

The Crystal Structure of Krupkaite, $\text{CuPbBi}_3\text{S}_6$, from the Juno Mine at Tennant Creek, Northern Territory, Australia

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Abstract

Krupkaite, $\text{CuPbBi}_3\text{S}_6$, from the Juno Mine at Tennant Creek, Northern Territory, Australia, is orthorhombic, space group $Pmc2_1$, with $a = 4.003(3)$, $b = 11.200(9)$, $c = 11.560(9)$ Å. Diffraction data were recorded with an equi-inclination diffractometer equipped with a proportional counter as detector. A least squares structural refinement, to an R value of 9.7 percent, permitted distinction between lead and bismuth on the basis of bond distances. The lead atom is coordinated to five sulfur atoms at distances from 2.89 to 3.02 Å; two additional sulfur neighbors are located at 3.27 Å. The Bi(1) atom has three sulfur neighbors at 2.65 Å and 2.79 Å and four more distant sulfur neighbors at 2.98 Å to 3.11 Å. The Bi(2) atom has three close sulfur neighbors at 2.54 Å and 2.79 Å and four more distant sulfur atoms at 2.99 Å to 3.38 Å. The Bi(3) atom has three neighbors at 2.64 Å and 2.63 Å, three more distant sulfur atoms at 3.00 Å to 3.10 Å and a seventh sulfur neighbor at 3.57 Å. The copper in the structure is mostly ordered (up to 80 percent) into one of the two sites available, to give the copper atoms a distorted tetrahedral coordination. In addition there is also an overall ordering of lead and bismuth atoms which is determined by the semi-exclusion of copper from one of its sites in order to avoid a close interaction between copper and bismuth atoms. The major distortions in the structure away from the bismuthinite and aikinite arrangements are the result of this effect. The structure of krupkaite is based on the c ribbon, a structural element of bismuthinite derivatives previously suggested by Ohmasa and Nowacki (1970) and which has recently been found in the structure of gladite, $\text{PbCuBi}_5\text{S}_8$, by Kohatsu and Wuensch (1973). Its structure as such is in disagreement with the extensive series of super-structures based on aikinite that have been proposed to occur in the Bi_2S_3 - $\text{CuPbBi}_3\text{S}_6$ system by Welin (1966) and Moore (1967).

Introduction

Large and Mumme (1974) and Mumme (in preparation) have described five distinct species of sulfosalts in the Juno Mine at Tennant Creek, Northern Territory, Australia. These included members of the bismuthinite-aikinite series Bi_2S_3 - $\text{CuPbBi}_3\text{S}_6$, one of which (R27792) gave analyses corresponding to $\text{CuPbBi}_3\text{S}_6$. Other members of this mineral series have been reported to occur at Gladhammer, Sweden, by Lindstrom (1887, 1889), Flink (1910), and Johansson (1924). These members, which were also associated with aikinite, were named rezbanyite, hammarite, lindstromite, and gladite.

Rezbanyite, originally described as $\text{Cu}_2\text{Pb}_3\text{Bi}_{10}\text{S}_{19}$ (in *Dana's System of Mineralogy*, 7th ed., Vol. 1, 1944, p. 471), was later suggested by Padera, Bouska, and Pelikan (1955) to be $\text{Cu}_3\text{Pb}_3\text{Bi}_{10}\text{S}_{19.5}$ a member of the bismuthinite-aikinite series. Gladite was determined by Johansson (1924) to have the composition $\text{CuPbBi}_5\text{S}_9$. The composition of hammarite, $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$, was originally erroneously determined

to be $\text{Pb}_5\text{Bi}_6\text{S}_{14}$ by Johansson (1924). For lindstromite from Gladhammer, Johansson derived a composition $\text{CuPbBi}_3\text{S}_6$. Padera (1956) later studied rezbanyite, hammarite, lindstromite, and gladite and considered them to be isomorphic mixtures of bismuthinite and aikinite. He proposed that the name rezbanyite had priority and that it should be used in place of hammarite, lindstromite, and gladite. Welin (1966) made further studies on some of these minerals in the collections of the Swedish Museum of Natural History, including those labelled rezbanyite, gladite, hammarite and, in particular, lindstromite (RM24100). He found from electron probe and single crystal studies that three complex minerals from Gladhammer—gladite, $\text{CuPbBi}_5\text{S}_9$; hammarite, $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$; and $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ —appeared to have super-structures based on aikinite. He concluded that continuous solid solution did not exist between bismuthinite and aikinite. Instead, he proposed a series of minerals with common substructures but with each possessing a different size unit cell and a particular composition. On the basis of this apparent

TABLE 1. Johansson's (1924) Analysis of Lindstromite Compared with Those of Ideal Krupkaite ($\text{CuPbBi}_3\text{S}_6$) and Ideal $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$

Gladhammer Material called Lindstromite (Johansson, 1924)	Krupkaite, $\text{CuPbBi}_3\text{S}_6$	$\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$
Pb 18.95	19.01	22.57
Cu 5.84	5.83	6.92
Bi 57.13	57.51	53.04
S [17.88]	17.65	17.47
Insol. 0.02	-	-

relationship, an extensive series of hypothetical aikinite derivatives was proposed by Moore (1967). Moore suggested a nomenclature in which each member of the series is given the prefix Z^n , where Z is the integral multiple of the a translation and n is the number of lead (= copper) atoms in the asymmetric unit (which equals $\frac{1}{4}$ of the lead [= copper] atoms of the structural cell). It was also suggested that the specific names rezbanyite, hammarite, lindstromite, and gladite should be dropped in favor of this new nomenclature.

Welin (1966, Table 4) later determined this same specimen to be $\text{Cu}_{2.24}\text{Pb}_{2.42}\text{Bi}_{5.72}\text{S}_{12.27}$ so that lindstromite would now be ideally defined as $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$, being thus an intermediate member of the bismuthinite-aikinite series. A crystal fragment of this specimen was found by Welin to have a superlattice based on a five-fold multiple of the a axis of bismuthinite and hence became known as "5³-aikinite". Consequently, the specimen with formula $\text{CuPbBi}_3\text{S}_6$ from the Juno mine must be considered to represent a new mineral. Concurrent with our studies, Zak, Syneck, and Hybler (1974) described a mineral of composition $\text{CuPbBi}_3\text{S}_6$ from Krupka, Czechoslovakia, this new mineral and name having been approved on June 22, 1974, by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Comparison of their data for krupkaite with the data for the $\text{CuPbBi}_3\text{S}_6$ specimen from Tennant Creek indicates the two specimens to be the same mineral. Henceforward, therefore, we shall refer to our specimen as krupkaite, rather than "2¹-aikinite" (the name that applies in Moore's nomenclature).

Other occurrences of bismuthinite-aikinite members have been described by Karup-Møller (1972) in specimens from the Bolivar Mine, Cerro Bonete, Lipez Province, Bolivar (specimen ROM M21003) and from Manhattan, Nevada, USA (specimen ROM M13805). Microprobe analyses of ROM M13805 gave an approximate formula $\text{Cu}_2\text{Pb}_2\text{Bi}_5\text{S}_{10.6}$, a composition close to that of krup-

kaite which is $\text{CuPbBi}_3\text{S}_6$. A similar phase was found in ROM M21003. While no composition was obtained for this latter sample, its unit cell parameters based on Guinier films were $a = 11.200 \text{ \AA}$, $b = 11.569 \text{ \AA}$, $c = 4.016 \text{ \AA}$, which corresponded with a lead content of 14-19 percent, using Welin's correlation of c axis dimensions with composition for members of the bismuthinite-aikinite join.

A full description of the structure of bismuthinite has appeared (Kupčík and Vesela-Novakova, 1970) and the crystal structure of aikinite has been determined, in part by Wickman (1953) who did not accurately find the sulfur atom positions, and in detail by Kohatsu and Wuensch (1971). An ideal structure for $\text{Cu}_{2.66}\text{Pb}_{2.66}\text{Bi}_{5.34}\text{S}_{12}$ (hammarite or "3²-aikinite") has been proposed by Welin (1966). Most recently the structure of the mineral gladite (or "3¹-aikinite") has been reported by Kohatsu and Wuensch (1973).

Electron probe analyses of the members of the bismuthinite-aikinite series found at Juno showed that one had a maximum lead content of 19.3 percent and a formula very close to the ideal composition of krupkaite (Table 2) (Large and Mumme, 1974).

A detailed X-ray study of this phase, krupkaite, was undertaken to provide further information about this complex mineral series, and to permit its comparison with related members.

Experimental

Several small crystals of krupkaite were obtained from a polished specimen R27792 (Large and Mumme, 1974) and Weissenberg X-ray films were taken of them. Most gave sharp X-ray spots and the smallest and most equidimensional was chosen for data collection. Precise lattice parameters (Table 3) were derived from X-ray powder data (Table 4) collected with a Guinier focusing camera using $\text{CuK}\alpha$ radiation and KCl ($a_0 = 6.2929 \text{ \AA}$) as an internal standard. Integrated intensities for 336 independent

TABLE 2. Electron Probe Analysis of Krupkaite in Specimen R27792 from the Juno Mine

R27792	Krupkaite, $\text{CuPbBi}_3\text{S}_6$
Bi 59.8	57.7
Pb 19.3	19.0
Cu 5.95	5.8
Ag Nd	-
Fe Nd	-
S 17.25	17.7
Se .95	-

TABLE 3. Unit Cell Dimensions for Bismuthinite, Krupkaite, and Aikinite

Mineral	Bismuthinite,	Krupkaite,	aikinite,
	Bi_2S_3	$\text{CuPbBi}_3\text{S}_6$	CuPbBiS_3
Lattice parameters	a = 11.28 Å b = 3.97 c = 11.11	c = 11.56 Å a = 4.00 b = 11.20	a = 11.5083 Å b = 4.0279 c = 11.2784
Space group	$Pnma$	Systematically absent reflections $h0l$ ($l \neq 2n$) (Alternatives) $Pmcm$, $P2cm$, $Pmc2_1$.	$Pnma$
	2	2	4

reflections from the single crystal were collected with $\text{CuK}\alpha$ using an ω -scan performed with a Stoe equi-inclination diffractometer equipped with a proportional counter. Background intensity was recorded for 100 sec at $\pm 2^\circ$ from the diffractometer maximum, and the total counts were accumulated as the crystal was rotated through 4° in ϕ at a scanning rate of $4^\circ/200$ sec. Subsequent data handling has been described by Mumme (1974).

Krupkaite has a high linear absorption coefficient for $\text{CuK}\alpha$ (1404 cm^{-1}); thus, the crystal's irregular shape made the calculation of absorption corrections difficult. The correction finally used was obtained by the empirical method attributed to North, Phillips, and Mathews by Arndt and Willis (1966) in which the variation of intensity with azimuth is observed for a low angle reflection whose scattering vector is parallel to the ϕ axis.

The Weissenberg films indicated orthorhombic symmetry for krupkaite and systematic absences for $h0l$ reflections with $l = 2n$, which permits $Pmcm$ (D_{2h}^5), $P2cm$ (C_{2v}^4) and $Pmc2_1$ (C_{2v}^2).

Structure Determination and Refinement

The absence of any super-lattice reflections, such as would be required by the doubling of the b axis predicted at this composition by Moore (1967), and the strong odd-order reflections along the $0k0$ axial row on the Weissenberg films, showed that while krupkaite had a unit cell of similar size to those of bismuthinite and aikinite, its space group was different (Table 1).

The intensity distribution of reflections on the $0kl$, $1kl$ and $2kl$ Weissenberg films indicated that the atomic distribution in krupkaite was close to that in bismuthinite and aikinite, thus eliminating two of the space group alternatives, $Pmcm$ and $P2cm$. Both of these would require mirror planes parallel to a , which is incompatible with the aikinite structure. In the set-

ting of axes used in Table 3, the mirror planes in aikinite and bismuthinite are perpendicular to the b axis in these structures. A similar conclusion was reached by Ohmasa and Nowacki (1970) when Welin (1966) attributed the space group $Pbmm$ to the aikinite derivative "5³-aikinite". They pointed out that of the alternatives available, the only possible space group compatible with the aikinite structure (in Welin's setting) was again $Pb2_1m$ (C_{2v}^2).

TABLE 4. Guinier Powder Data for Krupkaite

I	d (meas)	d (calc)	hkl
6	5.793	5.780	002
6	5.597	5.600	020
6	5.146	5.136	012
12	4.026	4.022	022
10	3.781	3.783	030
		3.772	110
30	3.645	3.644	013
20	3.594	3.586	111
24	3.552	3.553	031
7	3.294	3.293	102
		3.174	023
5	3.180	3.159	112
27	3.160	3.136	032
100	3.137	3.136	121
		2.884	004
37	2.841	2.838	122
		2.798	040
		2.721	041
13	2.732	2.731	130
26	2.660	2.658	131
		2.681	033
21	2.567	2.568	024
20	2.526	2.520	042
7	2.488	2.488	123
		2.469	132
19	2.343	2.344	104
12	2.294	2.285	034
		2.294	114
		2.295	140
6	2.250	2.251	141
10	2.229	2.228	133
16	2.133	2.137	025
		2.133	142
3	2.097	2.089	052
12	2.005	2.011	044
		2.003	200
26	1.970	1.966	035
		1.971	115
		1.972	143
		1.972	210
5	1.954	1.955	150
12	1.934	1.937	053
12	1.926	1.927	006
		1.928	151
5	1.864	1.867	060
		1.866	212
		1.861	221
2	1.841	1.843	061

TABLE 5. *R* Values and Temperature Factors for the Various Copper Occupancies of the Cu(1) and Cu(2) Sites

Model for copper ordering, Sites 1 : Site 2	1 : 0	1/2 : 1/2	1/3 : 2/3	1/5 : 4/5	0 : 1
<i>R</i> value	11.60	9.83	9.76	9.70	9.78
Temperature Factors, <i>U</i>					
Cu(1)	0.1116	0.095	0.083	0.060	—
Cu(2)	—	0.011	0.020	0.042	0.043

The data refinement used the least squares refinement program of Daly, Stephens, and Wheatley (1963) and the weighting scheme of Cruickshank *et al* (1961). All atoms were placed in the special positions 2(a) or 2(b) and the one copper atom was distributed equally between the two sites available to it. The original atomic positions used were those determined for aikinite by Kohatsu and Wuensch (1971), but transposed by $\frac{1}{4}b$. The refinement yielded a final *R* value of 9.83 percent when the shifts of all parameters except the isotropic temperature factor of Cu(1) were less than $\frac{1}{4}$ of their e.s.d.'s. The temperature factor of Cu(1) increased to the high value of $U = 0.0957$, while that of Cu(2) was much smaller at 0.0115. This behavior of the temperature factors suggested that the Cu(1) site contained much less copper than the Cu(2) site. Thus rather than the initial 1 : 1 distribution of copper which was, of course, only a computational device used in solving the structure, the refinement seemed to indicate that copper had a preference for site Cu(2). In fact, the lowest *R* value of 9.70 percent was obtained when Cu(1) contained 20 percent copper and Cu(2) contained 80 percent copper. Furthermore, the temperature factors of the copper atom sites behaved normally during this refinement (see Table 5).

Hamilton (1965) compiled tables in which the variance ratios $F_{b,n-m}$ (Hamilton, 1964) are converted to critical *R* factor ratios \mathcal{R} for comparing alternate hypotheses at a given significance level. In the present case we find that when 33 coordinates for the ordered copper model are replaced by 36 coordinates for the 20 percent disordered model:

$$\mathcal{R}_{36-33, 336-36, 0.10} = 1.0104,$$

$$\mathcal{R}_{36-33, 336-36, 0.25} = 1.0068.$$

The observed *R* factor ratio is $\mathcal{R} = 9.78/9.70 = 1.0082$, so that the probability of error if the hypothesis of 20 percent disordering is rejected lies between 10 percent and 25 percent. Usual practice would not demand the rejection of the hypothesis at this level. Therefore the results of the refinement do

not preclude the 20 percent disordered model. Also a three-dimensional Fourier synthesis calculated just before the final refinement cycle showed a residual peak associated with the Cu(1) site. Thus, even though *R* differs by only 0.08 percent for full occupancy of site Cu(2) as compared to 80 percent occupancy, a small amount of disorder in the copper must be considered a possibility.

The structure would certainly be a more pleasing one if it were comprised completely of ordered $[\text{CuPbBi}_3\text{S}_6]$ units and for this reason krupkaite is shown in Figure 1 as a completely ordered structure. The scaled observed data and the structure amplitudes calculated from the final model are listed in Table 6.

Results of Refinement

The asymmetric unit contains one lead, three bismuth, and one copper atom plus six sulfur atoms, all at special positions 2(a) and 2(b). The atomic coordinates (Table 7) permit distinction between the lead and bismuth positions on the basis of bond lengths. The copper atom in the structure is mostly ordered into one of the two sites available to it.

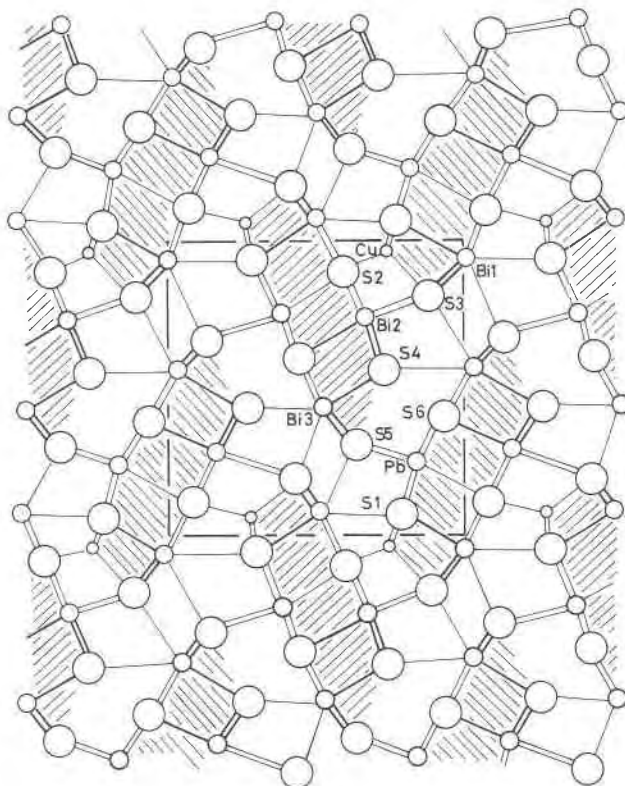


FIG. 1. The crystal structure of krupkaite projected onto (100). The shaded regions correspond to the stibnite quadruple chain.

TABLE 7. Atomic Coordinates in Krupkaite*

		x	y	z	B (Å ²)
Bi 1	(2a)	0	0.0629 (6)	0.9851 (7)	1.74 (14)
Bi 2	(2a)	0	.2882 (6)	.6563 (7)	1.78 (14)
Bi 3	(2b)	$\frac{1}{2}$.5777 (6)	.5217 (7)	1.98 (16)
Pb 1	(2b)	$\frac{1}{2}$.7503 (7)	.8305 (8)	2.33 (16)
Cu 1(.2)(2a)		0	.5465 (180)	.7652 (191)	4.73 (307)
Cu 2(.8)(2b)		$\frac{1}{2}$.0373 (33)	.7297 (32)	3.31 (61)
S 1	(2a)	0	.9463 (51)	.7853 (50)	2.54 (115)
S 2	(2b)	$\frac{1}{2}$.1231 (35)	.5491 (32)	1.60 (91)
S 3	(2b)	$\frac{1}{2}$.1919 (44)	.8725 (45)	1.85 (102)
S 4	(2b)	$\frac{1}{2}$.4513 (39)	.7142 (36)	1.57 (83)
S 5	(2a)	0	.6972 (38)	.6131 (41)	1.08 (85)
S 6	(2a)	0	.6100 (78)	.9594 (75)	3.87 (188)

* esd's in parentheses.

Discussion of the Structure

The seven lead-sulfur distances, ranging from 2.95 to 3.27 Å (Table 8), agree with those found in other lead sulfosalts (Nowacki, 1969; Mumme, 1974). The five closest sulfurs form a square pyramid about lead, with the lead atom displaced from the base of the pyramid so that all S-Pb-S angles are much less than 90°. The two more-distant sulfurs (at 3.27 Å) constitute a "split vortex" for octahedral coordination, as is found in aikinite (Kohatsu and Wuensch, 1971),

in B-type rare earth oxides (Cromer, 1957), and some zirconium oxy-salts (Bear and Mumme, 1971).

The bismuth atoms also have seven sulfur neighbors. Bond lengths range from 2.54 to 3.57 Å. In Bi(3) the seventh sulfur is nearly 0.5 Å further away than the other six and is not considered to be part of the nearest neighbor configuration. The coordination scheme differs from that for lead, with three sulfur atoms being close to bismuth and the other four at greater distances. The three closest constitute a BiS₃ trigonal pyramid which is characteristic of group V metals with p³ electron configuration. The sulfur atoms, when those at intermediate distances are included, become in the case of Bi(3) a distorted octahedron, and in the case of Bi(1) and Bi(2) constitute a split vortex octahedron. In each case the bismuth atom is distorted away from the plane of the square formed by the close and intermediate sulfur atoms.

Copper, in site Cu(2), has tetrahedral coordination, with Cu-S distances of 2.29 to 2.39 Å, which are normal for copper containing sulfosalts. The distortion of the tetrahedra is evidenced by the bond angles, which range from 97.1 to 118.2°.

TABLE 8. Interatomic Distances and Bond Angles in Krupkaite*

Interatomic Distances			Bond Angles					
**Cu1-S4	2.34(18)	x2	Copper					
S5	2.44(18)		S4-Cu1-S4	117.3(7)	S1'-Bi1-S3	81.2(1)	x2	
S6	2.36(19)		S4-Cu1-S5	97.7(6)	x2	S1'-Bi1-S2	82.8(1)	x2
Cu2-S1'	2.33(6)	x2	S5-Cu1-S6	118.6(7)		S3-Bi1-S3	91.6(1)	
S2	2.30(4)		S4-Cu1-S6	111.2(7)	x2	S3-Bi1-S2'	90.0(1)	x2
S3	2.39(5)					S2'-Bi1-S2'	89.2(1)	
Bi1-S1'	2.65(5)		S1'-Cu2-S1'	118.2(2)		S5'-Bi1-S3	76.8(1)	x2
S1''	3.11(5)		S1'-Cu2-S2	115.6(2)	x2	S1''-Bi1-S2'	74.1(1)	x2
S2'	2.98(3)	x2	S1'-Cu2-S3	97.1(2)	x2	S5'-Bi1-S1''	63.2(1)	
S3	2.79(4)	x2	S2-Cu2-S3	108.9(2)				
S5'	3.06(4)		Lead			S6'-Bi2-S4	85.6(1)	x2
Bi2-S6'	2.54(5)		S2-Pb1-S1''	78.3(1)	x2	S6'-Bi2-S2	84.5(1)	x2
S2	2.99(4)	x2	S2-Pb1-S6'	79.5(1)	x2	S2-Bi2-S2	83.9(1)	
S4	2.79(4)	x2	S1'''-Pb1-S1'''	83.1(1)		S4-Bi2-S4	91.5(1)	
			S6'-Pb1-S6'	85.4(1)		S2-Bi2-S4	91.5(1)	x2
			S6'-Pb1-S5''	91.5(1)	x2	S3-Bi2-S2	73.3(1)	x2
						S3-Bi2-S4	66.9(1)	x2
S3	3.38(5)	x2	S5'-Pb1-S1'''	113.9(1)	x2	S3-Bi2-S3	72.6(1)	
Bi3-S4	2.64(4)		S5'-Pb1-S6'	134.9(1)	x2	S3-Bi2-S2	120.3(1)	x2
S6'	3.00(5)	x2	S5'-Pb1-S1'''	66.0(1)	x2	S3-Bi2-S4	117.1(1)	x2
S5	2.63(5)	x2	S5'-Pb1-S6'	82.9(1)	x2			
S4'	3.57(4)		S5'-Pb1-S5'	75.5(1)		S4-Bi3-S6'	79.8(1)	x2
S3'	3.10(4)					S4-Bi3-S5	89.3(1)	x2
Pb1-S2	2.89(5)					S6'-Bi3-S6'	83.6(1)	
S''	3.02(4)	x2				S5-Bi3-S5	99.1(1)	
S5'	3.27(5)	x2				S5-Bi3-S6'	87.1(1)	x2
S6'	2.95(5)	x2				S4'-Bi3-S3'	61.6(1)	
						S3'-Bi3-S5	78.5(1)	x2
						S4'-Bi3-S6'	72.7(1)	x2

* Estimated standard deviations in parentheses.

** Cu1 is an almost empty site.

TABLE 9. Relative Metal Displacements in Bismuthinite, Krupkaite, and Aikinite

Bismuthinite			CuPbBi ₃ S ₆			% Expansion relative Bi ₂ S ₃			Aikinite			% Expansion relative Bi ₂ S ₃								
a =	11.28		c =	11.56	2.5	a =	11.61	2.9	b =	3.97	.8	b =	4.03	1.5	c =	11.10	.9	c =	11.28	1.5
Atom site	Type	z/Param	Type	y/Param*	ΔBi ₂ S ₃	Type	z/Param	ΔBi ₂ S ₃	ΔCuPbBi ₃ S ₆											
M1	Bi(1)	.1741	Bi(1)	.1871	+0.0130	Bi	.1812	+0.0071	-.0059											
M2	Bi(2)	.4660	Pb(1)	.4997	+0.0337	Pb	.4880	+0.0220	-.0107											
M3	Bi(1)	.6741	Bi(3)	.6723	-.0018	Bi	.6812	+0.0071	+0.0089											
M4	Bi(2)	.9660	Bi(2)	.9618	-.0042	Pb	.9880	+0.0220	+0.0262											

* y translation of $\frac{1}{4}b$. $y(\text{krupkaite}) \equiv z(\text{bismuthinite, aikinite})$.

Interstitial Copper

In comparing the addition of the interstitial copper and the substitution of lead for bismuth on the related arrangements in aikinite and bismuthinite, Kohatsu and Wuensch (1971) showed that the atomic positions of the two structures are nearly identical in spite of the addition of the copper atom. Aikinite is basically an expanded version of bismuthinite, with the significant exception of an alteration in the z coordinates of the lead atom. This suggested an overall repulsive interaction of lead with copper in aikinite, where the z parameter determines the lead-copper separation, which is mainly directed along [001].

The foregoing effect is also evident in krupkaite (Table 9); the largest distortion from the bismuthinite structure once again is the y ($\equiv z$, bismuthinite) coordinate of the one lead atom in the $M(2)$ site in the structure. The Bi(2)–Cu(1) separation in krupkaite is 3.16 Å while the Pb(1)–Cu(2) separation is 3.41 Å. In aikinite the lead-copper separation is 3.37 Å. The effect then is not so much a repulsive interaction between lead and copper as the fact that the short Bi(2)–S(4) bonds impose a short separation between Bi(2) and Cu(1) of 3.16 Å, which is only about 0.3 Å greater than the sum of their elemental radii. The copper is concentrated into the Cu(2) site in krupkaite because in this position there is not so close an interaction between Pb(1) and Cu(2) as there is between Bi(2) and Cu(1).

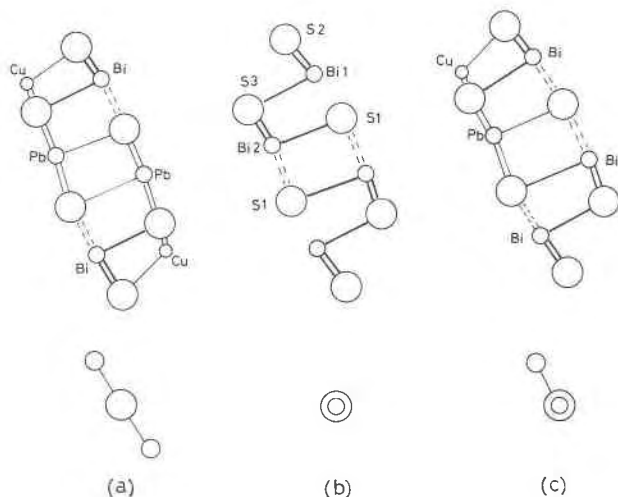


FIG. 2. The three possible ribbons in the structures of aikinite derivatives and their schematic representation as presented by Ohmasa and Nowacki (1970): (a) the a ribbon, (b) the b ribbon, (c) the c ribbon.

The c Ribbon

Ohmasa and Nowacki (1970) described the structures of bismuthinite, aikinite, and the aikinite derivatives in terms of three kinds of structural ribbons. In Figure 2 all three ribbons are projected normal to their elongated direction, that is the b axis of aikinite and bismuthinite, and the a axis of krupkaite. Two copper atoms, two lead atoms, and two bismuth atoms belong to an a ribbon, four bismuth atoms to a b ribbon, and one copper, one lead, and three bismuth atoms to a c ribbon. They assumed that copper cannot be coupled with the Bi₂S₃ ribbon of bismuthinite, presumably because this would have caused a lengthening of the Bi(2)–S(3) bonds. They argued that the Bi(2) atom in such a ribbon would have to form a trigonal pyramid with one S(1) and two S(1)' atoms in the bismuthinite structure (see Fig. 2 b). This would lead to a Bi₂S₃ ribbon with a con-

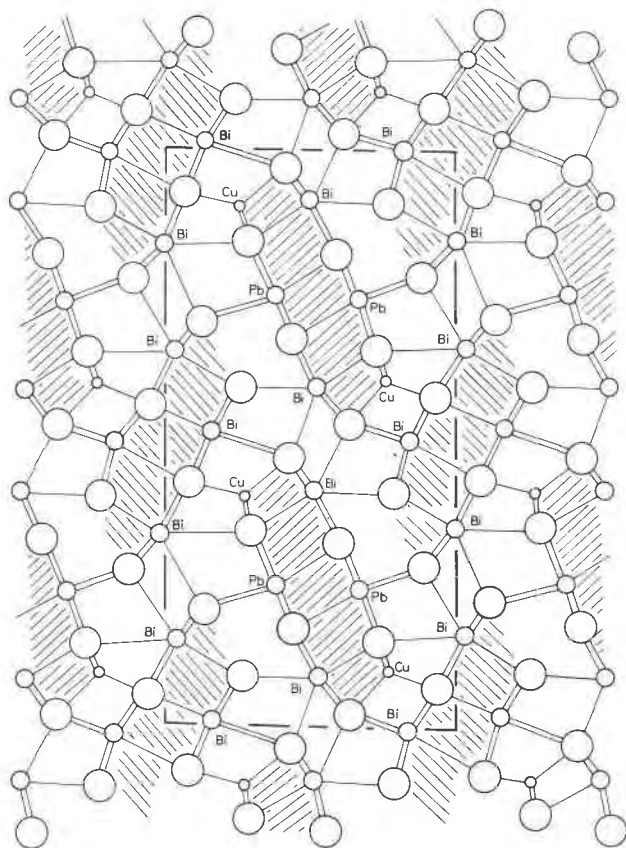


FIG. 3. A hypothetical crystal structure of "2'-aikinite", $2(\text{Cu}_2\text{Pb}_2\text{Bi}_6\text{S}_{12})$, as a super-structure of aikinite. This structure exemplifies one particular distribution of lead, bismuth, and copper in the four-fold positions. The dashed line surrounds the *a* and *b* ribbons.

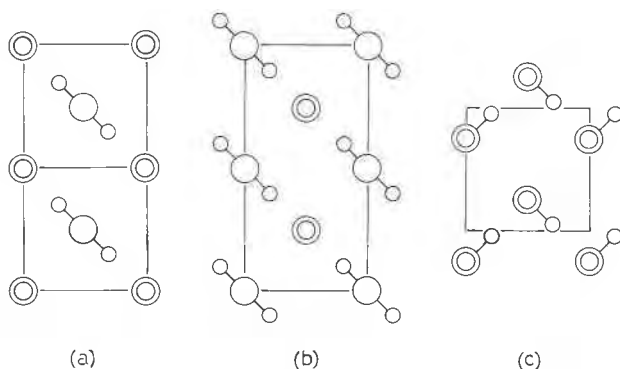


FIG. 4. Ribbon models for krupkaite. (a) and (b) are the hypothetical super-structure models based on the aikinite structure as predicted by Welin (1966) and Moore (1967). (c) The structure of krupkaite determined in this present investigation with the *c* ribbon as its basis.

figuration different from that of the Sb_2S_3 ribbon in stibnite (which has the same structure as bismuthinite) and from the similar ribbon found in aikinite.

Kohatsu and Wuensch (1973) have reported that the structure of gladite, $\text{CuPbBi}_5\text{S}_9$, is a super-structure based on Bi_2S_3 in which 1/6 of the Bi are replaced by Pb, and only 1/3 of a set of available tetrahedral interstices are occupied by copper. In spite of the close similarity between the stibnite-type ribbons in bismuthinite and in aikinite (Kohatsu and Wuensch, 1971), gladite contains one $[\text{Bi}_4\text{S}_6]$ and two $[\text{CuPbBi}_3\text{S}_6]$ slabs alternating along $[100]$ rather than a combination of aikinite and bismuthinite units. That is, gladite is found to consist of a mixture of "b-ribbons" and "c-ribbons", and not the mixture of "a-" and "b-ribbons" preferred by Ohmasa and Nowacki (1970). Also, Kohatsu and Wuensch (1973) found that the heavy metal positions in bismuthinite, aikinite, and gladite are similar when the site is occupied by the same species, but there are significant displacements of the locations of a Pb (or Bi) atom in gladite relative to a Bi (or Pb) atom in aikinite or bismuthinite.

The structure of krupkaite also shows that whereas there may be a limited association of copper atoms with bismuth atoms, the *c* ribbon does actually exist and is in fact the basis of the krupkaite structure. It is predicted that it also plays an important part in the formation of other structures in the Bi_2S_3 - CuPbBiS_3 series.

Existence of Bismuthinite Derivatives

One of the possible structures for "2'-aikinite", based on the super-structure arrangements of bismuthinite derivatives proposed by Welin (1966) and Moore (1967), is shown in Figure 3. This and a closely related structure are depicted using the ribbon notation of Ohmasa and Nowacki (1970) in Figure 4 a and b. Neither of these two structures brings copper into close association with bismuth—they are both made up of *a* and *b* ribbons alone—and for this reason their existence is a possibility. The metal ordering required in these two hypothetical structures and in the structure of krupkaite, determined here, is in contrast with the results of the experiments carried out by Springer (1971), which indicated that there is complete solid solution between bismuthinite and aikinite above 300°C . In further experimental runs of up to three months duration he found that complete equilibration between reactants and products was not achieved at temperatures below 300°C . Because the unit cell

of krupkaite resembles those of bismuthinite and aikinite, Springer may have overlooked it in his work, although a more recent study of this same system by Mumme and Watts (in preparation) has, also, not disclosed formation of krupkaite under laboratory conditions. Alternatively, and more likely, the conditions of relatively slow cooling which existed in the natural sulfide deposits as compared with laboratory experiments would favor an approach to equilibrium conditions in which the ordering of metals to form the *c* ribbon found in krupkaite has resulted (Fig. 4 c), perhaps at temperatures below 300°C. While it is possible that the hypothetical super-structures of Welin (1966) and Moore (1967) may represent an intermediate stage of crystallization, there must be some doubt now as to whether the extensive series that they propose does exist, in which case it may not be reasonable to use the Z^n type nomenclature to designate any member found in the series. In particular it does not apply to the structure of krupkaite determined here.

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