [plumbojarosite: a 7.3055, $c/2$ 16.838; jarosite: a 7.304, c 17.268 Å (Kato & Miura 1977)] would not have shown splitting of spots in the above-mentioned zone, but profile analysis of the high-angle 000/ reflections on a diffractometer could have shown the presence of the jarosite component if its X-ray scattering were significant. Thus, although it is known that the material examined is not strictly a single phase, the presence of the jarosite core can be ignored, particularly in view of the high degree of refinement, $R = 1.60\%$. It should be pointed out that Jambor & Dutrizac (1983) examined many crystals from the same locality, and found compositional zoning in most: the central core consists of plumbian jarosite surrounded by virtually K-free plumbojarosite, which in turn is surrounded by natrojarosite (their Table 4 and Fig. 10).

To confirm the above conclusion about the insignificance of the contribution to the scattering of the small jarosite core, and to show that the atomic species observed at the origin and identified as 0.039 of Pb and labeled Pb(1) was not in fact K, the following model was proposed and refined: the small jarosite core scatters in phase with the plumbojarosite surround, and the elements of the jarosite structure will virtually overlap those of the plumbojarosite structure with one exception. Pb at (0,0,½) will not be at full occupancy, the difference being K with equal occupancies at the (0,0,0) and (0,0,½) positions. This model could not be refined below

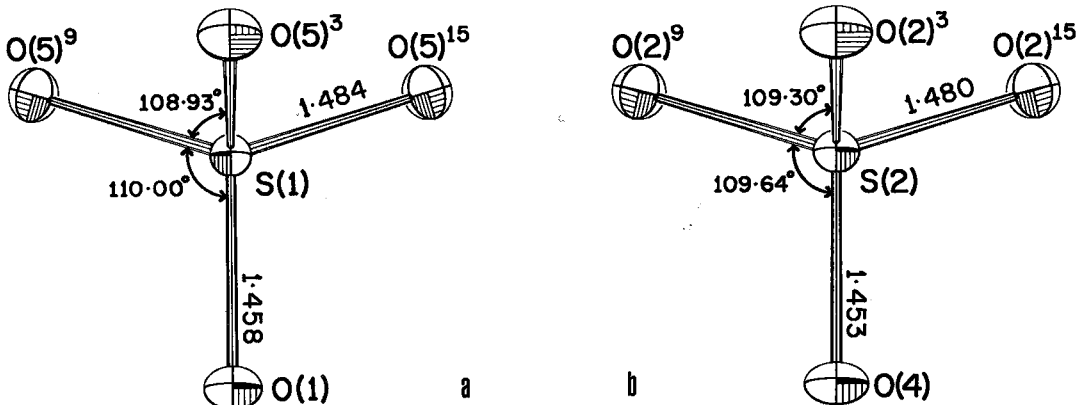


FIG. 3a, b. A comparison of the two sulfate groups. The S(1)-O(1) and S(2)-O(4) bonds lie on the threefold axis of the structure, whereas atoms O(5) and O(2) lie on the mirror planes. Unique bond-distances and angles are indicated.

$R = 2.2\%$, with the temperature factors of K at (0,0,0) refining to negative values. This model is therefore rejected in favor of the model described earlier.

DISCUSSION

The determination of the plumbojarosite structure by Kato (1979) gave the following bond-lengths for the two sulfate groups: S–O (apical) = 1.439, 1.447; S–O (basal) = 1.589 and 1.572 Å, respectively. These values are different from those reported here (Table 4, Figs. 3a, 3b). In fact the long basal bonds found by Kato are much closer to the bond distances reported by Kato & Miura (1977) for jarosite: [S–O (apical) = 1.468(8), S–O (basal) = 1.545(6) Å]. A further important difference between the present results and those of Kato is the occupancy of the mostly vacant Pb site (0,0,0). Kato found this to be 10%, whereas the present refinement shows 3.9(2)%. As plumbojarosite has basically a two-tiered jarosite structure, with alternate sites along z being "vacant" (0,0,0) and "occupied" (0,0,½), the anomalous results of Kato can be explained if one accepts that the "plumbojarosite" crystal of Kato had a large component of jarosite. The mean atomic positions would be altered from the plumbojarosite positions to a structure part-way between plumbojarosite and jarosite, and the occupancy of the "vacant" site would be increased by the presence of K at that position in the jarosite structure. No mention is made by Kato (1979) of any chemical analysis of the crystal of plumbojarosite he used, and in fact, no analysis was done and ideal composition was assumed (T. Kato, priv. comm.). The crystal used by Kato came from the same source as the present specimen (Tintic Standard mine, Dividend, Utah). Furthermore, a second crystal examined by the present author on the four-circle X-ray diffractometer, and considered nearly as good as the first from the point of view of spot shape, turned out to have a jarosite core of at least 30% by volume (Fig. 5). This grain still appeared to behave as a single crystal of plumbojarosite when judged by the singularity of diffraction spots, though the width of reflection peaks is greater, particularly for reflections with large l indices. It was because of this feature that the latter crystal was discarded and the first crystal was chosen for data collection. Intensities collected from the second crystal undoubtedly would have been affected by the jarosite core, and would have resulted in a composite jarosite–plumbojarosite structure.

NONSTOICHIOMETRY IN ALUNITE AND SYNTHETIC ALUNITE

The existence of apparent nonstoichiometry in synthetic jarosite and alunite is now well established

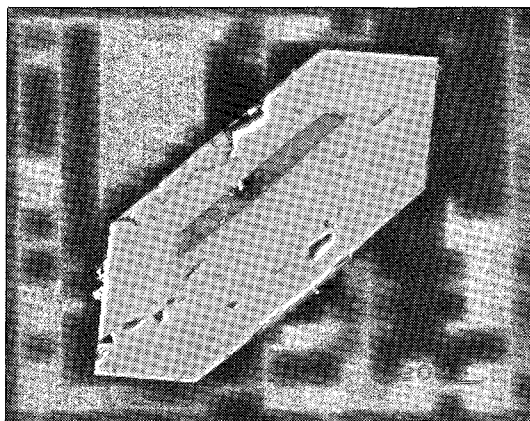


FIG. 4. Back-scattered electron micrograph of the single crystal of plumbojarosite used for structure determination, showing the tabular jarosite core (dark grey). Compositions are listed in Table 5. Scale bar 20 μm .

TABLE 5. ELECTRON-MICROPROBE DATA ON THE PLUMBOJAROSITE CRYSTAL WITH JAROSITE CORE THAT WAS USED FOR THE STRUCTURE DETERMINATION

Element	Plumbojarosite Crystal Matrix	Jarosite Core	Theoretical	
			Plumbojarosite	Jarosite
wt.% K	0.0	7.0	—	7.81
Pb	18.4	1.2	18.33	—
Fe	29.5	32.7	29.64	33.45
S	11.7	12.9	11.34	12.80

Probe conditions: accelerating voltage 15.9 kV, current 0.025 μA , counting time 10 secs. Data refined using EMPADR VII (Rucklidge & Gasparrini 1969). Standards: syn. PbSO₄ (Pb α & S α); syn. Fe₂O₃ (Fe α) and natural orthoclase (K α). Analyst: D.R. Owens.

(Härtig *et al.* 1984). This takes the form of deficiencies in both monovalent and trivalent cations. Deficiencies in the monovalent cation are usually considered to be balanced by inclusion into the cation site of a hydronium ion (H₃O⁺) [Kubisz 1970, 1971, 1972]. Whereas this may be a useful way of viewing the substitution, it is not yet proven that hydronium jarosite as such exists, although this matter is currently under active study (J.E. Dutrizac, priv. comm.). The present structure-determination shows that the hydrogen of the hydroxyl can move within the structure, depending on the element present at the cation site. There are six such hydroxyl groups in the immediate vicinity of the monovalent cation, and if a hydronium ion were introduced into the cation site, it is possible that it would be neutralized to a water molecule by one of the six hydroxyl groups, which would also be converted to a water molecule. There is certainly room enough in the structure to accommodate a second hydrogen on what was previously a hydroxyl. The transfer of a proton would not destroy the symmetry, as the proton would be statically or dynamically disordered among the six hydroxyl groups. However, with

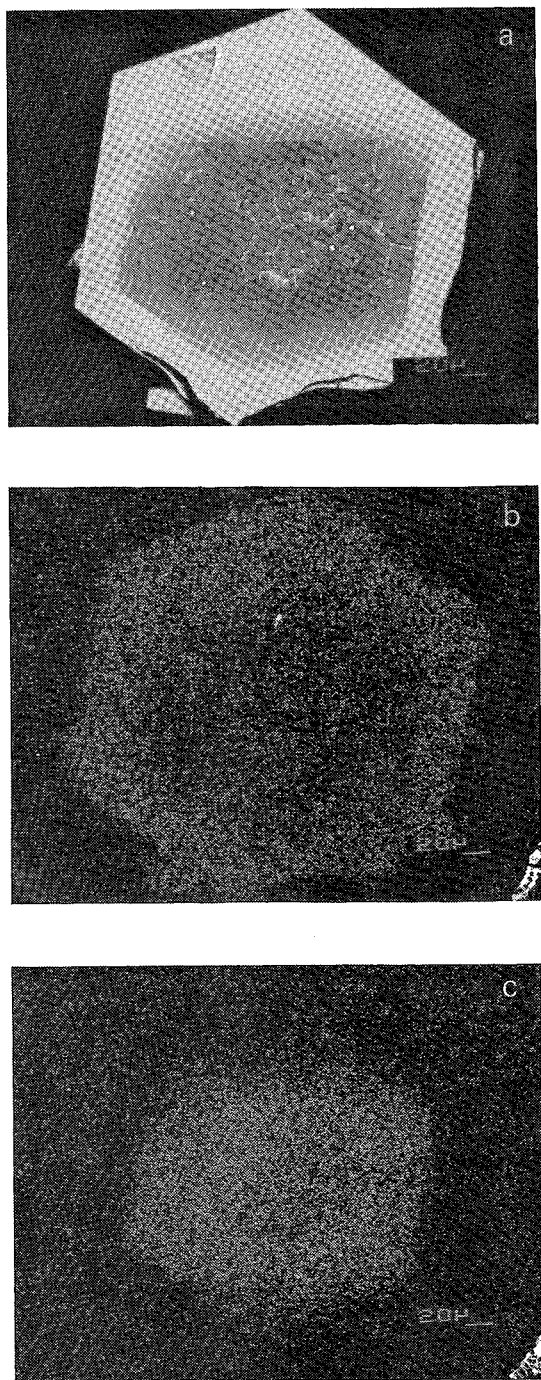


FIG. 5. a. Back-scattered electron micrograph of the second "good" crystal from the same batch, showing a large area of jarosite (dark) surrounded by plumbojarosite (light). b. X-ray micrograph of above crystal for PbL α . c. X-ray micrograph of above crystal for KK α . Scale bar 20 μ m.

increased "hydronium ion" substitution, the sharpness of the powder-diffraction patterns obtainable from these materials deteriorates (J.L. Jambor, priv. comm.), and this is usually a sign of decrease in degree of structural order. Corresponding deterioration is not as evident with cation-for-cation substitution (e.g., Na⁺ for K⁺).

The problem of deficiency in trivalent cations (Al³⁺ or Fe³⁺) is more difficult to rationalize, yet it has been reported to occur to the extent of 25% for Al³⁺ and 17% for Fe³⁺ (Härtig *et al.* 1984). Other authors (Jambor & Dutrizac 1983, Dutrizac & Jambor 1984) have reported similar deficiencies. The coordinating octahedron of oxygen atoms (four from hydroxyl and two from sulfate) is no more than 4.1 Å between diagonally opposite ligands. For a water molecule (minimum radius 1.3 Å) to replace a Fe³⁺ ion (radius 0.69 Å) or an Al³⁺ ion (radius 0.68 Å, Shannon 1976) is impossible without extreme distortion and breakdown of the structure. Charge neutralization to make up for a deficiency in trivalent cation can occur either by protonation of the sulfate oxygen to a bisulfate residue (H⁺ + SO₄²⁻ = SO₃·OH) or of hydroxyl groups to water (-OH + H⁺ = -OH₂). In either case, the oxygen content does not change, and no water has been added. Water can be added only in the monovalent site. However, water can be driven off from *both* sites in thermogravimetric analyses by the breakdown of the protonated ligands at the trivalent site and removal of substituting water (originating as a "hydronium ion") from the monovalent site.

Finally, there is the problem of the normalization of analytical data to give a chemical formula. In view of possible nonstoichiometry in the monovalent and trivalent sites, and substitution by the hydronium ion, normalization has to be carried out on the basis of two sulfate ions per formula unit. This method has been used by many authors, including Kubisz (1970, 1971, 1972), Jambor & Dutrizac (1983) and Härtig *et al.* (1984), in estimating the degree of nonstoichiometry of samples of synthetic alunite and jarosite. This procedure has a sound structural basis, however, in that the sulfate ions form the cohesive layer that is bonded to both types of cations. Although vacancies in the alkali sites are readily accommodated and vacancies in the trivalent cation can be accounted for, it is inconceivable to visualize a stable jarosite structure with vacancies in the sulfate layers as well. The necessity of normalization of a formula on the basis of S = 2 is rather unfortunate, however, as sulfur is usually the least precisely determined species in either classical chemical or microprobe analyses. There appears to be no obvious way out of the dilemma.

It is perhaps fortunate that of the many plumbojarosite and beaverite specimens examined in the laboratories at CANMET, the specimen of plum-

bojarosite used for this structure determination is stoichiometric (as shown by the population-parameter refinement and the featureless final difference-map), yet the sulfur determination is still 1½% high. Generally, deficiency of Pb^{2+} in an analysis is reflected in a deterioration of the quality of the X-ray-diffraction pattern.

SPACE-GROUP AMBIGUITY IN ALUNITE-JAROSITE STRUCTURES

In recent years, the technique of optical second harmonic analysis (SHA) (Dougherty & Kurtz 1976, Loiacono *et al.* 1982) has served to cast doubt on many previous structure-determinations of minerals in the alunite group. Some years ago, Menchetti & Sabelli (1976) pointed out that "in mineralogical handbooks (see for example Strunz, 1970) alunite and jarosite are still being reported as belonging to the acentric space group $R\bar{3}m$. The present refinement . . ." (*i.e.*, that of Menchetti & Sabelli 1976) ". . . leaves no doubt about the true symmetry; all terms of the solid solution within the alunite, woodhouseite and crandallite mineral series belongs to the space group $R\bar{3}m$." Support for this came from the work of Arkhipenko & Bokii (1979), who studied the IR and Raman vibrational spectra of alunite and jarosite, and from the observed and calculated numbers of frequencies for the two space groups $R\bar{3}m$ and $R3m$, concluded that the centrosymmetric space-group was correct. However, Loiacono *et al.* (1982) showed that alunite (identified as National Museum of Natural History, Smithsonian Institute Catalog # R-17342 from Tolfa, Roma, Laxio, Italy) exhibits a weak but reproducible signal in their SHA examination. This was taken as showing that the true space-group is noncentrosymmetric, presumably $R3m$. As this is in direct contradiction to the results of structural analyses of all samples of rhombohedral alunite and jarosite, the SHA results are worthy of comment.

In this group of minerals, quite substantial substitution for the monovalent cation is common, both cation (*e.g.*, Na^+ for K^+) and especially what has been termed hydronium for cation. Although a single cation, when occupying a position of possible centre of symmetry, can be truly centrosymmetric (both in terms of core and of bonding electrons), the hydronium ion, whether it remains in its original H_3O^+ form or whether it is reduced to water, *cannot have a centre of symmetry and cannot be located at a centre of symmetry*. Any hydronium-for-cation substitution will destroy the symmetry, and reduce the space group to $R3m$ or lower. This is not to say that the hydrogen atoms of the hydronium ion or the water molecule cannot be statistically distributed or dynamically disordered, and hence give the structure the overall appearance of having a centre of

symmetry. Furthermore, if the disordered hydrogen atoms are centrosymmetrically distributed around the oxygen atom, the symmetry is formally centrosymmetric, though in the event of static disorder, the disposition of hydrogen atoms around one particular site is not centrosymmetric. In the event of partial Na^+ for K^+ substitution, the local symmetry near the substituted site is obviously destroyed; Na^+ cannot be centrosymmetrically related to K^+ in the next unit cell. In this case, "average cation" considerations lead to an average structure with its consequent apparent centre. Such structures should be considered as centrosymmetric until the absence of a centre is definitely confirmed by structural analyses. Unless the alunite specimen of Loiacono *et al.* (1982) can be shown to be both stoichiometric and devoid of cation substitution (no composition was reported for the material), the space group of alunite-jarosite minerals should be considered as $R\bar{3}m$.

The above argument does not preclude the possibility that *structures derived from* the simple alunite model cannot have a symmetry lower than $R\bar{3}m$. In fact, Radoslovich & Slade (1980) and Radoslovich (1982) have successfully refined the structure of gorceixite in the noncentrosymmetric space-group Cm , and there appear to be sound structural reasons for the distortions observed.

In the present case, the plumbojarosite is stoichiometric within experimental error. Statistical tests done on the five segments of intensity-data indicate no difference between reflections where Friedel's Law would break down owing to the anomalous scattering component of the structure factor. Consequently, the centrosymmetric space-group was accepted in the intensity-averaging process. A residual R of 1.60%, with the hydrogen atoms clearly refined to the point where the hydroxyl bonds are shown to be equal [0.771(31), 0.775(15) Å], indicates that little is to be gained from attempting to refine the structure to a lower residual in the non-centrosymmetric space-group $R3m$. No such refinement was attempted.

ACKNOWLEDGEMENTS

The author thanks Mr. D.R. Owens, of CANMET, for the microprobe analyses (Table 5) and for the micrographs (Figs. 4, 5). Thanks are extended to Dr. J.E. Dutrizac, also of CANMET, for help in dealing with the mineralogy of jarosite, for providing the Introduction to this paper, and for supplying the crystals. The author acknowledges the assistance of Prof. Toshio Kato, of Yamaguchi University, Japan, for providing him with information about his work on plumbojarosite. The author thanks the referees, Drs. R.B. Ferguson and P. Bayliss, for their valuable comments.

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Received November 30, 1984, revised manuscript accepted April 19, 1985.