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LINDSTRÖMITE, $Cu_3Pb_3Bi_7S_{15}$: ITS SPACE GROUP AND ORDERING SCHEME FOR METAL ATOMS IN THE CRYSTAL STRUCTURE

HIROYUKI HORIUCHI* AND B. J. WUENSCH

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

ABSTRACT

Lindströmite, $Cu_3Pb_3Bi_7S_{15}$, is orthorhombic, *a* 56.115(4), *b* 11.5695(8), *c* 4.001(5)Å, D_{calc}=7.03 g/cm^3 for Z=4. The type crystal contains a small amount of exsolved krupkaite whose reflections mask an *n*-glide parallel to (010) to simulate space group $Pb2_1m$. The true space group is *Pbnm*. The structure is a superstructure with *a* five times that of bismuthinite and was solved in projection from visually-estimated intensities through examination of all 110 configurations which are permitted by the subgroup-supergroup relationship. Refinement was carried to R=16.3% by least-squares techniques. The structure contains 28 independent atoms (7Bi, 3Pb, 3Cu and 15S) and is built of $CuPbBi_3S_6$ krupkaite and $Cu_2Pb_2Bi_2S_6$ aikinite ribbons in the ratio 4:1.

SOMMAIRE

La lindströmite, $Cu_3Pb_3Bi_7S_{15}$, est orthorhombique, *a* 56.115(4), *b* 11.5695(8), *c* 4.001(5)Å et *D*(mes.) 7.03 avec Z=4. L'échantillon type contient une petite quantité de krupkaite dont les réflexions masquent un plan de glissement *n* parallèle à (010), simulant ainsi le group spatial $Pb2_1m$. Le vrai groupe spatial est *Pbnm*. Cette superstructure, avec *a* cinq fois celle de la bismuthinite, a été résolue en projection à partir des intensités estimées visuellement à l'examen des 110 configurations permises par la relation sousgroupe-supergroupe. L'affinement a été effectué jusqu'à R=16.3% par des méthodes de moindres carrés. La structure qui contient 28 atomes indépendants (7Bi, 3Pb, 3Cu et 15S), est construite de plaques de $CuPbBi_3S_6$ krupkaite et de $Cu_2Pb_2Bi_2S_6$ aikinite dans le rapport 4:1.

(Traduit par la Rédaction)

INTRODUCTION

A number of Cu-Pb-Bi sulfosalts (Lindström 1887, 1889; Flink 1910) were described from the copper and cobalt deposit at Gladhammar, Kalmar, Sweden. Johansson (1924) later reported a chemical analysis for a phase with composition close to $CuPbBi_3S_6$, an apparent new mineral for which he proposed the name lindströmite. In a reinvestigation of Gladhammar material preserved in the Naturhistoriska Riksmuseet, Stockholm, Welin (1966) obtained crystal data which confirmed the mineral as a new species. However, spectrographic analysis of material from the same hand specimen as Johansson's lindströmite (Naturhistoriska Riksmuseet Catalogue No. RM 24100:3) showed the composition to be $Cu_{2.40}Pb_{2.40}Bi_{5.60}S_{12} \approx Cu_3Pb_3Bi_7S_{15}$, and *not* the rather similar composition $CuPbBi_3S_6$. The identity of "lindströmite" was further complicated by the nearly simultaneous discovery by Zák *et al.* (1974), and Mumme (Large & Mumme 1975; Mumme 1975) that $CuPbBi_3S_6$ *per se* exists as a distinct mineral. It was proposed (Mumme *et al.* 1976) that the name lindströmite be retained for the $Cu_3Pb_3Bi_7S_{15}$ originally studied by Johansson (1924); $CuPbBi_3S_6$ was given the new name krupkaite (Zák *et al.* 1974). This nomenclature was approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

Lindströmite is one of five ordered phases presently known to be intermediate to bismuthinite, Bi_2S_3, and aikinite, $CuPbBiS_3$. One end member of the series, bismuthinite, has a structure composed of quadruple Bi_4S_6 chains (Kupčík & Veselá-Nováková 1970). Aikinite, with virtually the same lattice constants and the same space group as bismuthinite, has a structure which is built of similar chains (Wickman 1953), but the interior pair of Bi atoms in the quadruple chain is replaced by Pb, and Cu atoms are added to entirely fill a set of available tetrahedral interstices (Ohmasa & Nowacki 1970a; Kohatsu & Wuensch 1971). The intermediate phases are derivatives of the bismuthinite structure in which only a portion of the interior Bi atoms in the bismuthinite ribbon is replaced by Pb and the Cu atoms are ordered among a fraction of the tetrahedral interstices.

Structures (in order of increasing Pb:Bi) have been established for pekoite, $CuPbBi_{11}S_{18}$

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*Present address: The Institute of Scientific and Industrial Research, Osaka University, Japan

(Mumme & Watts 1976); gladite, $CuPbBi_5S_9$ (Kohatsu & Wuensch 1973, 1976; Syneček & Hybler 1974); krupkaite, $CuPbBi_3S_6$ (Syneček & Hybler 1974; Mumme 1975; and Kaplunnik *et al.* 1975, whose "lindströmite" is krupkaite in the revised nomenclature), and hammarite, $Cu_2Pb_2Bi_4S_9$ (Horiuchi & Wuensch 1976). The structure of lindströmite was heretofore undetermined. It is the most complex of the intermediate phases, having one lattice constant 5 times that of a corresponding translation of bismuthinite. (Pekoite, gladite and hammarite are 3-fold superstructures, whereas krupkaite has the same cell as bismuthinite but a space group of lower symmetry). Unlike the majority of the superstructures thus far established, lindströmite has Pb:Bi $> 1/3$. This, plus the greater structural complexity, made a structure determination of great interest toward establishment of the crystal chemical rules which govern this family of ordered minerals.

The present work describes a structural study of lindströmite which, though conducted in projection with visually-estimated intensities, established the ordering scheme with certainty. The probable space group deduced by Ohmasa & Nowacki (1970b) was found to be incorrect and it was necessary to revise the models permitted by the subgroup-supergroup relationship. The structure presently determined for lindströmite augments and confirms the principles which have emerged from study of the other bismuthinite derivative structures.

EXPERIMENTAL

The original single crystal of lindströmite (RM 24100:3) from Gladhammar, which had been isolated by Welin (1966), was employed in the study. The specimen consists of a slender fragment, approximately 0.50×0.07×0.05 mm, whose shape could be satisfactorily approximated by a set of five planar surfaces. The crystal is a unique specimen: most of the material in the original hand specimen was found to contain abundant lamellar exsolution (Welin 1966). Harris & Chen (1976) identified lindströmite from a second locality (Silver Miller mine, Cobalt, Ontario; Smithsonian Institution, Catalogue No. NMNH 106760), but report "only very weak streaky reflections were observed for the superlattice".

Diffraction patterns showed lindströmite to be orthorhombic. Lattice constants *a* 56.115(4) = 5×11.223, and *b* 11.5695(8)Å were determined from a least-squares fit (Burnham 1962) to 78 *hk*0 reflections recorded with Cu*Kα* radiation using a back-reflection Weissenberg camera. A value *c* 4.001(5)Å was measured from precession photographs. These data provide $D_{calc} = 7.03$ g/cm^3 for $Z=4$ ideal formula units. The lattice constants obtained in the present work are in good agreement with previous values *a* 56.07, *b* 11.45, *c* 4.02Å (Welin 1966) and *a* 56.15, *b* 11.56, *c* 3.99Å (Harris & Chen 1976).

The space group of lindströmite was reported by Welin (1966) as *Pbmm*. Ohmasa & Nowacki (1970b), however, showed that the derivative-structure relationship to bismuthinite permits only the noncentrosymmetric space group $Pb2_1m$, a result which was restated by Harris & Chen (1976). As described in detail in the following section, the present structure analysis revealed a centrosymmetric atomic arrangement and subsequent re-examination of the diffraction patterns showed that a small amount of exsolved second phase in the crystal produced extra reflections which insidiously masked the presence of an *n*-glide in the structure. The true diffraction symbol of lindströmite is *mmmPbn–* which permits $Pbn2_1$ (C^9_{2v}) or *Pbnm* (D^{16}_{2h}) as possible space groups. The latter proved to be necessary for description of the structure.

The intensity data employed in the analysis of the structure were photographically recorded with Ni-filtered Cu*Kα* radiation ($\mu = 1399$ cm^{-1}) using an equi-inclination Weissenberg camera and the multiple-film technique. The recorded intensities were estimated visually through comparison with a standard density wedge. Of 818 independent *hk*0 reflections with $2\theta \leq 157°$, a total of 317 was undetectable. Standard corrections for Lorentz, polarization and absorption factors were applied in converting the data to structure factors.

DETERMINATION OF THE STRUCTURE

The intensity distribution of strong substructure reflections confirmed Welin's observation that lindströmite is a superstructure based upon a bismuthinite-like arrangement of atoms. Zero through third level *c*-axis Weissenberg photographs apparently displayed systematic absences only for 0*kl* reflections with $k \neq 2n$. The noncentrosymmetric space group $Pb2_1m$, suggested by Ohmasa & Nowacki (1970b) was therefore assumed to be correct. For a bismuthinite-like arrangement of atoms this required 20 heavy-metal atoms (6 Pb and 14 Bi), 6 Cu and 30 S atoms in the asymmetric unit of the structure, all in special positions 2(*a*)*m xy*0 and 2(*b*)*m xy*½ of space group $Pb2_1m$. The Cu atoms must occupy 6 of the 10 available interstitial sites in the bismuthinite-like array:

$A(0.092, 0.268)$, $B(0.192, 0.232)$, $C(0.292, 0.268)$, $D(0.392, 0.232)$, $E(0.492, 0.268)$, $F(0.592, 0.232)$, $G(0.692, 0.268)$, $H(0.792, 0.232)$, $I(0.892, 0.268)$, or $J(0.992, 0.232)$, where the ideal coordinates were derived from the coordinates of Cu in the structure of aikinite (Kohatsu & Wuensch 1971). The copper atoms designated *B,D,F,H* and *J* occupy position $2(a)$, whereas *A,C,E,G* and *I* occupy $2(b)$. There exist 110 possible configurations for the arrangement of 6 Cu atoms among these sites.

Systematic examination in succession of all 110 models for the Cu distribution was considered too laborious to be practical, and a special procedure was devised for determination of the structure. The greater portion of the atoms in an idealized initial model occupy the positions of a bismuthinite-like array. The contribution of these atoms to a given structure factor therefore need be evaluated only once. The difference between alternative configurations for the structure consists only in the placement of the 6 Cu atoms (although, as discussed below, it proved necessary also to incorporate in the initial models the displacement of the metal position occupied by the substituted Pb atom). As the placement of Cu in a given site is common to a large fraction of the models, its contribution to a given structure factor may also be evaluated once and used subsequently as required. This approach to systematic examination of all possible models for the superstructure was implemented in a program written for an IBM 370/168 computer. The program accepted as data a limited subset of the diffraction data. For each structure factor the common contribution of the invariant atoms was computed. The contribution to each structure factor of the Cu atom in the individual interstices (plus displacement of the associated Pb) was then evaluated and stored for subsequent use in the various models. Through this procedure all 110 models for the structure could be examined in one set of computations with a surprisingly small expenditure of computer time. Two criteria were used to select the most probable model: the conventional R value $\Sigma||F_{\text{obs}}| - |F_{\text{calc}}||/\Sigma|F_{\text{obs}}|$ evaluated for both observed and unobserved structure factors, and, as a second useful index, ΣF_{calc} for the *unobserved* structure factors, a quantity which should ideally be close to zero.

All 110 possible arrangements of Cu among the interstices of an ideal bismuthinite array were examined for the separate subsets of reflections $h00$, $h10$, $h20$, $h30$ and $h40$. These computations gave no definitive indication of a most probable model. The reason for this lack of success was that, as in other bismuthinite derivatives (*e.g.*, Kohatsu & Wuensch 1976), the superstructure intensities are dominated by distortions in the array of heavy-metal atoms rather than by the placement of the interstitial Cu atom. The most important of these distortions is the displacement along a of the substituted Pb atom. This feature is illustrated in Figure 1 in which the $Cu_2Pb_2Bi_2S_6$ ribbon of aikinite (Kohatsu & Wuensch 1971) is superposed on the Bi_4S_6 unit of bismuthinite (Kupčík & Veselá-Nováková 1970). The x and y displacements of the Pb atom, as derived from the structure of aikinite, were accordingly taken into account in establishing ideal coordinates for the atoms in the initial models. The Pb atom was assumed to be coupled to the sites occupied by Cu as in the known structures of the other bismuthinite derivatives. Although this *assumes* a particular crystal chemical principle, the assignment of Pb atoms may be confirmed through examination of interatomic distances (which differ for Bi and Pb) in the final model. Moreover, since the Pb distortion determines the bulk of the superstructure intensities, the Cu atom distribution may be

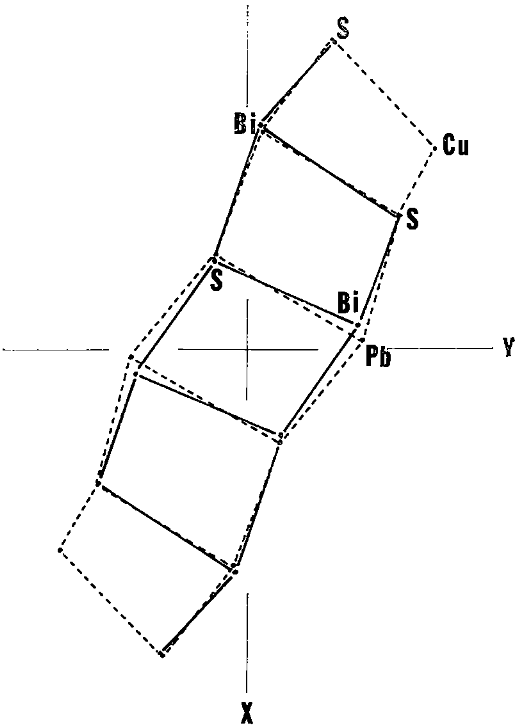

FIG. 1. Superposition of the $Cu_2Pb_2Bi_2S_6$ ribbon of aikinite (Kohatsu & Wuensch 1971) on the Bi_4S_6 unit of bismuthinite (Kupčík & Veselá-Nováková 1970) to indicate that the major distortion in bismuthinite derivatives is displacement of the substituted Pb atom.

TABLE 1. RESULTS OF STRUCTURE FACTOR CALCULATIONS (FOR FIVE SUBSETS OF hkO DATA) FOR THE 110 IDEAL CONFIGURATIONS PERMITTED BY THE INITIALLY-ASSUMED $Pb2_1m$-$Pbnm$ SUBGROUP-SUPERGROUP RELATIONSHIP BETWEEN LINDSTRÖMITE AND BISMUTHINITE. (The five most probable results are listed for each data subset and the most probable model is denoted by an asterisk.)

hk0 Total No. F's (No. F_{unobs})	Model Number	Cu atom Configuration	R(%)	ΣF_{cal} (for F_{obs} = 0)
h00	107	BCE(GHJ)*	45.5*	647*
75	109	ACD(FHI)	50.5	491
(35)	83	BCDGHJ	55.5	1507
	108	ABD(FGI)	56.1	709
	104	ACE(FHJ)	56.2	346
h10	95	ABDFHI	52.6	785
70	107	BCE(GHJ)*	52.8*	683*
(17)	23	ADFHIJ	54.0	917
	98	ABCDFI	54.5	1114
	13	ABDFIJ	54.6	1126
h20	23	ADFHIJ	50.5	1171
70	107	BCE(GHJ)*	52.1*	817*
(19)	2	ABGHIJ	52.1	1093
	3	ABDHIJ	52.2	1198
	100	ACFGHI	53.2	1301
h30	107	BCE(GHJ)*	57.5*	1442*
70	108	ABD(FGI)	63.1	1500
(29)	109	ACD(FHI)	65.1	1800
	95	ABDFHI	65.2	1978
	96	ABCDGI	65.3	1693
h40	107	BCE(GHJ)*	35.7*	652*
65	98	ABCDFI	37.6	1004
(17)	13	ABDFIJ	38.0	918
	95	ABDFHI	39.9	1046
	79	CEGHIJ	40.0	1085

The Cu distributions for which the last three sites have been enclosed within parentheses are centrosymmetric. The initial three positions and those included within parentheses are equivalent by inversion.

confirmed through use of difference Fourier syntheses.

The results of the calculations for the idealized starting models are presented in Table 1, in which an overall isotropic temperature factor of 1.2Å^2 was employed. The five most probable of the 110 Cu atom configurations are listed, along with R and the sum of $|F_{calc}|$ for the unobserved structure factors. For calculations performed with each of the five subsets of data, only two distributions appear among the five most probable more than twice: No. 95 (*ABDFHI*) and No. 107 (*BCEGHJ*). The latter is the only distribution to appear among the five most probable for all five subsets of data, has the lowest value of R for three of the five subsets, and has the smallest value of ΣF_{calc} for unobservable reflections for four of the five subsets. This was taken as definite indication that *BCEGHJ* is the correct configuration of Cu atoms. This ideal structure is unexpectedly centrosymmetric. Refinement of the model in the proposed noncentrosymmetric space group $Pb2_1m$ proceeded to R=13.8% but produced somewhat unreasonable interatomic distances. Another difficulty which was encountered was the appearance of pairs of "ghost" peaks along b on either side of the heavy-metal atoms in syntheses of the electron density of the projected structure. It was concluded therefore that the assignment of space group $Pb2_1m$ to the structure of lindströmite was suspect.

The precession and Weissenberg films which had been recorded previously were subjected to careful re-examination. An additional set of precession films, intentionally over-exposed to reveal the weak superstructure reflections, was prepared with Cu$K\alpha$ radiation to increase resolution. The experiments revealed the following features for the $h0l$ reflections with $h+l=$

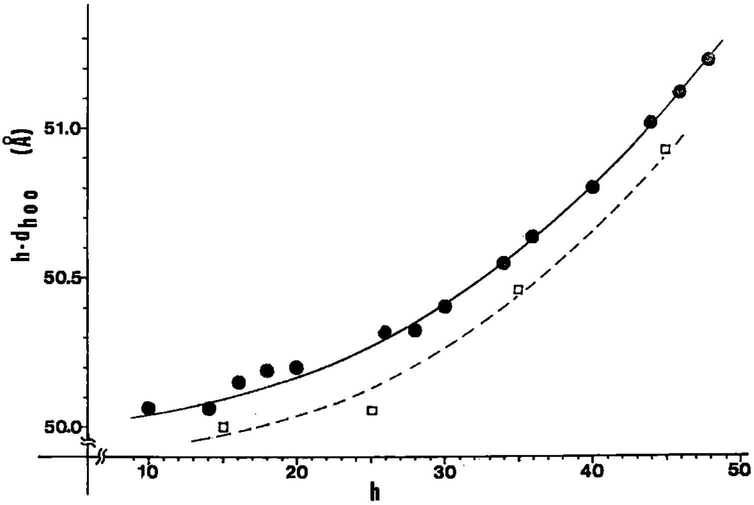

FIG. 2. Plot of values of $h \cdot d_{h00} = d_{100}$ as a function of h for $h00$ reflections on a c-axis Weissenberg photograph of lindströmite prepared with Cu$K\alpha$ radiation. The reflections fall into two groups: those with h=5(2n+1) correspond to an apparent a 55.90Å (5×11.18) and are interpreted as reflections from exsolved krupkaite.

$2n+1$ which violated the presence of an n-glide parallel to (010): (a) the $h0l$ reflections with $h+l=2n+1$ which appeared on precession films were present only when $h=5n$. (b) Such reflections were found to occur at diffraction angles which were slightly too large.

The latter feature is clearly indicated by Figure 2. Values of $h{\cdot}d_{h00}=d_{100}=a$, measured from the $h00$ reciprocal lattice row on a c-axis Cu$K\alpha$ Weissenberg film, are plotted as a function of h. (The values of $h{\cdot}d_{h00}$ differ significantly from a, 56.115Å, and show a systematic variation with h. This is due to a systematic error which arises, at least in part, from the high absorption of Cu$K\alpha$ radiation by the specimen). The reflections fall into two groups. Those with $h=5(2n+1)$ correspond to an apparent a (as measured more accurately on precession photographs) of 5×11.18Å, which is very close to the 11.200Å value of a reported for krupkaite (Mumme 1975), the neighboring phase of higher Bi content in the series. The unique type crystal of lindströmite was accordingly assumed to contain a small amount of exsolved krupkaite whose reflections ($h=5n$ relative to lindströmite) effectively mask the absences due to an n-glide for $h0l$ reflections with $h=5n$ and $h+l$ odd. Krupkaite reflections will be superposed on those of lindströmite for $h0l$ reflections with $h=5n$ and $h+l$ even but, since the volume fraction of krupkaite is small, the lindströmite reflections dominate, and no displacement of the angular position of any of these combined reflections is obvious. The manifestation of the exsolution is extremely subtle because of the close similarity in lattice constants for the two minerals: a 56.115, b 11.5695, c 4.001Å for lindströmite, and $5a$ 56.000, b 11.560, c 4.003Å for krupkaite (Mumme 1975).

The $h0l$ reciprocal lattice planes for lindströmite (assuming space group $Pbnm$) and krupkaite (space group $Pb2_1m$) are schematically shown in Figures 3a and 3b, respectively. One quadrant of a $h0l$ precession film of lindströmite prepared in Cu$K\alpha$ radiation is given in Figure 4a. The unequal spacing of reflections along a^* is particularly apparent in the trios of reflections 29 0 1, 30 0 1, 31 0 1 and 14 0 2, 15 0 2, 16 0 2. An interpretation of the photographs in terms of superposed reciprocal lattices of lindströmite and krupkaite is given in Figure 4b. The correct diffraction symbol for lindströmite is therefore $mmmPbn-$ which permits $Pbn2_1$ (C^9_{2v}) or $Pbnm$ (D^{16}_{2h}) as possible space groups. All diffraction patterns with l even had the same distribution of intensities, as did all those with l odd. This strongly suggests that all atoms occur on symmetry planes separated by $c/2$. In addition, the emergence of a centrosymmetric model as the most probable structure also supports the designation of $Pbnm$ as the correct space group.

REFINEMENT OF THE STRUCTURE

The centrosymmetric configuration which had been determined as the most probable structure in space group $Pb2_1m$ was redescribed as an asymmetric unit in $Pbnm$. (The position ¼ 0–¼ of $Pb2_1m$ was used as the origin for the unit cell in space group $Pbnm$). This halved the number of independent atoms in the structure to 7 Bi, 3 Pb, 3 Cu and 15 S atoms. The 3 Cu atoms, which previously had been denoted by H, J and B, were designated Cu(1), Cu(2), and Cu (3), respectively. The contribution to the structure factors with $h=5n$ from the exsolved krupkaite was evaluated using the structure reported by

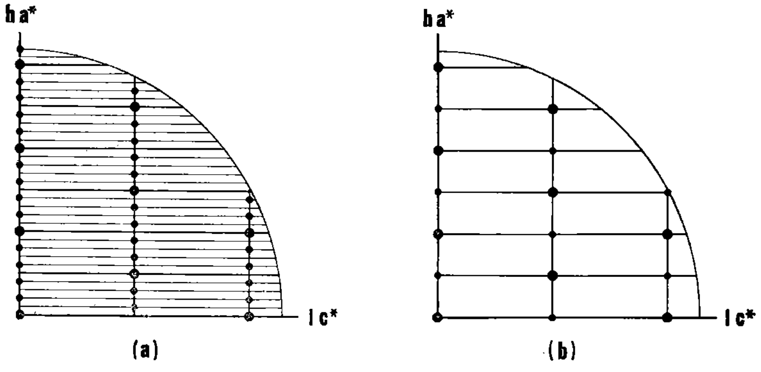

FIG. 3. Reciprocal lattice planes $h0l$ for (a) lindströmite, assuming space group $Pbnm$, and (b) krupkaite, space group $Pb2_1m$. The smaller circles represent superstructure reflections and the large circles indicate intense reflections due to the bismuthinite substructure.

Mumme (1975). This contribution was subtracted from the observed structure factors for lindströmite using a scaling factor (which corresponded to 6.3 vol. % krupkaite) derived from the measured krupkaite structure factors which were not superposed with a lindströmite reflection. Least-squares refinement of the idealized atomic coordinates was performed with the aid of the full-matrix program RFINE2 (Finger & Prince 1975). Neutral-atom scattering curves obtained from *International Tables for X-ray Crystallography*, Vol. IV were used. Each structure factor was given weight $1/\sigma^2$ in the refinement, with σ estimated as 0.1 F_{obs} for $|F_{obs}| \geq 100$ and 0.5 F_{obs} for $|F_{obs}| < 100$.

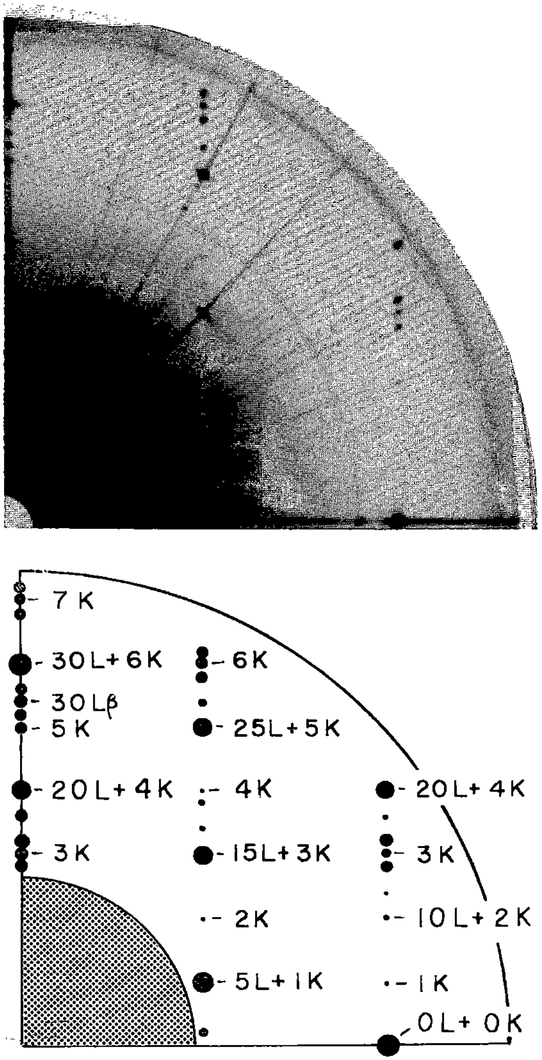

FIG. 4. (a) One quadrant of a *h0l* precession photograph of lindströmite. Ni-filtered Cu$K\alpha$ radiation, 34 kV 14 mA, 161 hr. exposure. The unequal spacing of reflections is particularly apparent for the 29, 30, and 31 0 1 and 14, 15 and 16 0 2 reflections. (b) Interpretation of the photograph in terms of superposed reciprocal lattices of lindströmite (L) and krupkaite (K). The integer gives the value of *h* relative to the true reciprocal cell of each phase (*e.g.*, 3K corresponds to $h=3$ for krupkaite) and β indicates a Cu$K\beta$ reflection.

The 491 detectable *hk*0 reflections and a single overall temperature factor 1.2Å were employed to first refine the heavy-metal atom coordinates. This resulted in the reduction of *R* from an initial value of 40% for the ideal coordinates to 33%. Eleven very intense substructure reflections were found to be overexposed and were eliminated from the data set. Further cycles of refinement, in which the coordinates of all atoms were adjusted, produced convergence at $R = 17.4\%$. Refinement of separate isotropic temperature factors for the metal atoms improved *R* to 16.8%. Introduction of separate isotropic temperature factors for the sulfur atoms reduced *R* only slightly to a final value of 16.3%. The small improvement in the final stage is due to the fact that the sulfur atoms account for only 20.8% of the electrons contained within the cell. The temperature factors for S therefore display large standard deviations. As the essential features of the structure seemed firmly established, additional refinement was deferred to a future study planned with three-dimensional data. A table of observed and calculated structure factors has been deposited and is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

RESULTS AND DISCUSSION

Temperature factors and coordinates obtained for the 28 atoms contained in the asymmetric unit of lindströmite are presented in Table 2. A projection of the electron density in the structure is given[1] in Figure 5. No evidence is found

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[1] In Figure 5 and in subsequent discussion a superscript is used to designate an atom related by symmetry to an atom in the asymmetric unit. The value of this integer corresponds to the order of the coordinates for the atom in the equipoints tabulated for space group *Pbnm* in the International Tables for X-ray Crystallography, Vol. I. Atoms which are related by translation are not distinguished.

TABLE 2. ATOMIC COORDINATES AND TEMPERATURE FACTORS FOR LINDSTRÖMITE
(Estimated standard deviations in parentheses; $z = ¼$ for all atoms)

Atom	x	y	B(Å^2)	Atom	x	y	B(Å^2)
Bi(1)	.0383(1)	.0185(7)	2.3(1)	S(1)	.1291(6)	.044(4)	1.3(7)
Bi(2)	.2376(1)	.0202(7)	2.4(1)	S(2)	.3271(5)	.051(3)	0.5(6)
Bi(3)	.4355(1)	.0222(8)	2.8(1)	S(3)	.5272(7)	.048(4)	1.5(7)
Bi(4)	.6350(1)	.0174(7)	2.1(1)	S(4)	.7279(10)	.055(6)	4.0(13)
Bi(5)	.8334(1)	.0150(7)	2.5(1)	S(5)	.9241(4)	.052(3)	0.0(5)
Bi(6)	.1925(1)	.3469(7)	2.8(1)	S(6)	.0587(8)	.211(5)	2.5(9)
Bi(7)	.3916(1)	.3456(6)	2.0(1)	S(7)	.2631(6)	.215(4)	1.3(6)
Pb(1)	.6008(1)	.3266(6)	1.9(1)	S(8)	.4599(7)	.211(4)	1.9(8)
Pb(2)	.7992(1)	.3248(7)	2.4(1)	S(9)	.6608(9)	.212(6)	3.2(11)
Pb(3)	.9983(1)	.3317(8)	2.6(1)	S(10)	.8620(7)	.213(5)	2.1(8)
Cu(1)	.5419(4)	.228(2)	2.6(5)	S(11)	.1083(9)	.389(5)	2.4(9)
Cu(2)	.7419(5)	.228(3)	3.8(6)	S(12)	.3106(8)	.369(5)	2.9(11)
Cu(3)	.9413(3)	.225(2)	1.2(3)	S(13)	.5105(10)	.389(5)	3.5(11)
				S(14)	.7117(10)	.368(5)	3.2(11)
				S(15)	.9115(7)	.368(4)	1.5(7)

for electron density in the unoccupied tetrahedral sites. Since the signs of the superstructure reflections are controlled by distortion in the array of heavy-metal atoms, a difference Fourier synthesis using $F_{obs} - F'_{calc}$ as coefficients (where F'_{calc} is the structure factor computed without the contribution of the Cu atoms) was evaluated to confirm the Cu distribution. This synthesis (Fig. 6) clearly reveals the presence of Cu (1), Cu (2) and Cu (3). Only weak features, barely above background variation, are found at the unoccupied sites *T* and *T'*. These weak maxima were not reproduced in a conventional difference synthesis and thus were not taken as a suggestion that the Cu atom arrangement is other than completely ordered.

The interatomic distances in the structure (Table 3) are similar to those found in other bismuthinite derivatives. The heavy-metal atoms have sulfur atom neighbors at positions close to 5 of the 6 vertices of an octahedron. Sixth and seventh neighbors are present at larger distances. The minimum approaches of an S atom to Pb (2.88 to 2.96Å) are larger than the minimum bond distances to Bi atoms (2.50 to 2.73Å). This characteristic is in accord with results obtained for other Pb-Bi sulfosalts and confirms the correctness of the designation of Pb and Bi in the ordering scheme. The Cu atoms in lindströmite occupy tetrahedral interstices, but the Cu atom is displaced towards one triangular face of the tetrahedron [S (3) – Cu (1) = S (6^3), S (4) – Cu(2) = S(7^3) and S(5) – Cu(3) = S(8^3), where the double dash signifies bonds to a pair of atoms equivalent by translation]. This feature has also been found in the other bismuthinite derivatives.

The structure of lindströmite consists of a combination of $Cu_2Pb_2Bi_2S_6$ aikinite-like ribbons and $CuPbBi_3S_6$ krupkaite units in the ratio 1:4. Lindströmite is the only bismuthinite derivative other than hammarite, $Cu_2Pb_2Bi_4S_9$ (Horiuchi & Wuensch 1976) found to contain an aikinite chain; these are the only two known derivatives with Pb:Bi > ⅓.

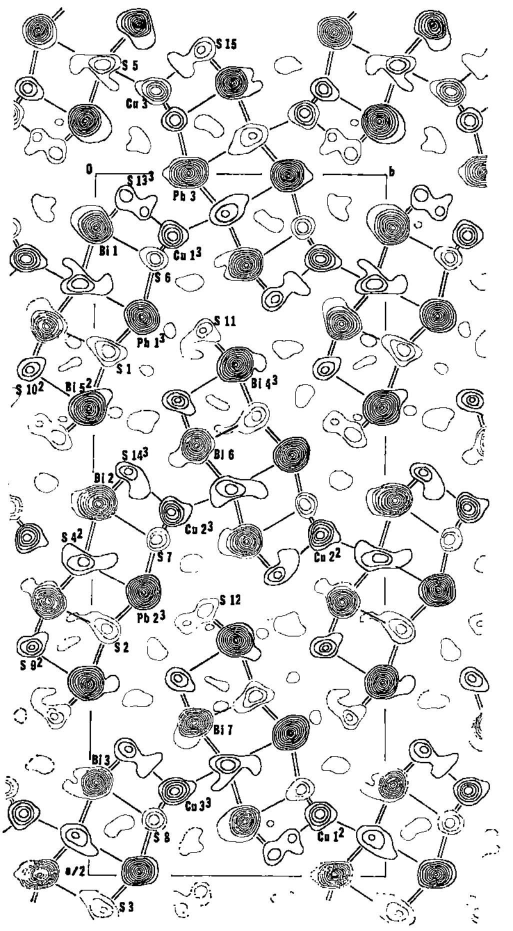

FIG. 5. Electron density in lindströmite projected along *c*. Contours begin at 10 $e/Å^2$; intervals of 20 $e/Å^2$ for heavy-metal atoms, 10 $e/Å^2$ elsewhere. The bold contours arise from atoms located at $z = ¾$, the lighter contours from atoms at $z = ¼$.

The crystal chemical rules which have emerged from determination of the other derivative structures in the bismuthinite-aikinite series are followed also in lindströmite: (a) the Pb atoms are ordered among one or both of the pair of interior metal-atom positions of the bismuthinite ribbon. (The Pb atoms remain confined to these sites even in disordered structures — Mumme & Watts 1976). The outer pair of heavy-metal sites in the ribbon is always occupied by Bi atoms. (b) The Pb atoms are distributed among the maximum possible number of ribbons. Krupkaite, $CuPbBi_3S_6$ with Pb:Bi = ⅓ is thus com-

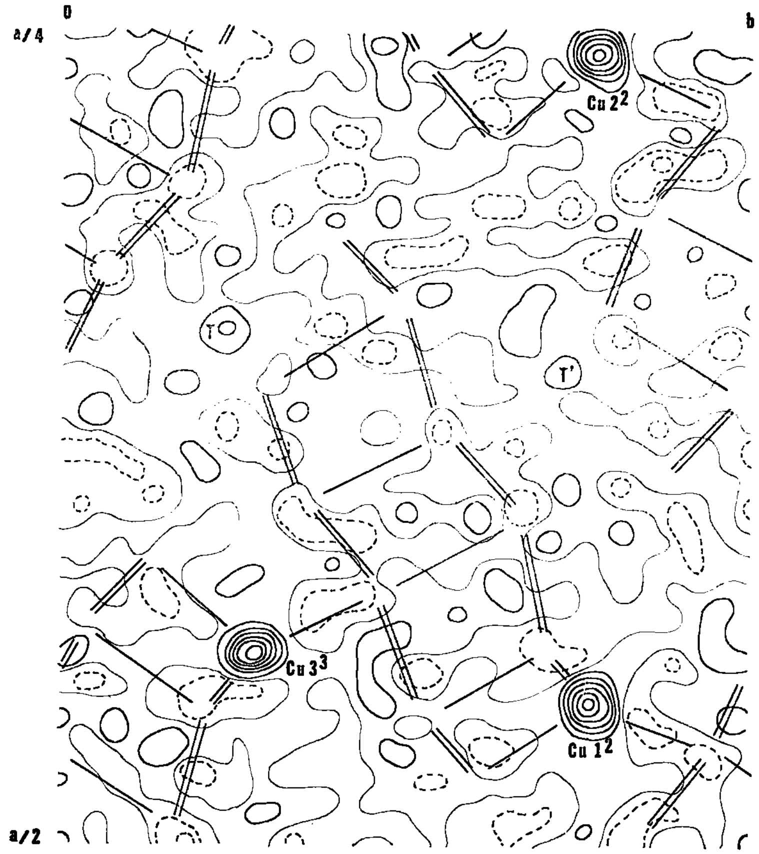

FIG. 6. Projection along *c* of the difference electron density in lindströmite synthesized using $F_{obs} - F'_{calc}$ as coefficients, where F'_{calc} are structure factors computed without Cu atoms. Contours begin at 0 $e/Å^2$, intervals of 5 $e/Å^2$; negative contours are shown as broken lines. *T* and *T'* are unoccupied tetrahedral interstices.

TABLE 3. INTERATOMIC DISTANCES IN LINDSTRÖMITE

Bi(1) -	S(6)	2.50Å	
	S(13^3)	2.75	2X
	S(5^2)	3.02	2X
	S(13^4)	3.12	
Bi(2) -	S(7)	2.67	
	S(14^3)	2.79	2X
	S(4^2)	2.92	2X
	S(12^4)	3.22	
Bi(3) -	S(8)	2.57	
	S(15^3)	2.73	2X
	S(11^4)	2.90	
	S(3^2)	3.01	2X
Bi(4) -	S(9)	2.68	
	S(11^3)	2.72	2X
	S(2^2)	3.02	2X
	S(15^4)	3.13	
Bi(5) -	S(12^3)	2.73	2X
	S(10)	2.80	
	S(1^2)	2.98	2X
	S(14^4)	3.05	
Bi(6) -	S(2^4)	2.60	
	S(9^3)	2.76	2X
	S(4^3)	3.04	2X
	S(14^3)	3.37	2X
Bi(7) -	S(1^4)	2.57	
	S(10^3)	2.69	2X
	S(5^3)	2.96	2X
	S(15^3)	3.37	2X
Cu(1) -	S(3)	2.23Å	
	S(6^3)	2.33	2X
	S(13)	2.56	
Cu(2) -	S(4)	2.14	
	S(14)	2.34	
	S(7^3)	2.42	2X
Cu(3) -	S(5)	2.22	
	S(15)	2.35	
	S(8^3)	2.38	2X
Pb(1) -	S(5^4)	2.96	
	S(1^3)	2.96	2X
	S(6^3)	3.13	2X
	S(11^3)	3.23	2X
Pb(2) -	S(7^3)	2.89	2X
	S(2^3)	2.92	2X
	S(4^4)	3.07	
	S(12^3)	3.08	2X
Pb(3) -	S(3^4)	2.88	
	S(3^3)	2.93	2X
	S(8^3)	2.99	2X
	S(13^3)	3.32	2X

posed entirely of ribbons of that composition. Superstructures with Pb:Bi<⅓ (pekoite and gladite) are built of mixtures of krupkaite and bismuthinite ribbons whereas those with Pb:Bi >⅓ (lindströmite and hammarite) contain mixtures of krupkaite and aikinite units. (c) The addition of a Cu atom to a tetrahedral interstices is coupled with substitution of Pb for a Bi atom. The interstitial Cu always occupies that site which is adjacent to the substituted Pb atom on the same side of the bismuthinite ribbon.

The structures of all of the derivatives known in the system have now been determined. In order of increasing lead content of each phase, the minerals bismuthinite < pekoite < gladite < krupkaite < lindströmite < hammarite < aikinite have structures which contain bismuthinite (*b*), krupkaite (*k*) and aikinite (*a*) ribbons in ratios given by *b*, 2*b*+*k*, *b*+2*k*, *k*, 4*k*+*a*, 2*k*+*a*, *a*, respectively.

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REFERENCES

Burnham, C. W. (1962): Lattice constant refinement. *Carnegie Inst. Wash. Year Book* **61**, 133-135.

Finger, L. W. & Prince, E. (1975): A system of Fortran IV computer programs for crystal structure computations. *U.S. Nat. Bur. Stand. Tech. Note* **854.**

Flink, G. (1910): Bidrag till Sveriges mineralogi. *Arkiv Mineral. Geol.* **3**, 1-166.

Harris, D. C. & Chen, T. T. (1976): Crystal chemistry and re-examination of nomenclature of sulfosalts in the aikinite-bismuthinite series. *Can. Mineral.* **14**, 194-205.

Horiuchi, H. & Wuensch, B. J. (1976): The ordering scheme for metal atoms in the crystal structure of hammarite, $Cu_2Pb_2Bi_4S_9$. *Can. Mineral.* **14**, 536-539.

Johansson, K. (1924): Bidrag till gladhammargruvornas mineralogi. *Arkiv Mineral. Geol.* **9**, 1-22.

Kaplunnik, L. N., Pobedimskaya, E. A. & Belov, N. V. (1975): The crystal structure of lindströmite, $CuPbBi_3S_6$. *Kristallografiya* **20**, 1037-1039.

Kohatsu, I. & Wuensch, B. J. (1971): The crystal structure of aikinite, $PbCuBiS_3$. *Acta Cryst.* **B27**, 1245-1252.

——— & ——— (1973): The crystal structure of gladite, $PbCuBi_5S_8$. *Amer. Mineral.* **58**, 1098 (Abstr.).

——— & ——— (1976): The crystal structure of gladite, $PbCuBi_5S_9$, a superstructure intermediate in the series $Bi_2S_3 - PbCuBiS_3$ (bismuthinite-aikinite). *Acta Cryst.* **B32**, 2401-2409.
Kristallstruktur des Bismuthinits, Bi_2S_3. *Tscher-*

Kupčík, V. & Veselá-Nováková, L. (1970): Zur
maks Mineral. Petrogr. Mitt. **14**, 55-59.

Large, R. R. & Mumme, W. G. (1975): Junoite, "wittite" and related seleniferous bismuth sulfosalts from Juno Mine, Northern Territory, Australia. *Econ. Geol.* **70**, 369-393.

Lindström, G. (1887): Om förekomsten av wismutmineral vid Gladhammar. *Geol. Fören. Förh.* **9**, 523-528.

——— (1889): Ytterligare om wismutmineral från Gladhammar. *Geol. Fören, Förh.* **11**, 171-172.

Mumme, W. G. (1975): The crystal structure of krupkaite, $CuPbBi_3S_6$, from the Juno Mine at Tennant Creek, Northern Territory, Australia. *Amer. Mineral.* **60**, 300-308.

——— & Watts, J. A. (1976): Pekoite, $CuPbBi_{11}S_{18}$, a new mineral of the bismuthinite- aikinite series: its crystal structure and relationship with naturally- and synthetically-formed members. *Can. Mineral.* **14**, 322-333.

———, Welin, E. & Wuensch, B. J. (1976): Crystal chemistry and proposed nomenclature for sulfosalts intermediate in the system bismuthinite-aikinite ($Bi_2S_3 - CuPbBiS_3$). *Amer. Mineral.* **61**, 15-20.

Ohmasa, M. & Nowacki, W. (1970a): A redetermination of the crystal structure of aikinite $[BiS_2|S|Cu^{IV}Pb^{VII}]$. *Z. Krist.* **132**, 71-86.

——— & ——— (1970b): Note on the space group and on the structure of aikinite derivatives. *Neues Jahrb. Mineral. Monatsh.* 158-162.

Syneček, V. & Hybler, J. (1974): The crystal structures of krupkaite, $CuPbBi_3S_6$, and of gladite, $CuPbBi_5S_9$, and the classification of superstructures in the bismuthinite-aikinite group. *Neues Jahrb. Mineral. Monatsh.*, 541-560.

Welin, E. (1966): Notes on the mineralogy of Sweden, 5. Bismuth-bearing sulfosalts from Gladhammar, a revision. *Arkiv Mineral. Geol.* **4**, 377-386.

Wickman, F. E. (1953): The crystal structure of aikinite, $CuPbBiS_3$. *Arkiv Mineral. Geol.* **1**, 501-507.

Žák, L., Syneček, V. & Hybler, J. (1974): Krupkaite, $CuPbBi_3S_6$, a new mineral of the bismuthinite-aikinite group. *Neues Jahrb. Mineral. Monatsh.*, 533-541.

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