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THE CRYSTAL STRUCTURE OF BEUDANTITE, $Pb(Fe,Al)_3\ [(As,S)O_4]_2(OH)_6$

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ABSTRACT

The crystal stucture of beudantite, $PbFe_3[(As,S)O_4]_2(OH)_6$, has been determined and refined to 3.7% from 644 unique reflections, obtained by averaging the whole sphere of absorption-corrected intensity data collected to $2\theta = 80°$ using Mo$K\alpha$ X radiation. No evidence was found for ordering of the As and S atoms within the cell; the structure is centrosymmetric, $R\bar{3}m$, with *a* 7.3151(9), *c* 17.0355(5) Å. The Pb^{2+} cation, which is expected to occupy the 3*a* site (origin) in $R\bar{3}m$, is disordered, its position being about 0.28 Å from the origin along *x*. Thus, together with its space-group-equivalent positions, the electron density appears as a regular hexagon with sides 0.28 Å in the *x–y* plane. Owing to electron-density overlap of these positions, the figure appears to be a toroid, centered on the origin and surrounded by a cage of 12 oxygen atoms. This effect of displacement of Pb from its expected special position has been attributed to Pb(II) $6s^2$ lone-pair interaction with neighboring atom bond-pairs. The bond lengths from Pb to the oxygen atoms vary between 2.64 and 3.10 Å, these being longer (in the maximum) and shorter (in the minimum) than the corresponding distances in plumbojarosite.

Keywords: beudantite, crystal-structure refinement, jarosite-like structure, disordered (As,S), disordered Pb cation, lone-pair interaction.

SOMMAIRE

La structure cristalline de la beudantite, $PbFe_3[(As,S)O_4]_2(OH)_6$, a été affinée jusqu'à un résidu *R* de 3.7% à partir de 644 réflexions uniques, corrigées pour l'absorption, et obtenues en faisant la moyenne des réflexions équivalentes d'une sphère complète mesurée jusqu'à $2\theta = 80°$ en utilisant le rayonnement $K\alpha$ du molybdène. Aucune évidence d'une structure ordonnée du point de vue des atomes de As et S n'a été trouvée. La structure est centrosymétrique, $R\bar{3}m$, avec *a* 7.3151(9), *c* 17.0355(5) Å. Le cation Pb^{2+}, attendu à la position 3*a* (origine) de $R\bar{3}m$, est désordonné, étant situé à 0.28Å de l'origine, le long de l'axe *x*. Ainsi, en vertu des opérations de symétrie du groupe spatial, la densité électronique associée au plomb se présente sous forme d'un hexagone à côtés égaux de 0.28 Å, dans le plan *x–y*. Mais, comme ces positions se recouvrent au niveau de la densité électronique, la figure prend plutôt l'aspect d'un tore centré à l'origine et entouré d'une cage de 12 atomes d'oxygène. Cet effet de déplacement du Pb de cet équipoint particulier, assumé en premier lieu, a été attribué à l'interaction de la paire isolée d'électrons $6s^2$ du Pb(II) avec les paires d'électrons liant des atomes voisins. La longueur des liaisons Pb–O varie de 2.64 à 3.10 Å, les distances maximales et minimales étant systématiquement plus longues et plus courtes, respectivement, que les distances correspondantes observées dans la plumbojarosite.

Mots-clés: beudantite, affinement de la structure cristalline, structure de type jarosite, (As,S) désordonné, Pb désordonné, interaction d'une paire isolée d'électrons.

INTRODUCTION

Beudantite, a lead-containing species structurally related to the alunite $[KAl_3(SO_4)_2(OH)_6]$ family of minerals, is characterized by roughly equal proportions of As and S instead of S only, and by a predominance of Fe rather than Al as the trivalent cation. Generally, the crystal symmetry of the alunite minerals and chemically related minerals is rhombohedral, $R\bar{3}m$, though some exceptions are well documented, *e.g.*, gorceixite, $BaAl_3(PO_4)_2(OH)_5 \cdot H_2O$, which is pseudorhombohedral, but actually monoclinic *Cm* (Radoslovich 1982). A wide range of substitutions occurs in these minerals, starting with the alunite formula:

a) for the monovalent cation K: Na, NH_4, H_3O, Ag, Pb, Ca, Sr, Ba, vacancy;
b) for the trivalent cation Al: Fe, Cu, vacancy;
c) for $(SO_4)^{2-}$: $(AsO_4)^{3-}$, $(PO_4)^{3-}$.

Adopting the ionic model, there are valence changes associated with many of these substitutions, both at the monovalent cation site, and by virtue of the negative triply-charged phosphate or arsenate groups substituting for the doubly-charged sulfate group. Hydronium substitution for the monovalent cation (Ripmeester *et al.* 1986), and the occurrence of vacancies in both the monovalent and trivalent cation sites, together with substitution of water for hydroxyl [see discussion of nonstoichiometry in Szymański (1985)], further complicate the chemistry of these minerals.

Where a divalent cation substitutes for the monovalent cation at the origin of the cell, rhombohedral symmetry is typically retained, but the 17 Å *c* axis is doubled as a consequence of the alternation of filled and vacant sites along *c*, as in plumbojarosite (Szymański 1985). Beaverite also shows indications of a doubled cell in some compositions, and this is evidenced by the presence of an 11.3 Å (003) line in the powder pattern (Jambor & Dutrizac 1983).

The structure of beudantite was studied to determine whether there is evidence of ordering of As and S between the tetrahedral sites, which in the structures of alunite and jarosite are related by a center of symmetry. Any such ordering would lower the symmetry of the structure from $R\bar{3}m$, and raise the possibility of such ordering in other more complex substituted members of the alunite family. There is interest at CANMET in the role of arsenic in jarosite precipitation during hydrometallurgical circuits controlling iron (Dutrizac & Jambor 1987*a*, Dutrizac *et al.* 1987), and in silver losses to jarosite precipitation in such reactions (Dutrizac & Jambor 1987*b*). The role of "lead jarosite" (the precipitated equivalent of natural plumbojarosite) in this latter capacity has been studied (Dutrizac & Chen 1984), but the role of arsenic when present in solution, on silver losses, is not known. The incorporation of arsenic into a jarosite-like structure, and the subsequent discarding of this as part of the hydrometallurgical circuit, have serious implications in terms of possible water pollution by arsenic. In order to try to relate crystal structure to bonding strength within such compounds, the structure of plumbojarosite (Szymański 1985) was previously studied. Following upon this, it was hoped that a study of beudantite would provide information on a "model compound" for examining the effect of arsenic on the bonding within a jarosite-like structure, compared to an analogous arsenic-free jarosite (plumbojarosite). It has been shown (Jambor & Dutrizac 1983) that there is very little change in the unit-cell parameters upon replacement of a sulfate group by an arsenate; a study of an ordered sulfate-arsenate would provide precise information on the relative sizes of these two groups in a jarosite-like structure, and show how the stress, caused by the incorporation of the presumably larger arsenate group, is taken up by the structure.

COMPOSITION

The beudantite examined, from Tsumeb, Namibia, was kindly donated by Mr. William Pinch. The material is coarse grained, with slabs in excess of 5 mm across intergrown to form an irregular mass. The majority of the pieces examined have a reddish core, with a predominantly yellow outer edge. Typical electron-microprobe results for the red and yellow zones are listed in Table 1. There is a substantial variation in composition, even within a monochromatic zone, but red beudantite has less Al in substitution for Fe than the yellow variety. The As:S ratio is variable, and is as high as 1.22:0.78 in the yellow zones, though some are close to 1:1. The red zone has an As:S ratio significantly less than 1:1. Certainly, there is no evidence of a consistent 1:1 stoichiometry in either red or yellow zones. No F was found in any of the analyses.

EXPERIMENTAL

Crystal-structure determinations were attempted on three different crystals, but two gave apparently unsatisfactory results, and are discussed later. Fragments of potential single crystals were separated from the massive blocks, and were examined for color zoning and presence of twinning. Most fragments had to be rejected because twinning or intergrowths were present; this was seen as splitting of spots on precession photographs. The experimental details and the

TABLE 1. CHEMICAL COMPOSITION OF BEUDANTITE (ELECTRON-MICROPROBE DATA)

Element	Analysis line	Standard	Crystal	1	2	3	4	5	6
wt.% Pb	Pb*M*α	syn. PbS	PET	29.6	28.8	28.6	29.0	29.5	29.11
Fe	Fe*K*α	syn. Fe_2O_3	LiF	18.8	19.5	21.8	21.4	20.2	23.54
Aℓ	Aℓ*K*α	syn. $A\ell_2O_3$	TAP	2.0	1.7	0.7	1.0	1.8	—
As	As*L*α	syn. InAs	TAP	10.6	12.3	9.9	12.8	11.4	10.53
S	S*K*α	syn. $PbSO_4$	PET	4.4	3.7	4.8	3.5	4.2	4.50
Total:				65.4	66.0	65.8	67.7	67.1	67.68

Analyst: D.R. Owens, CANMET. 15kV accel. voltage; 20 nanoamps beam current. Data reduced by ZAF program of Tracor 5500. PET=pentaerithrol, TAP=thallium acid phthalate. Points 1 through 5 are: 1, Area 1, yellow, av. of 10 spots; 2, Area 2, yellow, av. of 4 spots; 3, Area 3, red core, av. of 5 spots. 4, Crystal #1, yellow; 5, Crystal #2, yellow. Above analyses correspond to:-

Area 1, Yellow: $Pb_{1.03}(Fe_{2.43}A\ell_{0.53})_{\Sigma 2.96}(As_{1.02}S_{0.99})_{\Sigma 2.01}O_8.(OH,H_2O)_6$

Area 2, Yellow: $Pb_{1.00}(Fe_{2.52}A\ell_{0.46})_{\Sigma 2.98}(As_{1.19}S_{0.83})_{\Sigma 2.02}O_8.(OH,H_2O)_6$

Area 3, red: $Pb_{0.99}(Fe_{2.80}A\ell_{0.19})_{\Sigma 2.99}(As_{0.95}S_{1.08})_{\Sigma 2.03}O_8.(OH,H_2O)_6$

Cryst.1, yellow: $Pb_{1.00}(Fe_{2.73}A\ell_{0.27})_{\Sigma 3.00}(As_{1.22}S_{0.78})_{\Sigma 2.00}O_8.(OH,H_2O)_6$

Cryst.2, yellow: $Pb_{1.00}(Fe_{2.54}A\ell_{0.46})_{\Sigma 3.00}(As_{1.07}S_{0.93})_{\Sigma 2.00}O_8.(OH,H_2O)_6$

Point 6 is theoretical composition for Aℓ-free As:S 1:1 end member.

limits of the subsequent structure refinement will be dealt with sequentially for the three crystals examined.

Crystal #1

What appeared to be a yellow single-crystal fragment was selected from a larger block by saw-cutting and trimming to form an irregular rhombic grain, 0.20 × 0.18 × 0.12 mm. The faces still present were (012), (10$\bar{2}$), (001) and (00$\bar{1}$). Microprobe data for the remaining adjacent portion of the larger fragment are given in Table 1. Precession photography showed the crystal to be single, within the limits of such observation, and confirmed what had been noted from powder diffraction, namely that there is no doubling of the *c* axis. The cell dimensions were obtained from a least-squares refinement of the angular positions of 64 reflections in the range $39° < 2\theta < 51°$, using the routine TRUANG of the NRC–CAD system of programs for the Nonius CAD–4 diffractometer (LePage *et al.* 1986). In this routine, the angular values are averaged from the equivalents of the measured values at $+H+\theta$, $+H-\theta$, $-H+\theta$ and $-H-\theta$, where H represents the *hkl* index, and θ is the diffraction angle. The refined values are *a* 7.3125(8), *c* 17.0217(7) Å. Differences in angles from values expected in a truly hexagonal crystal were found to be less than 1.5σ (0.008°).

The whole of the diffraction sphere was collected with Mo$K\alpha$ radiation to a limit in 2θ of 80° using ω scans. The reason for the latter, rather than the more usual θ–2θ scans, is that detailed analysis of some low-angle intense reflections showed multiple diffraction-maxima within a single peak. Whether this was an artifact of twinning, of unit-cell variation with compositional zoning, or was caused by the high X-ray absorption at the center of the crystal, or by a combination of any of the above, could not be determined. A gaussian integration procedure was used to correct the intensity data for absorption, using the best possible attempts to describe and measure the crystal in terms of its irregular "faces". The absorption-corrected data set was examined to see whether there was any systematic difference between a) the *hkl* reflections and their equivalents in space group $R3m$, and b) the $\bar{h}\bar{k}\bar{l}$ reflections and their equivalents. Possible differences due to differences in anomalous dispersion between As and S, should the space group be noncentrosymmetric, were not observed; there was no statistical difference between the two sets, indicating the probable space-group to be $R\bar{3}m$. The data were merged and reduced to a unique set of 644 reflections, of which 70 had an intensity less than $1.65\sigma(I)$ and were considered as "unobserved". The disagreement factor between equivalent measurements of intensity was R_{sym} 4.1%, indicating that, with a correct model, a refinement on *F* should be possible down to an R_F of about 2.1%.

Starting from the alunite parameters (Menchetti & Sabelli 1976), refinement was attempted both in space groups $R\bar{3}m$ and $R3m$. However, even with anisotropic thermal parameters and the inclusion of an extinction parameter (Larson 1970), the refinement would not converge below an R_F of 10.7%. Examination of the thermal parameters for all atoms revealed that the thermal motion of the Pb atom at the origin had refined to totally unacceptable and anomalous values. The U_{11} and U_{22} temperature factors were found to be between five and six times larger than U_{33}, which itself was reasonable. A difference synthesis showed large residual electron-density in the form of a ring around the center of the icosahedral oxygen cage containing the Pb atom, with a severe negative area near the center (at and near the origin). Less prominent residual positive peaks were scattered near most of the other atomic positions. The implications of this pattern in the difference synthesis were not understood, and they were presumed to relate to the non-singularity of maxima in the diffraction-peak profiles, with the strong suspicion that the crystal had been multiply-twinned. Refinement of these data was not pursued further.

Crystal #2

A better crystal was found, cut into a roughly equidimensional block, and ground to a sphere 0.24 mm in diameter using the Bond (1951) method. Examination of the peak profiles on the diffractometer showed that this sphere exhibited none of the multiple maxima typical of the preceding crystal. The cell dimensions, obtained using the same reflections and the same experimental conditions as for crystal #1, are: *a* 7.3151(9), *c* 17.0355(5) Å. Deviations in angles from values expected for true hexagonal symmetry were found to be similar to those found for crystal #1. A complete sphere of reflection was collected using the same experimental conditions as before, but this time spherical absorption corrections were applied at the time of data reduction. The intensity averaging was done in two ways: one set of data was prepared using $R\bar{3}m$ (centrosymmetric) as the space group, whereas the second set had the *hkl* reflections and their Friedel-related pairs included separately so that refinement could be carried out in $R3m$. No statistical difference was observed between these two sets, the inference being that the structure is centrosymmetric. The $R\bar{3}m$ set contained 644 reflections, of which 59 were considered as "unobserved" on the same criterion as before, and with a disagreement factor of R_{sym} 2.8%. Structure refinement was done using, as a starting set, the final parameters for the first crystal; refinement rapidly converged to an R_F of 9.3%. Very similar, and again totally unacceptable, thermal parameters were observed for the Pb atom. A difference synthesis indicated a toroid of electron density, of radius about 0.3 Å, in the plane $z = 0$, with a negative trough at the Pb position (origin). This was interpreted as a disorder of the Pb position away from the origin. Various models were tried for the location of the disordered Pb atom and its space-group-related positions. The one giving the best agreement involves a 1/6 Pb atom at 0. 28 Å along the x axis. The space-group symmetry results in six such fractional atoms around the origin in the x–y plane. The thermal parameters of this disordered Pb atom were refined anisotropically with reasonable values resulting, and the residual decreased to R_F 3.7%, but a difference synthesis still showed the presence of further disorder; remaining electron density was found at about 0.28 Å from the origin along the (hexagonal) c axis. However, attempts to include single additional peak positions (at ± z) into the refinement were not successful, as there was little improvement with the additional fractional atoms refined isotropically; anisotropic refinement gave nonpositive temperature-factors (U_{33} negative, with excessive values of U_{11} and U_{22}). It seemed as though additional light toroids[1] of electron density (amounting in total to about 3% of a Pb atom), and of a radius significantly less than the original Pb "doughnut" (0.28 Å), would have to be introduced to account for these excursions. Such refinement, however, proved impossible. There were additional electron-density excursions near the As/S tetrahedral sites, indicating some disorder along z, as though the refined atomic position lies part-way between two disordered real-atom sites. Attempts to resolve this in terms of refinement of As and S occupancy in two possible sites close together along z, were unsuccessful. Furthermore, the U_{33} thermal parameter of O(1) is three times larger than that of any other atom in the structure, and has a correspondingly large standard deviation. There is no apparent reason for this anomalous value, other than to suspect that it relates to further positional disorder in O(1) [bonded to As/S at 1.565(8) Å along z]. This disorder is quite probable, as the mean bond is the average of an S–O bond (d 1.52Å) and an As–O bond (d 1.69Å). Thus, although it is apparent that the proposed model does not account for all the disorder present in the structure, it was thought that all possible avenues of refinement had been explored within the limits of the data, and that little could be gained by further computation on minor variations of the same disordered model. The essential physical details of the specimen used in this refinement are summarized in Table 2.

TABLE 2. CRYSTAL DATA

Beudantite, $Pb(Fe,Al)_3[(As,S)O_4]_2(OH)_6$ As ≃ S
Ideal formula weight: 711.75 Daltons
Source: Tsumeb, Namibia
Crystal System: Rhombohedral, (hexagonal axes)
Cell dimensions (Crystal#2): a = 7.3151(9), c = 17.0355(5)Å
Systematic absences: $hkil$, $-h + k + l \neq 3n$.
Space group: $R\bar{3}m$, (#166).
Density: D_m = 4.48 ± 0.02, D_x = 4.49 g cm^{-3}
Linear absorption coefficient: μ(Mo$K\alpha$) = 235 cm^{-1}; μr = 2.82
X-ray data: whole sphere of data collected with Mo radiation to 2θ=80°, absorption corrected and averaged to give 644 unique reflections, (59 "unobserved" with $I < 1.65\sigma(I)$).

Crystal #3

In the course of looking for single crystals after the non-convergence of the refinement of the data from crystal #1, a peculiar anomaly was discovered. A crystal fragment, which gave extremely sharp diffraction-maxima, was ground to a sphere 0.18 mm in diameter, and the cell dimensions were examined prior to data collection. The routine TRUANG was used as before, but this time the unit-cell refinement was based on 128 reflections in the triclinic system. Refinements of the unit cell for crystals #1 and #2 also were carried out in the triclinic system, but showed no significant difference from rhombohedral symmetry. The anomalous results for crystal #3 are: a 7.3191(5), b 7.3087(5), c 17.0316(3) Å, α 90.004(4), β 90.022(4), γ 119.974(5)°. The difference between a and b is 0.0104(7) Å, *i.e.*, unacceptably large for an equivalence, as are the differences from 90 and 120° in β and γ, though these are not as marked. However, if the triply-primitive hexagonal cell is reduced to the "primitive rhombohedral" cell, the result is very noteworthy: a 7.0754(3), b 7.0756(3), c 7.0756(3) Å, α 62.211(4), β 62.271(4), γ 62.296(4)°. The three cell edges remain identical; the angles have become slightly but significantly distorted from equality. The result is a truly triclinic beudantite cell, but so close to a rhombohedral cell that only very precise single-crystal analysis can show the difference. In the hope of determining the structure of beudantite from what was most certainly a single crystal, a complete sphere of diffraction data was measured using the same experimental conditions as for the other two data sets; the data, however, were collected out farther, to 2θ = 100°, and more slowly than the other two sets in order to improve the count-

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[1] It was pointed out to the author by both referees that the term "toroid" implies a *smooth* annular distribution of electron density, and that this is strictly incorrect in the present structure; a better description is a "bracelet with six beads" around the origin. However, with the fairly large thermal parameters found for the Pb "beads", it is impossible to resolve the six fractional Pb atoms, each separated by 0.28 Å from its neighbors, and the description of the observed electron-density around the origin as a "toroid", although not correct, is an appropriate first approximation.

ing statistics on the weak high-angle reflections, with which it was hoped to resolve the disorder. A total of 10,988 unique reflections was measured (keeping *hkl* and $\bar{h}\bar{k}\bar{l}$ as valid separate reflections). The structure proved totally intractable; the very severe correlation between previously equivalent parameters, and the lack of an ordered, even moderately heavy atom necessary to define the origin in $P1$, resulted in divergent refinement. Even starting from the refined parameters of data set #2, and despite the inclusion of heavy "damping", the refinement was divergent and uncontrolled. No agreement better than R_F 12% was achieved for all data (5.0% for low-angle data), and no clear indication of the true nature of the disorder in the Pb site(s) could be obtained. Because the triclinic data-set (#3) could not be refined, the structure reported here is based on the second (rhombohedral) data set with R_F 3.7%.

In all structural computations and refinement for crystal #2, the XRAY–76 system of crystallographic programs was used (Stewart *et al.* 1976). For all atom types refined, the scattering curves used were the neutral atom type and were calculated from the coefficients given by Cromer & Mann (1968). The probable position of the hydrogen atom of the hydroxyl group [based upon the geometry around the filled Pb site in plumbojarosite (Szymański 1985)], was found to be in a residual positive area of the final difference synthesis, but the atomic position was not clearly resolved and was somewhat ambiguous; its inclusion in the structure-factor calculation (though not refinement) made no difference in the overall agreement, and is not reported here. It should be stressed that there were several peaks in the map, associated with atomic positions, that were higher than this, so no valid conclusions can be drawn about the H position. The anomalous scattering components for all atom types were taken from Cromer & Liberman (1970). The final positional and thermal parameters, with standard deviations, are given in Table 3. The observed and calculated structure-factors are given in Table 4, available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0S2.

DESCRIPTION OF STRUCTURE

Despite the atomic positional disorder identified in the Pb site, and suspected in the (As,S)O_4 tetrahedron, the structure of beudantite closely follows the alunite–jarosite model, which has been well-studied. A brief description of the present structure has been published (Szymański 1987). The icosahedron of six oxygen atoms [O(2)] and six hydroxyl oxygen atoms [O(3)] is somewhat different in shape from that found around the near-fully occupied site in plumbojarosite (Szymański 1985). Figure 1 shows the icosahedron found in the present structure. The separation between the O(3) face at the top (where

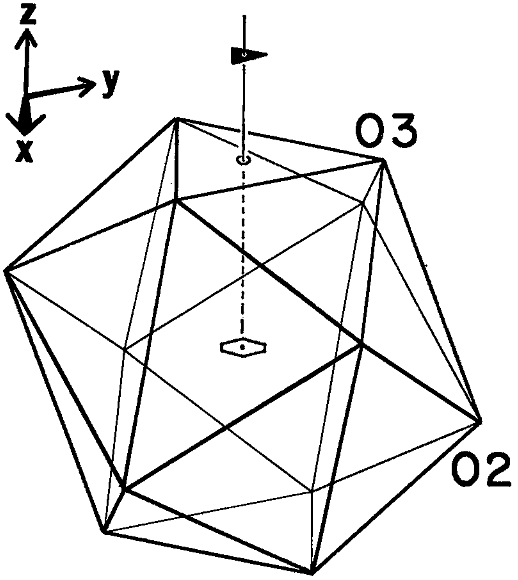

FIG. 1. The Pb–O icosahedron. The disordered Pb site is represented by the vertices of the small hexagon around the center and in the x–y plane. Unique oxygen atoms (coordinates in Table 3) are labeled. The axial directions are indicated; the $\bar{3}$ axis (designated by the solid triangle) is shown emergent through the center of the triangle of O3 oxygen atoms.

TABLE 3. POSITIONAL AND THERMAL (x100) PARAMETERS WITH STANDARD DEVIATIONS

Atom	site*	site symmetry	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	18*f*	2	.0383(31)	.0	.0	2.26(15)	$2xU_{12}$	1.63(3)	1.41(34)	-.01(2)	$2xU_{13}$
As/S	6*c*	3*m*	.0	.0	.31490(5)	$2xU_{12}$	$2xU_{12}$	1.15(4)	0.40(1)	.0	.0
Fe/Aℓ	9*d*	2/*m*	.0	.5	.5	$2xU_{12}$	0.76(3)	1.14(3)	0.27(2)	$2xU_{23}$	-.02(1)
O 1	6*c*	3*m*	.0	.0	.4068(5)	$2xU_{12}$	$2xU_{12}$	5.29(48)	0.70(8)	.0	.0
O 2	18*h*	*m*	.2145(3)	2*x*	-.0532(2)	1.94(10)	$2xU_{12}$	1.33(11)	1.08(12)	-.07(5)	$2xU_{13}$
O 3	18*h*	*m*	.1254(3)	2*x*	.1343(2)	0.96(8)	$2xU_{12}$	1.73(11)	0.47(9)	.09(5)	$2xU_{13}$

Population parameter of Pb = 1/6 (fixed)
Occupancy ratios: As:S = 1.07(1):0.93; Fe:Aℓ = 2.54(1):0.46

Anisotropic temperature factors are expressed as follows: $T=\exp[-2\pi^2(U_{11}a^{*2}h^2...+2U_{12}a^*b^*hk .+.)]$
*The "site" column is a combination of the multiplicity and the Wyckoff letter (International Tables, A, 1983).

the *z* direction emerges from the geometric figure) and the other O(3) face (at the bottom) is larger than in plumbojarosite, 4.569 *versus* 4.388 Å. Across the center of symmetry, the O(3)-O(3) distance is increased from 5.380 in plumbojarosite to 5.570 Å, and the corresponding O(2)-O(2) distances are 5.730, decreased from 5.906 Å. This means that the atoms of the icosahedron are now much closer to being on the surface of a sphere than they are in plumbojarosite, where there is a significant "flattening" along *z* to form an oblate spheroid. The projection of this figure down *z* is a hexagon at the edges, and the distances between the sides of this hexagon are 4.708, decreased from 4.891Å. The disordered Pb site is shown near the center of Figure 1. In view of the nature of this disorder, the bond lengths from only one of the six Pb positions are indicated in Table 5, and no Pb-Pb-O bond angles are given, as in no case can two Pb atoms be in the icosahedral cage at the same time. This more nearly spherical icosahedron, smaller in the *x-y* direction, is all the more remarkable in view of the Pb-atom disorder exhibited in the *x-y* plane. The shortest and longest bond-lengths to an oxygen atom are 2.64(2) and 3.10(2), and to hydroxyl oxygen atom are are 2.66(1) and 2.93(1) Å; these are shorter (in the minimum) and longer (in the maximum) than the corresponding distances in plumbojarosite.

The (Fe,Al)$(OH)_4O_2$ octahedron is quite normal (Fig. 2), with bond lengths of 4 × 1.983(1)Å to hydroxyl [O(3)] and 2 × 2.026(2) Å to oxygen [O(2)]. The observed geometry (Fig. 3) of the arsenate-sulfate tetrahedron, as already indicated, is probably a composite figure, involving disorder in both the (As,S) and O(1) sites, which is the explanation offered for the anomalous thermal parameters of

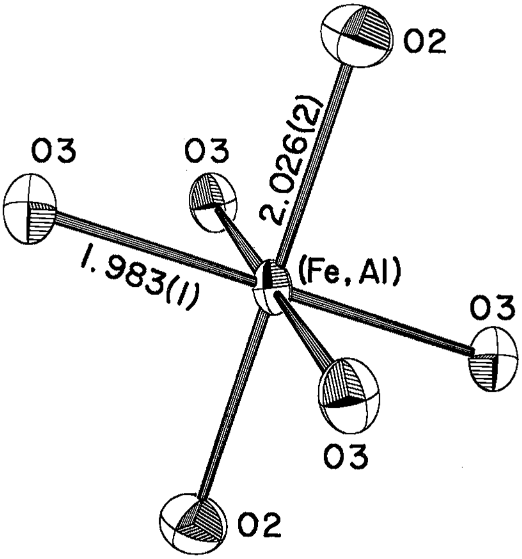

FIG. 2. The $Fe(OH)_4O_2$ octahedron, with Fe at a center of symmetry (0, ½, ½).

TABLE 5. BOND LENGTHS (Å) AND INTERBOND ANGLES (°) WITH STANDARD DEVIATIONS

1. Coordination of Pb, (0.0383, .0, .0):

Atom	d(Å)	$O(2)^{3}$	$O(2)^{5}$	$O(2)^{8}$	$O(2)^{10}$	$O(2)^{12}$	O(3)	$O(3)^{3}$	$O(3)^{5}$	$O(3)^{8}$	$O(3)^{10}$	$O(3)^{12}$
O(2)	2.879(2)	168.8(9)	103.8(5)	72.5(2)	117.0(5)	66.1(3)	73.2(1)	105.6(1)	116.5(5)	59.1(1)	126.4(3)	56.2(2)
$O(2)^{3}$	2.879(2)	—	66.1(3)	117.0(5)	72.5(2)	103.8(5)	105.6(1)	73.2(1)	56.2(2)	126.4(3)	59.1(1)	116.5(5)
$O(2)^{5}$	3.100(20)	—	—	173.6(5)	110.0(1)	63.6(4)	113.7(7)	55.0(3)	68.2(4)	103.3(3)	118.1(4)	53.9(3)
$O(2)^{8}$	2.640(18)	—	—	—	76.5(6)	110.0(1)	60.4(2)	130.7(7)	108.4(1)	79.5(5)	62.3(4)	129.4(3)
$O(2)^{10}$	2.640(18)	—	—	—	—	173.6(5)	130.7(7)	60.4(2)	124.9(2)	63.2(4)	79.5(5)	108.4(1)
$O(2)^{12}$	3.100(20)	—	—	—	—	—	55.0(3)	113.7(7)	53.9(3)	118.1(4)	103.3(3)	68.2(4)
O(3)	2.799(3)	—	—	—	—	—	—	168.5(9)	57.3(2)	125.1(3)	60.5(1)	115.3(5)
$O(3)^{3}$	2.799(3)	—	—	—	—	—	—	—	115.3(5)	60.5(1)	125.1(3)	57.3(2)
$O(3)^{5}$	2.934(13)	—	—	—	—	—	—	—	—	170.0(8)	58.7(1)	111.2(7)
$O(3)^{8}$	2.658(10)	—	—	—	—	—	—	—	—	—	131.3(9)	58.7(1)
$O(3)^{10}$	2.658(10)	—	—	—	—	—	—	—	—	—	—	170.0(8)
$O(3)^{12}$	2.934(13)	—	—	—	—	—	—	—	—	—	—	—

2. Coordination of Fe, (0, ½, ½):

Atom	d(Å)	$O(2)^{9}$	$O(3)^{1}$	$O(3)^{4}$	$O(3)^{11}$	$O(3)^{13}$
$O(2)^{6}$	2.026(2)	180.0	93.8(1)	86.2(1)	93.8(1)	86.1(1)
$O(2)^{9}$	2.026(2)	—	86.2(1)	93.8(1)	86.1(1)	93.8(1)
$O(3)^{1}$	1.983(1)	—	—	180.0	87.9(1)	92.1(1)
$O(3)^{4}$	1.983(1)	—	—	—	92.1(1)	87.9(1)
$O(3)^{11}$	1.983(1)	—	—	—	—	180.0
$O(3)^{13}$	1.983(1)	—	—	—	—	—

3. Coordination of (As/S), (.0, .0, 0.31490):

Atom	d(Å)	$O(2)^{2}$	$O(2)^{7}$	$O(2)^{11}$
O(1)	1.565(8)	111.5(1)	111.5(1)	111.5(1)
$O(2)^{2}$	1.618(2)	—	107.4(1)	107.4(1)
$O(2)^{7}$	1.618(2)	—	—	107.4(1)
$O(2)^{11}$	1.618(2)	—	—	—

Superscripts used above refer to the following equivalent positions:-

1. $-1/3 + x, 1/3 + y, 1/3 + z$
2. $-1/3 + x, -2/3 + y, 1/3 + z$
3. $-x, -y, -z$
4. $1/3 - x, 2/3 - y, 2/3 - z$
5. $-y, x-y, z$
6. $1/3 - y, 2/3 + x-y, 2/3 + z$
7. $2/3 - y, 1/3 + x-y, 1/3 + z$
8. $y, -x+y, -z$
9. $-1/3 + y, 1/3 - x+y, 1/3 - z$
10. $-x+y, -x, z$
11. $-1/3 -x+y, 1/3 -x, 1/3 + z$
12. $x-y, x, -z$
13. $1/3 + x-y, 2/3 + x, 2/3 + z$

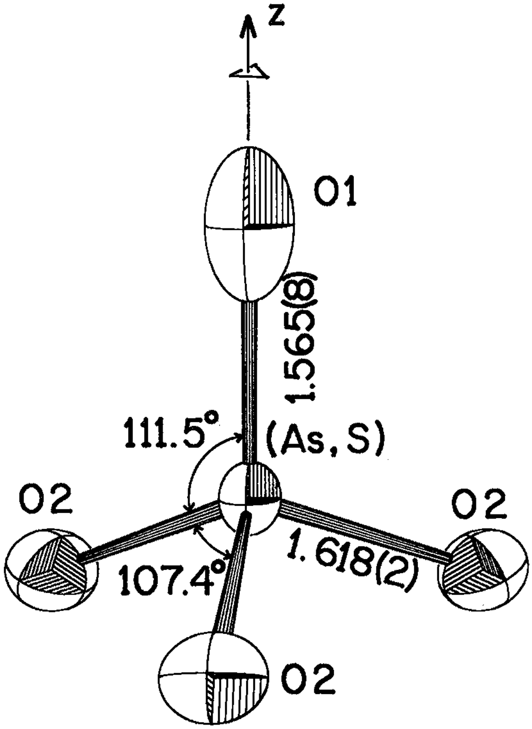

FIG. 3. The $(As,S)O_4$ tetrahedron, lying on the threefold axis of the structure. Figures 2 and 3 were prepared using the program ORTEP-II (Johnson 1965), and the thermal ellipsoids are drawn at 50% probability.

O(1) and the spurious peaks in the difference synthesis around (As,S). The bond lengths to oxygen in this type of tetrahedron are generally dependent upon the hydrogen-bonding network, in which the oxygen atoms are involved, and on whether the oxygen is in fact a hydroxyl. A review (Ferraris & Ivaldi 1984) of bond-length variation with oxyanion (including arsenate) protonation indicates that generally there is a distortion in the oxyanion from regular tetrahedral symmetry, with one bond being shorter than the other three. In jarosites, this distortion is caused by the unique bond being to an oxygen which itself is hydrogen-bonded. The bond lengths in the present structure are part-way between those found in sulfate tetrahedra (as in jarosites and alunites) and those found in arsenate tetrahedra. Thus in $Pb(II)Cu(I)[AsO_4]$ (Pertlik 1986), where there is no hydrogen bonding, the other oxygen bond always being to a metal, the distortion is quite small: 3 × 1.697(7), 1.681(6)Å, $\Delta = 0.016$ Å. The present structure has bonds of 3 × 1.618(2) and 1.565(8) Å, $\Delta = 0.053$ Å. Full details of the bond lengths and interbond angles are given in Table 5.

Discussion

The beudantite unit cell can be transformed into an F-centered, nearly cubic cell, with a 10.178 Å, and a maximum angular deviation Δ of 2.73°. Such small distortion from higher symmetry may account for the prevalence of twinning in the specimens examined. This twinning, together with the compositional zoning, which is visible in the limit as a red–yellow interface, severely limits the quality of the crystals for structure analysis.

Crystal #1, with its multiple maxima within a single peak-profile, may have been multiply twinned or compositionally zoned, but provided in essence the same structural model as that derived from the sharp and single reflections of crystal #2. The author has no simple explanation for the nature and apparently lower symmetry of crystal #3. While admitting that the lower symmetry identified for crystal #3 weakens the conclusion that the structure of beudantite is centrosymmetric, $R\bar{3}m$, the detection and description of this anomaly leave the door open for further investigation on the lowering of the symmetry of this specimen, and do not detract from the argument that the most stringent examination revealed no deviation from $R\bar{3}m$ in the case of crystal #2. The chemical composition of crystal #3 was not determined, and it is not known whether the lower symmetry is an artifact of composition.

In addition to geometrical factors of bond lengths and spatial distribution of bonds and neighbors, one of the factors most sensitive to the correctness of a structure is the magnitude and variation of the anisotropic thermal parameters (provided the diffraction data are sufficiently extensive in 2θ, and the data have been adequately corrected for absorption). The present paper lists all thermal parameters as U_{ij}, defined in Table 3, where $U_{ij} = <u^2>$, the root mean square thermal displacement of the given atom in the particular direction.

Cruickshank (1965) pleaded the case for publication of anisotropic thermal parameters as U_{ij}, rather than B_{ij} (the anisotropic equivalent of the isotropic B), or even worse, β_{ij}, parameters which by themselves have little physical significance. It is therefore distressing to find that these latter *still* appear in print and often serve to mask serious problems with structure refinement.

In a recent paper, an ordered arrangement of S and P atoms is claimed to occur in corkite, $PbFe_3(SO_4)(PO_4)(OH)_6$ (Giuseppetti & Tadini 1987) in space group $R3m$. Corkite is chemically very close to beudantite, the only difference being replacement of half the S by P instead of by As. Table 4 of this paper lists anisotropic thermal parameters (given as B_{ij}, but mathematically actually β_{ij}) which, when converted to U_{ij}, show that the thermal parameters for their now identified S and P atoms have diverged grossly in opposite directions. The U_{33} for S is now

14.4 times larger than its U_{11} value, whereas for P, the factor is 14.5, *but in the reverse sense, i.e.*, the thermal ellipsoid is extremely prolate for S, and extremely oblate for P. Furthermore, the U_{ij} for Pb is a factor of 4.9 times larger than U_{33}, a situation very similar to that found here when the Pb atom was constrained to be at the origin (*i.e.*, not disordered). The S–O and P–O bond lengths in corkite are consistent with the chemical-type identification, but the P and S scattering curves differ by no more than, and over most of the sin θ/λ range by much less than, one electron so it is difficult to differentiate these two atom types with certainty. Refinement of a centrosymmetric structure in a noncentrosymmetric space-group, commonly leads to a false minimum in the least-squares procedure, with the previously equivalent parameters diverging as a result of near-singularity in the least-squares matrix (Ermer & Dunitz 1970). Such singularity may not be apparent if the block-diagonal approximation is used in the least-squares matrix. Slight positional shifts often serve to "take up" random errors in the data, and the result is an apparently noncentric structure. This is *not* to claim that the structure of corkite as published is necessarily wrong, but it casts doubt on the correctness of the interpretation of the data, in view of the magnitudes of the published thermal parameters.

In the present structure, the "reasonableness" of the thermal parameters was monitored at every stage of the refinement, and was the motivating force in the proposal of the disordered-Pb model. Even so, the refined thermal parameters of O(1) in the $(As,S)O_4$ tetrahedron are anomalous, probably because of positional disorder. This inference is quite reasonable, as the O(1) position can vary along *z* without much distortion of the structure, depending on whether there is As or S in the given tetrahedron.

It is evident that the structures of alunite- and jarosite-like minerals may retain the gross features of the jarosite model, but positional disorder of the type found here in the Pb site is more common than had been appreciated. The author has encountered this in the structure of the yet unnamed mineral $PbFe_3(PO_4)_2(OH)_5H_2O$ (Szymański, unpubl. data), where there are two independent disordered Pb sites very similar to the one in the present structure. The reasons for the disorder in the Pb position were not originally understood. It was suspected that bond-valence considerations might be favoring an "off-center" position; bond strength is not a linear function of distance but is a higher power function. Charge-balance calculations, according to the method of Brown & Wu (1976), showed only minor differences between the the two models, one with Pb at the origin and the other with Pb at the disordered off-center site. The differences between the two were scarcely significant, and not enough to explain the disorder. The probable reason for the disorder was pointed out to the author by one of the referees of this paper, who drew the author's attention to the recent work of Moore (Moore 1988, Moore *et al.* 1985, 1982), who has identified this effect as being due to the Pb(II) $6s^2$ lone-pair interaction with adjacent bond-pair electrons. In the structure of joesmithite (Moore 1988), the Pb atom is displaced 0.601 Å from the special position site (¼, ¼, 0; an inversion center) as a result of this type of interaction with bond-pairs from neighboring atoms of oxygen. The Pb(II) $6s^2$ lone pair cannot be accommodated at an inversion center in joesmithite, and in the present (beudantite) structure it cannot be accommodated at a $\bar{3}m$ inversion site. In the synthetic phase $K_2Pb_4Si_8O_{21}$ (Moore *et al.* 1985), the separation between half-occupied K(I) and Pb(II) atom sites is 0.59 Å, which is very comparable to the value found in the present structure (0.56 Å between 1/6-occupied Pb(II) sites across the center of symmetry). For a full discussion of the results of lone-pair bond-pair interactions, the reader is directed to the above references.

As already mentioned, there are significant deviations from 1:1 As:S stoichiometry in beudantite, and Table 1 shows the range of values, between 1.28:0.78 and 0.95:1.08 in the specimens analyzed. The formula of beudantite, as given in the Title, implies a 1:1 ratio, with $(OH^-)_6$ required to balance the charges. It has been shown (Ripmeester *et al.* 1986) that charge balance is achieved in cation-deficient jarosites by hydronium substitution for the cation, or by protonation of hydroxyl to water. All beudantite analyses in Table 1 show virtually stoichiometric composition as far as Pb and (Fe + Al) are concerned. However, the question of charge balance, changing with As:S ratio, needs to be raised. At the As-rich composition, the excess negative charge can be balanced by protonation of hydroxyl groups to water, but it is difficult to balance the S-rich composition without proposing some O^{2-} substituting for OH^-, and this would weaken the hydrogen-bonding network that is present in these minerals. It should also show up as differences from expected values in bond-valence analyses. However, the incompletely described Pb disorder and the additional disorder found in the $(As,S)O_4$ tetrahedron inhibit the precise refinement required to make significant the minor deviations found from the expected bond-valence values. This proposed substitution in S-rich compositions must remain a hypothesis.

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