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THE CRYSTAL STRUCTURE OF NORDSTRÖMITE $CuPb_3Bi_7(S,Se)_{14}$, FROM FALUN, SWEDEN: A MEMBER OF THE JUNOITE HOMOLOGOUS SERIES

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ABSTRACT

Nordströmite from Falun, Sweden, is monoclinic, *a* 17.97(8), *b* 4.11(2), *c* 17.62(8) Å, β 94.3(2)°, space group $P2_1/m$, $Z = 2$. Its crystal structure has been determined from 1548 independent reflections recorded with Cu $K\alpha$ radiation using a single-crystal diffractometer. There are 10 *Me*, 1 Cu and 14 S atoms in two asymmetric units. *Me*3 [Bi], *Me*4 [Bi], *Me*6 [Bi,Pb] and *Me*8 [Bi,Pb] have slightly distorted octahedral coordinations; *Me*2 [Pb] and *Me*5 [Bi] have trigonal prismatic coordinations with two other bonds through faces; *Me*9 [Bi,Pb] and *Me*10 [Bi] have seven-fold split-vertex octahedral coordinations, whereas *Me*1 [Bi,Pb] and *Me*7 [Bi] have highly distorted octahedral coordinations that, in the case of *Me*1 closely approach seven-fold. Cu is in near-planar coordination to three sulfur atoms. The structure consists of two sets of alternating slabs. In one, atoms have (predominantly) little distorted octahedral coordinations. The orientation of the octahedral groups in these *regular*-octahedral slabs is such that $[110]_{PbS}$ corresponds with $[010]_{nordströmite}$, and their boundary planes, parallel to $(10\bar{1})_{nordströmite}$, are $(111)_{PbS}$. The second slab is composed of fragments of double layers of metal atoms with irregular coordinations to sulfur atoms. These are the fragments of more highly distorted double-galena layers, with boundary planes parallel to $(001)_{PbS}$, that join to form the slabs of *distorted*-galena structure.

Keywords: nordströmite, Falun, Sweden, selenian copper–lead–bismuth sulfosalt, crystal structure.

SOMMAIRE

La nordströmite de Falun (Suède) est monoclinique: *a* 17.97(8), *b* 4.11(2), *c* 17.62(8) Å, β 94.3(2)°, $P2_1/m$, $Z = 2$. Sa structure a été établie, à partir de 1548 réflexions indépendantes enregistrées en rayonnement Cu $K\alpha$ sur diffractomètre à cristal unique. Le domaine asymétrique contient 10 *Me*, 1 Cu et 14 S. Quatre métaux, *Me*3 [Bi], *Me*4 [Bi], *Me*6 [Bi,Pb] et *Me*8 [Bi,Pb] ont une coordination octaédrique légèrement difforme; *Me*2 [Pb] et *Me*5 [Bi] combinent une coordination en prisme trigonal avec deux liaisons supplémentaires à travers des faces; *Me*9 [Bi,Pb] et *Me*10 [Bi] sont heptacoordonnés (octaèdre à sommet dédoublé), alors que *Me*1 [Bi, Pb] et *Me*7 [Bi] ont chacun comme polyèdre de coordination un octaèdre extrêmement difforme, au point que celui de *Me*1 est proche de l'heptacoordination. Quant à Cu, il se trouve entouré de trois atomes S avec lesquels il est presque complanaire. La structure consiste en deux séries de plaquettes alternantes. Dans l'une des deux, les atomes sont essentiellement en coordination octaédrique légèrement difforme. L'orientation des groupes octaédriques dans ces plaquettes à octaèdres *réguliers* fait correspondre $[110]_{PbS}$ à $[010]_{nordströmite}$ et leurs plans de jonction, || $(10\bar{1})_{nordströmite}$, à $(111)_{PbS}$. La seconde plaquette comporte des fragments de couches doubles d'atomes métalliques irrégulièrement coordonnés aux atomes de soufre. Quant aux plaquettes à structure galène-déformée, elles sont constituées de fragments de couches doubles de galène plus fortement déformées, dont les plans de jonction sont || $(001)_{PbS}$.

(Traduit par la Rédaction)

Mots-clés: nordströmite, Falun, Suède, sulfosel sélénifère de cuivre, plomb et bismuth, structure cristalline.

INTRODUCTION

Nordströmite is the recently defined seleniferous lead–bismuth sulfosalt from Falun, Sweden; it is named after T. Nordström, who contributed to the very early studies of Falun minerals (Mumme 1980b). Its history follows.

Peacock & Berry (1940) examined "galenobismutite" from Falun and reported that it contained several minerals, one with unit-cell parameters 18.03, 4.04, 17.53 Å, $\beta = 94.29°$. They designated this mineral weibullite [*i.e.*, the Falun mineral named by Flink (1910)]; subsequently the above unit cell, together with an indexed powder-pattern, was published in the Peacock atlas (Berry & Thompson 1962) as weibullite, thus characterizing a Pb,Bi,S,Se mineral of unknown composition. However, more recent studies of Falun specimens (Karup-Møller 1970, Johan & Picot 1976, Mumme 1976, 1980a) now support the argument that weibullite, as originally defined by Flink, is the orthorhombic mineral with $a \sim 53.7$, $b \sim 4.1$, $c \sim 15.4$ Å which can be isolated from Falun specimens. Thus for many years *nordströmite* was not recognized as an independent species in its own right. This anomaly originates from what obviously was an inevitable conclusion on the part of Peacock & Berry (1940) and Berry & Thompson (1962), in view of the information available to them at the time of their studies.

[The "weibullite" single crystal films were obtained in 1939 by Professor L.G. Berry from a selected single crystal fragment (from ROM *M*12992); a powder pattern (282 UT, 13/2/40) was also obtained from this specimen. The sample for the powder film was scraped from a polished section and was therefore not representative of the single crystal fragment. UBC 530 (Peacock atlas, p. 164) refers to a Straumanis film obtained by R.M. Thompson on a specimen whose number is now lost (it may have been a UBC specimen), but the film was obtained some years after 1940. Thompson spent the summer of 1950 working with Berry on the Peacock atlas; they chose UBC 530 as the best film to represent weibullite which, in their opinion, was the only fibrous selenide phase present in their Falun specimens. Other relevant powder films still available are UT 126 (on NRM 24083, 8/5/39) and UT 172 (on USNM 84460, 5/12/39). The space group $P2/m$ reported for "weibullite" in the Peacock atlas was not unequivocally determined, as no record was made of $0k0$ reflections. A recent study (October 1978) of the powder films by Berry revealed that UBC 530 and UT 282 are virtually identical, as are UT 172 and UT 126; with the four films side by side there is little doubt that they should be paired as noted. There are obvious differences between 530 and 172, although these reflect only minor differences in any tabulated data measured from the films. The cell data listed under "weibullite", no. 205 in the Peacock atlas, thus represent nordströmite, whereas the powder spacings may possibly represent weibullite or even a mixture of the two minerals. (Priv. comm., L.G. Berry 1978.)] A comparison of the powder patterns of weibullite and mineral no. 205, Peacock atlas (Table 3, Mumme 1976) with nordströmite (Table 3C, Mumme 1980b) shows great similarities.

TABLE 1. CHEMICAL AND CRYSTALLOGRAPHIC DATA FOR NORDSTRÖMITE

Space Group	:	$P2_1/m$	Radiation	:	CuKα
Unit cell	:	a = 17.97(8)Å b = 4.11(2)Å c = 17.62(8)Å β = 94.3(2)°	μ	:	1421
			Total number of reflections	:	1548
D (calc)	:	7.12	Derived formula, $Cu_{.94}Pb_{3.05}Bi_{7.24}Se_{4.12}S_{9.89}$		
Z	:	2	Structural formula, $CuPb_3Bi_7Se_4S_{10}$		

Returning to the identity of these Falun minerals, it has proved impossible to locate a specific specimen (or holotype) of weibullite amongst those in the Naturhistoriska Riksmuseet, Stockholm. In his search for one, Dr. Bengt Lindquist of that institution has kindly made available for study fragments from several of the Falun specimens. One of them [810203] was from the original material analyzed by Nordström (1879), for which he obtained Se 5.11–4.79, Bi $\sim$ 50, Pb 17–20 wt. %. Single crystal X-ray studies here have shown that this specimen contains galenobismutite and the mineral presently called wittite (Mumme 1980b).

EXPERIMENTAL

The nordströmite crystal used for the present investigation was isolated from specimen ROM *M*12992, kindly provided by the Royal Ontario Museum. Microprobe analysis of adjacent material gave Cu 2.04, Pb 21.73, Bi 51.95, Se 11.16, S 10.88 wt. %, Σ 97.75 (Mumme 1980b). Weissenberg and refined powder-data (from a Debye-Scherrer film internally calibrated with KCl) collected with Cu $K\alpha$ radiation gave the unit-cell parameters presented in Table 1. The only other bismuth-containing minerals found associated with nordströmite in ROM *M*12992 are bismuthinite and wittite.

The systematic extinctions ($0k0$, $k \neq 2n$) indicated $P2_1/m$ and $P2_1$ as the possible space groups. $P2_1/m$ was chosen as the more probable of these two, and was subsequently confirmed by the results of the structure determination.

The crystal obtained from the museum specimen was best approximated by a six-sided prism $\sim$ 0.002 x 0.020 x 0.006 cm. Intensity data were collected from it with Cu $K\alpha$ radiation using ω-scans performed with a 2-circle Stoe single crystal diffractometer [see Makovicky & Mumme (1979)]. Corrections for absorption were performed with ABSNTST (Blount 1966). A total of 1548 independent reflections were obtained by averaging all the equivalent ones measured; the discrepancy between equivalent reflections, averaged overall, was 5%. Intensities were corrected for Lorentz and polarization effects.

STRUCTURE DETERMINATION AND REFINEMENT

Assuming a density of 7.0 g/cm³ for nordströmite (a value about average for Cu–Pb–Bi sulfosalts), the structural formula $CuPb_3Bi_7(S,Se)_{14}$ ($Z = 2$) was deduced from the microprobe analysis as most probable for the mineral. The alternative with Σ S + Se = 30 (for the unit cell), which requires only a slightly higher density, results in a somewhat less satisfactory formula because the derived metal-atom contents become nonintegral to conform with the chemistry.

The structure was solved by Patterson and reiterative structure-factor/Fourier-analysis methods. The concept that a significant part of the structure would be a galena-like fragment with metal atoms having minimally distorted octahedral coordinations was the basis upon which the structure solution proceeded in the early stages; this concept eventually led to a correct solution, with all the atoms occupying special positions (2*e*) in the structure.

Structural parameters were refined by a full-matrix least-squares version of ORFLS (Busing *et al.* 1962) using the weighting scheme of Cruickshank *et al.* (1961). Neutral scattering curves (Cromer & Waber 1965) were used for all the atoms, and anomalous dispersion corrections (Ibers & Hamilton 1962) were made for Bi and Pb.

An average of $f = (0.7\ S + 0.3\ Se)$ was applied for the scattering factor of the anions during the initial refinements, carried out using isotropic temperature factors. These converged to give $R = 12.6$, at which stage an examination of the Fourier maps indicated that 5 of the "sulfur" peaks had higher-than-average electron densities. In the subsequent refinements, therefore, all the selenium was ordered equally in these sites, resulting in a lowering of R to 12.3. Individual anisotropic temperature factors were then introduced (Table 2), and the structure was finally refined to give an R value of 11.7.

As evidenced by the Weissenberg films, the crystals of nordströmite studied here all contain, to some extent, fine-grained oriented intergrowths of wittite. This defect, together with the high absorption coefficient and irregular shape of the crystal fragment used for data collection, explains why we did not achieve a lower agreement factor.

DESCRIPTION

General

The crystal structure of nordströmite (Fig. 1) is composed of two types of slabs, parallel to $(10\bar{1})$. One slab represents segments of a regular-octahedral, little-distorted galena-like structure, joined by paired columns of distorted octa-

TABLE 2. ATOMIC PARAMETERS AND ANISOTROPIC TEMPERATURE-FACTORS COEFFICIENTS FOR NORDSTRÖMITE

ATOM	PROBABLE OCCUPANCY	COORDINATES x	y	z	TEMPERATURE FACTORS β11	β22	β33	β13
Me1	Bi/Pb	.0909(4)	¼	.0540(4)	.0023(2)	.0516(152)	.0027(2)	.0001(2)
Me2	Pb	.3268(4)	¼	.0441(5)	.0030(2)	.0445(158)	.0035(3)	.0004(2)
Me3	Bi	.2133(4)	3/4	.2238(4)	.0020(2)	.0489(149)	.0023(2)	.0001(2)
Me4	Bi	.4521(4)	3/4	.2364(4)	.0021(2)	.0597(152)	.0023(2)	.0001(2)
Me5	Bi	.0496(4)	¼	.3947(4)	.0025(2)	.0505(155)	.0032(3)	-.0002(2)
Me6	Bi/Pb	.3210(4)	¼	.4060(4)	.0021(2)	.0633(149)	.0023(2)	-.0001(2)
Me7	Bi	.1519(4)	¼	.6121(4)	.0026(2)	.0514(150)	.0025(2)	.0001(2)
Me8	Bi/Pb	.4377(4)	3/4	.5818(4)	.0024(2)	.0457(149)	.0023(2)	.0001(2)
Me9	Bi/Pb	.1071(4)	3/4	.8140(4)	.0034(3)	.0552(154)	.0023(2)	.0002(2)
Me10	Bi	.3134(4)	¼	.8122(4)	.0028(2)	.0451(153)	.0032(3)	-.0003(2)
Cu1	Cu	.4786(16)	3/4	.9305(16)	.0033(9)	.0846(371)	.0044(11)	.0003(8)
S1	S	.0016(24)	¼	.9121(25)	.0030(14)	.0087(540)	.0034(16)	.0003(11)
S2	S	.2113(20)	3/4	.0709(23)	.0017(11)	.0152(487)	.0030(14)	-.0001(9)
S3	S	.4572(19)	3/4	.0863(21)	.0015(10)	.0335(530)	.0020(12)	-.0003(9)
S4	1/5S+4/5Se	.1106(13)	¼	.2187(13)	.0032(8)	.0662(334)	.0025(8)	.0002(6)
S5	S	.3381(18)	¼	.2253(20)	.0012(9)	.0351(508)	.0018(11)	-.0002(8)
S6	1/5S+4/5Se	.2167(12)	3/4	.3969(14)	.0024(7)	.0321(305)	.0032(8)	-.0001(5)
S7	S	.4439(20)	3/4	.4106(19)	.0017(10)	.0482(488)	.0009(9)	-.0001(7)
S8	S	.0728(28)	3/4	.5245(23)	.0043(18)	.0106(534)	.0021(13)	.0002(12)
S9	1/5S+4/5Se	.3262(12)	¼	.5670(13)	.0018(6)	.0391(290)	.0030(8)	-.0001(5)
S10	S	.0399(22)	¼	.6919(20)	.0024(12)	.0393(532)	.0013(10)	-.0014(9)
S11	S	.2131(22)	3/4	.7128(23)	.0019(12)	.0374(542)	.0021(13)	-.0002(10)
S12	1/5S+4/5Se	.4382(14)	3/4	.7371(15)	.0026(8)	.0988(394)	.0035(9)	.0001(7)
S13	1/5S+4/5Se	.1885(17)	¼	.8893(18)	.0037(10)	.0761(400)	.0048(12)	-.0009(9)
S14	S	.3526(22)	3/4	.9157(26)	.0017(12)	.0885(655)	.0026(14)	-.0003(10)

ANISOTROPIC TEMPERATURE-FACTOR EXPRESSION: $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})\}$

with $\beta_{12} = 0$ and $\beta_{23} = 0$ for all atoms.

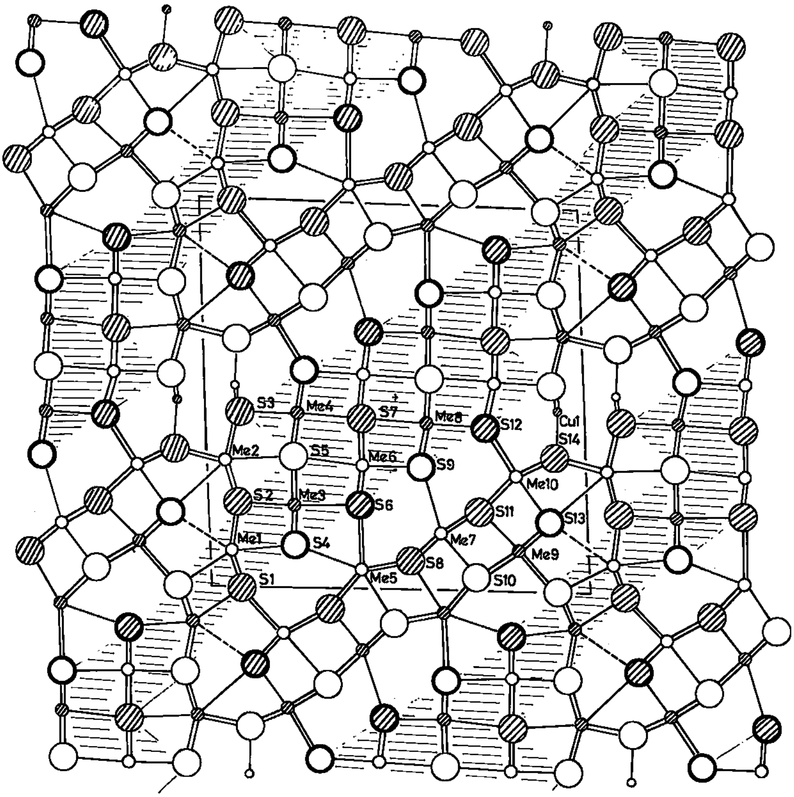

FIG. 1. Crystal structure of nordströmite drawn as an assemblage of octahedra and other coordination polyhedra. The shaded portions are, for the most part, equivalent to the PbS structure type. Small circles are Cu, medium circles are (Pb,Bi), large circles are S. Significant Se replacement is in heavy outline. The projection is onto (010). Hatched circles are at ¾, open circles are at ¼.

hedra (*Me*1–*Me*1); the other is a disjointed double layer in which most of the metal atoms have irregular coordinations; only one of them approaches octahedral coordination.

The octahedral segments in the first type of slab all have identical orientation and, notably, their continuity across the gap occupied by the other, intermediate, slabs is almost exactly in phase along the direction $[001]_{\mathrm{PbS}}$ (*i.e.*, $[001]_{\mathrm{nordstr\ddot{o}mite}}$). In total, these slabs are made up of alternate single-layer and double-layer sections that combine to produce an overall zigzag pattern. The coordinations of most of the metal atoms in this slab are scarcely deformed from those of ideal galena (Fig. 2a). It is only in the central region of the single layer section that distortions from a regular octahedron become considerable, and the coordination of *Me*1 actually approaches seven-fold. For ease of reference, however, these slabs are referred to in later discussions as the *regular*-octahedral or *regular*-galena slabs. The orientation of the octahedral groups in these slabs is such that $[110]_{\mathrm{PbS}}$ corresponds with $[010]_{\mathrm{nordstr\ddot{o}mite}}$, and the boundary planes of the groups parallel to $(10\bar{1})_{\mathrm{nordstr\ddot{o}mite}}$ are $(111)_{\mathrm{PbS}}$.

The second type of slab contains only one octahedron (somewhat distorted), that of *Me*7. *Me*2 and *Me*5 have trigonal prismatic coordinations with two additional bonds through faces; *Me*9 and *Me*10 have seven-fold coordinations (which may be described as octahedral with split vertex or as trigonal prismatic plus one extra bond), and Cu1 is in three-fold planar coordination (Fig. 2b). Except in the immediate region of disjointing, these slabs may be considered basically as fragments of distorted double-galena layers that have their boundary planes

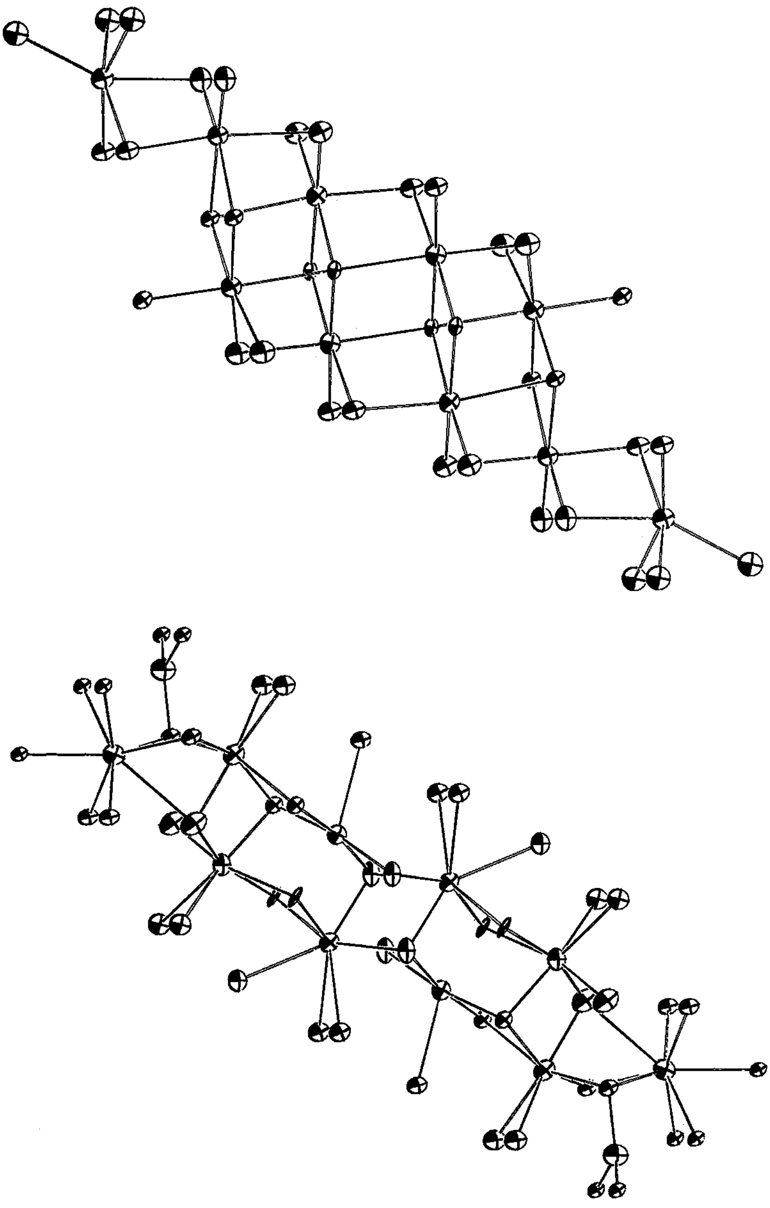

FIG. 2. Drawings of (a) the octahedral fragments and (b) the fragments of distorted-galena structure, which join to form the alternating regular-octahedral and distorted-galena slabs in the crystal structure of nordströmite. ORTEP plot drawn with 50% probability ellipsoids (Johnson 1965). Projection is along a direction close to $[0\bar{1}0]$.

parallel to $(001)_{\text{PbS}}$. Near the dislocations *Me*2 (and Cu1) does not occupy positions consistent with those of metal atoms in galena; to achieve this the levels they occupy in nordströmite would have to be reversed. However, *Me*2 closely coincides with the expected metal-atom position in the projection of the galena structure on $(110)_{\text{PbS}}$. In all later discussions these slabs are referred to as being composed of *distorted-galena* fragments.

The spaces occupied by the distorted-galena fragments in the structure of nordströmite (Fig. 1) may appear at first to have been produced from an original galena structure by a stepped shear of ~ ½ [112] $(111)_{\mathrm{PbS}}$. However, closer examination of the structure (see Fig. 4b) shows that an undulation within the regular-octahedral slab occurs where it is a single layer (at *Me*1), and a uniform stepped shear would only prevail for an ideal structure in which this does not occur. In fact, owing to this distortion in the regular-octahedral slabs, the stepped shear actually varies from ~ ½ [112] $(111)_{\mathrm{PbS}}$ to ~ ⅝ [112] $(111)_{\mathrm{PbS}}$.

Metal position and selenium ordering

Bond-length calculations (Table 3) show that *Me*3, *Me*4, *Me*5, *Me*7, *Me*9 and *Me*10 all have bonds of 2.71 Å or less, with [1+2] shortest bonds set apart from the remaining larger bonds; therefore all are probably Bi-atom sites. (*Me*3, *Me*4 and *Me*7, with bonds of 2.69, 2.64 and 2.54 Å, respectively, are more definitely so.) Of the remaining metal sites, *Me*2 has no bond shorter than 2.98 Å and in addition has a trigonal prismatic coordination configuration typical of Pb. *Me*1, *Me*6 and *Me*8 are less clear-cut in their bond-length characteristics. *Me*1 and *Me*8 both have shortest distances of 2.74 Å and a [1+2] short-bond to long-bond configuration typical of Bi; *Me*6 has no bond shorter than 2.78 Å (x2) and a [2+1] short-bond to long-bond configuration not so typical of Bi. If both *Me*1 and *Me*8 are considered to be Bi (and *Me*6 to be Pb), overall only two Pb atom sites are established in the structure instead of the three required by the microprobe data. Such

TABLE 3. INTERATOMIC DISTANCES AND BOND ANGLES IN NORDSTRÖMITE

Interatomic distances		
Me1 - S1	2.74(2)	x 2
S1'	2.87(3)	x 1
S4	2.90(2)	x 1
S2	2.98(2)	x 2
Me2 - S2	2.98(2)	x 2
S14	3.12(2)	x 2
S3	3.16(3)	x 2
S5	3.18(3)	x 1
S13	3.55(3)	x 1
Me3 - S2	2.69(2)	x 1
S4	2.76(2)	x 2
S5	3.04(3)	x 2
S6	3.05(2)	x 1
Me4 - S3	2.65(2)	x 1
S12	2.86(2)	x 2
S5	2.90(2)	x 2
S7	3.08(3)	x 1
Me5 - S8'	2.71(2)	x 1
S10	2.96(2)	x 2
S8	3.08(3)	x 2
S4	3.37(3)	x 1
S6	3.64(3)	x 2
Me6 - S6	2.78(2)	x 2
S9	2.83(2)	x 2
S7	3.01(2)	x 2
S5	3.22(3)	x 1
Me7 - S10	2.54(2)	x 1
S8	2.88(2)	x 2
S11	2.88(2)	x 2
S9	3.29(3)	x 1
Me8 - S12	2.74(2)	x 1
S9	2.87(2)	x 2
S7	2.96(2)	x 1
S7'	3.03(2)	x 2
Me9 - S13	2.71(2)	x 1
S14	2.80(2)	x 2
S11	3.17(2)	x 2
S12	3.38(3)	x 2
Me10 - S13	2.71(2)	x 1
S14	2.80(2)	x 2
S11	3.17(2)	x 2
S12	3.38(3)	x 2
Cu1 - S14	2.26(2)	x 1
S3	2.39(2)	x 2

Bond angles	
S1' - Me1 - S1	83.7
S1' - Me1 - S2	116.2
S4 - Me1 - S1	79.2
S4 - Me1 - S2	82.3
S1 - Me1 - S1	97.3
S2 - Me1 - S2	87.1
S1 - Me1 - S2	84.8
S3 - Me2 - S14	66.1
S14 - Me2 - S2	78.7
S2 - Me2 - Se	91.6
S3 - Me2 - S3	81.0
S14 - Me2 - S14	82.5
S2 - Me2 - S2	87.1
S2 - Me3 - S5	87.9
S2 - Me3 - S4	90.5
S6 - Me3 - S5	91.8
S6 - Me3 - S4	89.8
S5 - Me3 - S5	85.1
S4 - Me3 - S4	96.3
S4 - Me3 - S5	89.3
S3 - Me4 - S12	95.0
S3 - Me4 - S5	90.6
S7 - Me4 - S12	85.5
S7 - Me4 - S5	88.9
S12 - Me4 - S12	91.8
S5 - Me4 - S5	90.3
S5 - Me4 - S12	88.7
S3 - Cu1 - S14	118.4 x 2
S3 - Cu1 - S3	118.9
S'8 - Me5 - S10	80.8
S'8 - Me5 - S8	71.3
S10 - Me5 - S10	87.9
S8 - Me5 - S8	83.7
S8 - Me5 - S10	87.6
S5 - Me6 - S7	84.4
S5 - Me6 - S6	93.3
S9 - Me6 - S7	90.2
S9 - Me6 - S6	91.7
S7 - Me6 - S7	86.0
S6 - Me6 - S6	95.4
S6 - Me6 - S7	89.3
S10 - Me7 - S8	85.2
S10 - Me7 - S11	86.6
S9 - Me7 - S8	108.1
S9 - Me7 - S11	79.8
S8 - Me7 - S8	91.0
S11 - Me7 - S11	91.1
S8 - Me7 - S11	88.4
S7 - Me8 - S7'	88.0
S7 - Me8 - S9	89.3
S12 - Me8 - S7'	90.4
S12 - Me8 - S9	92.3
S9 - Me8 - S9	91.5
S7' - Me8 - S7'	88.0
S7' - Me8 - S9	90.2
S11 - Me9 - S10	78.6
S11 - Me9 - S13	86.8
S10 - Me9 - S10	81.5
S13 - Me9 - S13	94.5
S10 - Me9 - S13	90.3
S13 - Me10 - S11	79.6
S13 - Me10 - S14	81.4
S11 - Me10 - S11	80.7
S14 - Me10 - S14	94.3
S11 - Me10 - S14	89.4

Estimated standard deviation for bond angles is .7°.

an analysis of bond lengths therefore suggests that significant (Pb,Bi) disorder occurs, confined mostly to *Me*1, *Me*6 and *Me*8, but probably extending to *Me*5, *Me*9 and *Me*10.

Metal-anion bond distances in nordströmite will, however, be influenced to a degree by the ordering of selenium in the structure (up to 80% in S4, S6, S9, S12 and S13), and this should also be taken into consideration in any interpretation of the overall metal-ordering. In the case of the less well defined (possibly disordered) sites *Me*1, *Me*5, *Me*6, *Me*8, *Me*9 and *Me*10, where any increase in the magnitude of bond lengths due to selenium occupancy of anion sites may have significance in establishing the (Pb,Bi) ordering, there are two "characteristic" short bonds that could be affected, *i.e.*, *Me*8–S12 = 2.74 Å and *Me*10–S13 = 2.71 Å. As these bonds may well be equivalent to somewhat shorter metal–sulfur bonds, *Me*8 and *Me*10 are additionally substantiated as being Bi-atom sites. Thus, the high degree of (Pb,Bi) disorder inferred before the effect of Se ordering is considered may in fact be somewhat less, and confined only to *Me*1, *Me*5, *Me*6 and *Me*9.

Most of the selenium ordering in nordströmite (as determined from this refinement) takes place in the boundary layer of anions between the two slabs, an effect that was also observed in the structure of weibullite (Mumme 1980a). The significance of this location therefore seems to be in providing the distorted-galena fragments with critically placed longer bonds that help bridge the gap between the regular-octahedral slabs in the structures (*e.g.*, in nordströmite *Me*5–S6 = 3.64, *Me*7–S9 = 3.29 and *Me*10–S12 = 3.38 Å). Also noticeable is the fact that in the structure of nordströmite the selenium ordering is related to sites in which the distorted double-galena layers thicken slightly in sympathy with the undulation of the regular-octahedral layers, at *Me*1. Details of thermal and disorder ellipsoids in nordströmite (Table 4) may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

Copper

The coordination of Cu1 is described as threefold planar with bonds of 2.39 (x2) and 2.26 Å. A departure from a true planar coordination is evidenced by the sum of the S–Cu–S bond angles, which is 355.7° for the Cu–S_3 polyhedron, compared with 360° for an ideal situation. The copper groups in wittichenite (Kocman & Nuffield 1973) also are nearly planar, with bonds for Cu1 ranging from 2.26 to 2.31 Å (sum of angles 359.3°), for Cu2 from 2.26 to 2.31 Å (358.8°), and for Cu3 from 2.26 to 2.35 Å (359.0°). [Matzat's (1972) results for wittichenite are virtually identical.] A closer approach of a fourth sulfur atom S3^1, 2.80 Å in nordströmite, is the reason for the greater distortion (from planar coordination) in this case.

CHEMICAL AND STRUCTURAL RELATIONSHIPS

Chemical series

Nordströmite is closely related to the previously studied seleniferous Cu–Pb–Bi–sulfosalt junoite [$CuPb_{1½}Bi_4(S,Se)_8$] (Mumme 1975), from the point of view of both its chemistry and its crystal structure. A chemical series, based on their composition, may be formulated thus:

n	Mineral	Composition
1	Emplectite	$Cu_2Pb_0Bi_2S_4$
2	—	$Cu_2Pb_1Bi_4S_8$
3	Krupkaite	$Cu_2Pb_2Bi_6S_{12}$
4	Junoite	$Cu_2Pb_3Bi_8S_{16}$
5	—	$Cu_2Pb_4Bi_{10}S_{20}$
6	—	$Cu_2Pb_5Bi_{12}S_{24}$
7	Nordströmite	$Cu_2Pb_6Bi_{14}S_{28}$
etc.		
∞	Galenobismutite	$PbBi_2S_4$

i.e., $Cu_2S{\bullet}(n-1)PbS{\bullet}nBi_2S_3$. This series (Fig. 3) is seen to describe the composition of other known minerals, but overall there is no exten-

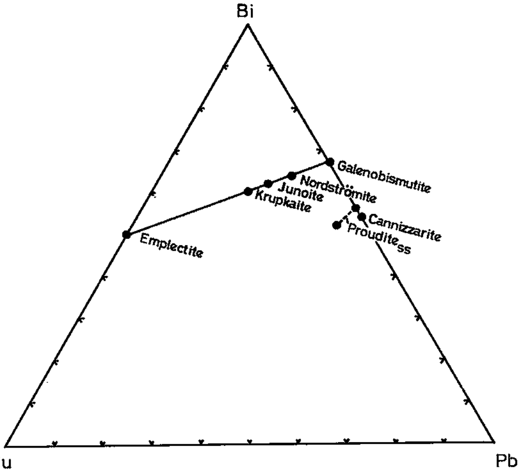

FIG. 3. Compositional plot Cu–Bi–Pb showing the junoite–nordströmite chemical series (emplectite, krupkaite, junoite, nordströmite and galenobismutite) in relation to proudite and cannizzarite.

sion of the structural similarity that exists between junoite and nordströmite (see below) to any of the other members. Krupkaite, for example, is a bismuthinite derivative (Mumme *et al.* 1976) that has been found associated with junoite in ore deposition (Large & Mumme 1975). Galenobismutite is more closely related to the lillianite homologous series structure-types (Makovicky 1977, Mumme 1978); therefore junoite and nordströmite are the only known members of the *junoite homologous series* of analogously built structures, of which proudite (Mumme 1976) and $Pb_3In_{6.67}S_{13}$ (Ginderow 1978) are related members (E. Makovicky, priv. comm.).

Related structures

Representations of the structural frameworks in junoite and nordströmite are given in Figure 4; only octahedra are delineated (in ideal form, except for *Me*1 in nordströmite). These demonstrate the close relationship between the two structures. In junoite (Fig. 4a) the regular-

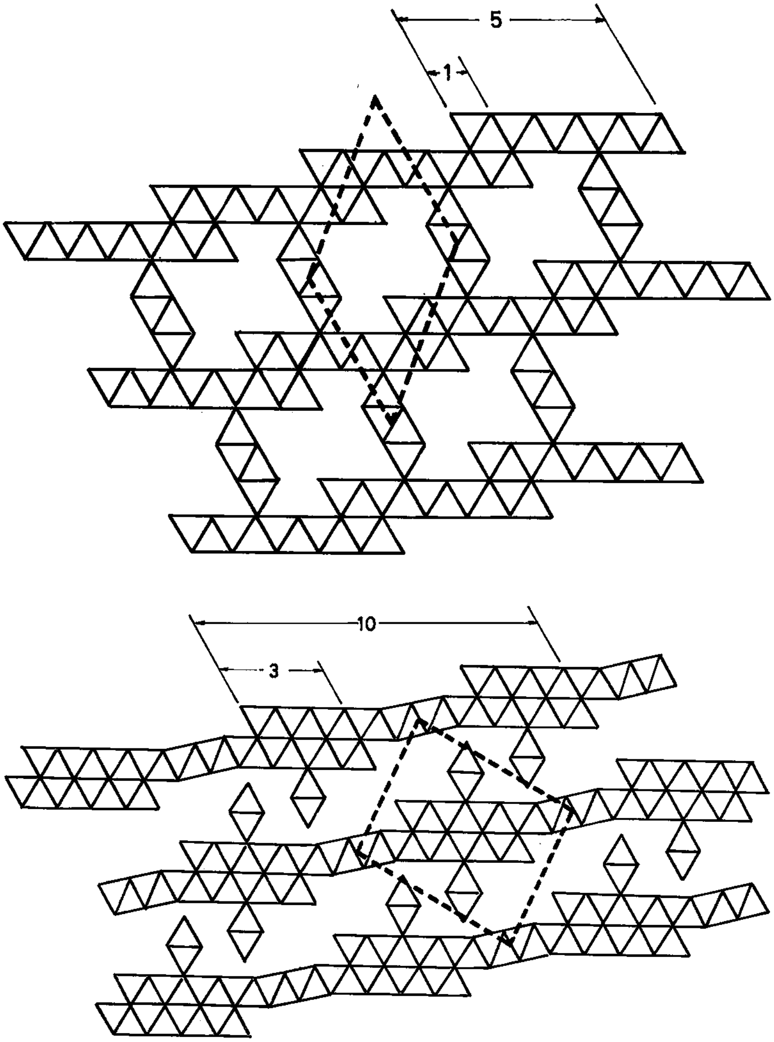

FIG. 4. Octahedral frameworks (idealized) in the structures of (a) junoite and (b) nordströmite, projected onto (010). Unit cells are outlined by heavy dashed lines. Sheared single octahedral layer segments and the overlapped sections discussed in the text are indicated.

octahedral slab may be considered to derive from the shearing of a continuous single octahedral layer. This layer, oriented such that (1) $[110]_{PbS}$ corresponds to $[010]_{nordströmite}$, (2) the boundary planes are parallel to $(111)_{PbS}$, is sheared into segments five octahedra in length, which are rejoined by means of overlapped sections each one octahedron long. These segments alternate with intermediate, disjointed, double-layer fragments made up of three-long-by-two-wide arrays of Pb and Bi atoms in irregular coordinations (plus Cu), which are segments of distorted double-galena layers, with their boundary planes parallel to $(001)_{PbS}$. In nordströmite (Fig. 4b) (disregarding the distortion at *Me*1) the regular-octahedral slabs may be derived from the shearing of the single octahedral layer into segments ten octahedra long, then rejoining with overlapped sections three octahedra long. These segments, again, alternate with the intermediate disjointed double-layer segments of (basically) highly distorted galena structure, which contain five-by-two arrays of Pb and Bi atoms (plus Cu), as already discussed in Figure 4 above. It is suggested that other members of the above chemical series, particularly $Cu_2Pb_4Bi_{10}(S,Se)_{20}$ and $Cu_2Pb_5Bi_{12}(S,Se)_{24}$ may also exist with similarly derived structures.

Relationship to cannizzarite

The crystal structures discussed above are all built up of slabs derived from regular-octahedral and distorted-galena fragments that have orientations the same as the two alternating layer sets in cannizzarite (Matzat 1979). Compounds of this type, with two noncommensurate layer sets periodically modified, interrupted and displaced by crystallographic shear planes, were first recognized by Makovicky & Hyde (1977, 1979). In particular, they discussed both junoite and proudite (a related seleniferous Pb–Bi sulfosalt: Mumme 1976) in terms of the cannizzarite structural arrangement.

A similar relationship between cannizzarite and weibullite, another selenium-bearing mineral from Falun, has also been demonstrated recently (Mumme 1980a). The continuous layers, which persist in the cannizzarite structure, are modified, disjointed and kinked in junoite, nordströmite and proudite in much more complicated ways than those observed in weibullite, but the general relationship of alternating layers is maintained. Cannizzarite may therefore be regarded as a parent structure from which all four derive.

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