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WEIBULLITE $\text{Ag}_{0.32}\text{Pb}_{5.09}\text{Bi}_{8.55}\text{Se}_{6.08}\text{S}_{11.92}$ FROM FALUN, SWEDEN: A HIGHER HOMOLOGUE OF GALENOBISMUTITE

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ABSTRACT

Weibullite from Falun, Sweden, is orthorhombic $a = 53.68(9)$, $b = 4.11(1)$, $c = 15.40(2)$ Å, space group $Pnma$, $Z = 4$. Its crystal structure has been determined using 1186 independent reflections recorded with Cu $K\alpha$ radiation and multiple-film packs. Eight Pb and Bi atoms are coordinated by S (and S, Se) atoms in octahedral coordination, whereas five other Pb and Bi atoms have more irregular seven- and eight-fold coordinations. $Me(11)$ is the site of up to one-third Ag substitution. The ideal end-member composition of weibullite is $\text{Pb}_8\text{Bi}_8(\text{S},\text{Se})_{18}$ whereas the structurally derived composition of $\text{Ag}_{0.33}\text{Pb}_{5.33}\text{Bi}_{8.33}(\text{Se},\text{S})_{18}$ is in good agreement with the microprobe analysis $\text{Ag}_{0.32}\text{Pb}_{5.09}\text{Bi}_{8.55}\text{Se}_{6.08}\text{S}_{11.92}$. The structure consists of two types of blocks: one has a 7×2 array of metal atoms in octahedral coordinations, the other a 6×2 array of metal atoms in irregular coordinations, aligned along [001] and [100]. A distorted trigonal prism $Me(4)$ occupies a position between the two blocks, and the overall structural arrangement thus formed represents a higher CaFe_2O_4 or galenobismutite homologue.

Keywords: weibullite, Falun, Sweden, lead-bismuth-selenium sulfosalt, galenobismutite homologues, lillianite homologues.

SOMMAIRE

La weibullite de Falun (Suède) est orthorhombique, $Pnma$, avec $a = 53.68(9)$, $b = 4.11(1)$, $c = 15.40(2)$ Å, $Z = 4$. On en a déterminé la structure cristalline, sur 1186 réflexions indépendantes enregistrées en radiation Cu $K\alpha$ sur films multiples. De 14 atomes Pb et Bi, huit sont entourés d'atomes S ou (S,Se) en coordination octaédrique, et cinq

autres ont une coordination 7 ou 8 plus irrégulière. La position $Me(11)$ est occupée par Ag jusqu'à concurrence de $\frac{1}{3}$. Le pôle weibullite de la solution solide a pour composition $\text{Pb}_8\text{Bi}_8(\text{S},\text{Se})_{18}$; la composition déduite de la structure, $\text{Ag}_{0.33}\text{Pb}_{5.33}\text{Bi}_{8.33}(\text{Se},\text{S})_{18}$, s'accorde avec celle que donne l'analyse à la microsonde, $\text{Ag}_{0.32}\text{Pb}_{5.09}\text{Bi}_{8.55}\text{Se}_{6.08}\text{S}_{11.92}$. La structure comporte des blocs de deux types: dans l'un, 7×2 atomes en coordination octaédrique, dans l'autre, 6×2 atomes en coordination irrégulière, sont alignés suivant [001] et [100] respectivement. Un prisme trigonal difforme $Me(4)$ se trouve entre les deux blocs; l'arrangement structural ainsi formé représente un homologue supérieur de CaFe_2O_4 ou de la galenobismutite.

(Traduit par la Rédaction)

Mots-clés: weibullite, Falun, Suède, sulfosel de plomb, bismuth et sélénium, homologue de la galenobismutite, homologue de la lillianite.

INTRODUCTION

Most specimens of seleniferous lead-bismuth sulfosalts from Falun, Sweden are closely intergrown mixtures of chemically related minerals, all of which have generally similar physical characteristics. The old chemical analyses of these minerals usually are misleading because, of necessity, they were carried out on gram amounts of material, which in most cases represented such mixtures. A nomenclature has now been established for three of the Falun minerals (Mumme 1980); it retains the old names *weibullite* (Flink 1910) and *wittite* (Johansson 1924) for two, and introduces the new name *nordströmite* for the third (accepted

by the Commission on New Minerals and Mineral Names, I.M.A. in December 1978). The present paper describes the results of a crystal-structure analysis of weibullite as defined in that nomenclature.

EXPERIMENTAL

The crystal of weibullite used in this analysis was isolated from a Falun specimen, BSF 1753, originally obtained from Dr. S. Solver, Bergskolan (Filipstad) by Dr. S. Karup-Møller, who then kindly made some of the specimen available for study here. The precise unit-cell parameters, a 53.68(9), b 4.11(1), c 15.40(2) Å, were derived by refining Guinier powder X-ray data internally calibrated with KCl (a 6.929 Å), and indexed with the aid of the Weissenberg films. These cell parameters may be compared with the values obtained by Johan & Picot (1976) from data obtained using Debye-Scherrer methods (53.8, 4.068, 15.39 Å, respectively).

The systematic absences of the $h0l$, $h1l$ and $h2l$ Weissenberg films recorded about the short (4 Å) axis, namely, $hk0$, $h \neq 2n$; $0kl$, $k + l \neq 2n$, defined the space-group alternative as $Pnma$ and $Pn2_1a$. Reflections with $k = 0, 2$ have the same distribution of intensity, which indicates that all atoms in the structure are in planes normal to b , separated by half the repeat distance of 4 Å; thus the atoms occupy the positions 4(a), 4(b) and 4(c) of the centrosymmetric space group $Pnma$.

Many crystal fragments were investigated, but only one small, irregular fragment ($\sim 0.02 \times 0.03 \times 0.07$ mm) was isolated that gave relatively sharp reflections. An attempt to use an automatic Stoe diffractometer to obtain a set of data from it was not successful because of the low count rates encountered owing to the small size of the crystal. Thus, intensity data were collected using an integrating Weissenberg camera, multiple-film packs and Cu $K\alpha$ radiation. A much smaller integration range than usual was set to eliminate the overlap of high-angle reflections, which made intensity measurement impracticable when the normal range for film measurement was used.

A linear absorption-coefficient of $ca.$ 1494 cm^{-1} was deduced; owing to the impossibility of measuring a detailed crystal-shape, the absorption correction applied was simply that of a thin rectangular prism bounded by six surfaces.

Corrections for absorption were performed with the program ABSNTST (Blount 1966). Because of the large number of reflections

involved and the necessity for visual measurement, agreement between equivalent reflections in the Weissenberg films, after correction for absorption, was estimated using fifty reflections from each level. The discrepancy between the equivalent reflections (averaged overall) was only 5.5%, in reasonable agreement with the assumption of rotational symmetry about [010].

STRUCTURE DETERMINATION AND REFINEMENT

Determination

This investigation was commenced before Johan & Picot (1976) published their chemical data and when the probe data of Karup-Møller (1970) were the only reliable analyses available. An analysis of weibullite from BSF 1753 was also performed here by electron-probe microanalysis; the fragment used was confirmed as weibullite from zero-level Weissenberg data collected about its 4 Å axis.

Apart from a lower Pb content, this analysis agrees reasonably well with Karup-Møller's average analysis and also confirms the presence of Ag: KM, Karup-Møller, av. of three: Cu 0.1, Pb 30.8, Ag 0.8, Bi 47.53, Se 11.63, S 10.30; M, Mumme: Pb 28.33, Ag 0.96, Bi 48.04, Se 12.83, S 10.28. On the other hand, the analyses of Johan & Picot (1976) gave a significantly higher Se content; more notably, they reported As in the mineral, but no Ag: J & P, Johan & Picot, av. of two: Pb 28.95, Bi 46.7, Se 15.3, S 9.7, As 0.4.

Assuming the monoclinic unit cell of Peacock & Berry (1940) (now known to be the unit cell for nordströmite; Mumme 1980), Karup-Møller's average analysis agrees best with the formula $\text{Bi}_6\text{Pb}_4\text{S}_6\text{Se}_4$ ($Z = 2$). However, volume relationships with proudite (Mumme 1976), based on Karup-Møller's chemical data, and the correct, larger, orthorhombic unit-cell indicate that the formula would be closer to $\text{Bi}_8\text{Pb}_8(\text{S},\text{Se})_{17}$ ($Z = 4$). As Karup-Møller's analyses and ours had both detected the presence of Ag (½ to 1% by weight) it was anticipated that the structure would contain an atom site that had a significant partial occupancy by silver. Up to one-third occupancy was suggested by the chemical analyses recorded.

Because of the short repeat-distance of 4 Å, the structure solution was initially attempted using only the $h0l$ data, from which a Patterson projection $\rho(u, 0, w)$ was calculated. Both of the selenium-bearing bismuth-lead sulfosalts junote and proudite (Mumme 1975, 1976) had previously been determined to have struc-

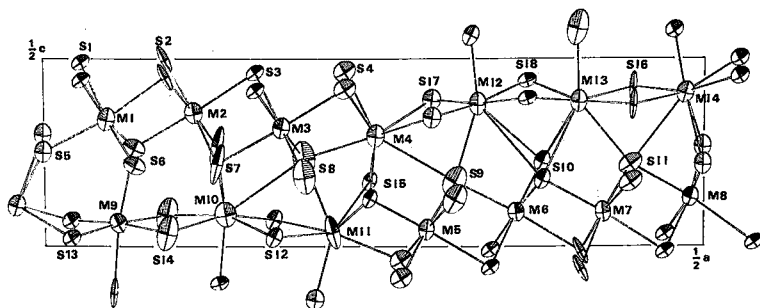


FIG. 1. Asymmetric unit of weibullite drawn with 50% probability ellipsoids. This ORTEP drawing is a projection along a direction close to $[0\bar{1}0]$.

tures containing PbS-type fragments, and it was anticipated that this would also be the case in the structure of weibullite. Furthermore, the "predictive" classification of Takéuchi & Sadanaga (1969) supported this premise. The starting model for the structure, which was supported by examination of the Patterson projection, incorporated a pair of edge-shared octahedra related by a centre of symmetry as part of a larger PbS-type fragment. From the very basic model most of the atomic positions were determined by reiteration of structure-factor and electron-density calculations using the $h0l$ data. Three-dimensional Fourier calculations were then carried out until finally all the atoms were located.

Refinement

Atomic positions were refined with a local version of the least-squares-refinement program ORFLS (Busing *et al.* 1962), using the weighting scheme of Cruickshank *et al.* (1961). Neutral-atom scattering curves were employed (Cromer & Waber 1965), and anomalous dispersion corrections were made for lead and bismuth in the final stages. The average scattering-curve f $[(2S + Se)/3]$ was initially used for the nonmetal atoms and an average of Pb and Bi for the metals.

The asymmetric unit of weibullite, as finally determined and shown in Figure 1, contains 32 atom sites: 14 heavy-metal atom sites designated $Me(1)$ to $Me(14)$, and 18 sulfur-selenium atom sites, all located in special positions of the space group $Pnma$. Once the correct atom-positions were established, refinement using average scattering-factors and isotropic temperature-factors proceeded smoothly to give an R of 0.16. At this stage a detailed study of the Fourier synthesis showed that S(4), S(5), S(6), S(7), S(8), S(9), S(10), S(11) and S(14) all had

higher maxima than the other nonmetal sites, whereas $Me(11)$ had a significantly lower maximum than the other metals. Compositions based on $\Sigma S, Se = 18$ were derived for the above three analyses, and then were calculated to be $Ag_{0.28}Cu_{0.08}Pb_{5.71}Bi_{8.73}Se_{5.06}S_{12.34}$ (KM), $Pb_{5.06}Bi_{8.10}As_{0.16}Se_{7.03}S_{10.97}$ (J & P) and $Ag_{0.32}Pb_{5.09}Bi_{8.55}Se_{8.08}S_{11.82}$ (M). For KM, ΣMe is 0.78 higher than the structurally derived value of 14, whereas for J & P it is 0.71 lower. For M, $\Sigma Me = 13.96$. Thus, of the three formulae, the one recorded here is the most consistent with structural features, presumably because it is obtained from a fragment adjacent to the crystal used in the structure analysis. If the six selenium atoms mentioned above, each containing ($\frac{2}{3}$ Se, $\frac{1}{3}$ S), and if $\sim (\frac{1}{3}$ Ag, $\frac{2}{3}$ Pb+Bi) in the structure is ordered in $Me(11)$, the variations in the electron densities are readily explained and the resulting structural formula, $Ag_{0.33}Pb_{5.33}Bi_{8.33}(Se_6, S_{12})$, compares favorably with the formula derived from the analytical data.

With this ordering scheme and the addition of an anomalous-dispersion correction, the R value was reduced from 0.16 to 0.14. Three more cycles with individual anisotropic temperature-factors reduced the R value to 0.12, at which stage parameter shifts were less than one-third their $esds$ (Table 1). Observed and calculated structure factor may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

METAL POSITIONS AND THE SUBSTITUTIONS

Metal positions

A survey of the bond lengths (Table 2) shows that $Me(2)$, $Me(5)$, $Me(6)$, $Me(7)$, $Me(8)$, $Me(12)$ and $Me(14)$ all have bonds less than

TABLE 1A. ATOMIC PARAMETERS, ISOTROPIC AND ANISOTROPIC TEMPERATURE FACTORS FOR WEIBULLITE

Atom	Occup.	x	y	z	Final isotropic B	Results of anisotropic refinement [*]			
						β_{11}	β_{22}	β_{33}	β_{13}
Me1	Pb	.0515(2)	1/4	.3631(10)	5.38(33)	3(1)	790(712)	75(8)	2(2)
Me2	Bi	.1170(2)	3/4	.3525(9)	4.97(31)	4(1)	920(703)	63(8)	-1(2)
Me3	Bi	.1822(2)	1/4	.3323(8)	4.28(27)	3(1)	500(699)	60(7)	1(1)
Me4	Pb	.2524(2)	3/4	.2845(9)	5.16(30)	4(1)	630(697)	72(7)	1(2)
Me5	Bi	.2894(2)	1/4	.0580(9)	4.20(27)	3(1)	750(692)	61(7)	1(1)
Me6	Bi	.3563(2)	3/4	.0768(8)	4.15(28)	3(1)	740(703)	51(6)	-1(1)
Me7	Bi	.4212(2)	1/4	.0974(8)	4.66(29)	3(1)	750(703)	60(7)	-1(1)
Me8	Bi	.4865(2)	3/4	.1091(8)	4.56(28)	3(1)	850(701)	53(6)	2(1)
Me9	Pb	.0596(2)	3/4	.0648(9)	4.77(30)	3(1)	1030(698)	54(7)	-3(2)
Me10	Pb	.1396(3)	3/4	.0827(9)	6.04(37)	5(1)	720(709)	89(10)	-1(2)
Me11	1/3 Ag + 2/3 (Bi,Pb)	.2195(2)	3/4	.0311(15)	5.40(41)	3(1)	90(714)	153(17)	-9(2)
Me12	Bi	.3287(2)	3/4	.3641(9)	4.94(29)	3(1)	770(705)	73(8)	1(2)
Me13	Pb	.4042(2)	3/4	.3667(9)	4.88(30)	3(1)	800(698)	69(8)	1(2)
Me14	Bi	.4837(2)	3/4	.3848(9)	4.35(28)	3(1)	710(700)	64(7)	2(1)
S1	S	.0332(15)	3/4	.4905(42)	2.6(1.3)	4(3)	200(982)	34(30)	4(8)
S2	S	.0960(10)	1/4	.4715(47)	2.0(1.1)	2(2)	750(890)	93(40)	-12(7)
S3	S	.1634(9)	3/4	.4549(42)	2.1(1.3)	4(2)	170(950)	34(33)	4(6)
S4	2/3 Se + 1/3 S	.2300(7)	1/4	.4325(24)	6.2(1.0)	5(2)	920(811)	56(20)	3(5)
S5	2/3 Se + 1/3 S	.0039(6)	1/4	.2802(25)	5.6(0.9)	3(1)	840(800)	64(20)	1(4)
S6	2/3 Se + 1/3 S	.0721(8)	3/4	.2630(25)	6.0(1.0)	5(2)	1250(788)	46(20)	-4(5)
S7	2/3 Se + 1/3 S	.1340(6)	1/4	.2397(38)	6.4(.9)	2(1)	80(792)	226(47)	16(6)
S8	2/3 Se + 1/3 S	.1987(9)	3/4	.2271(44)	7.1(1.0)	6(2)	1120(866)	178(48)	-4(8)
S9	2/3 Se + 1/3 S	.3108(8)	3/4	.1611(34)	7.3(1.1)	7(2)	800(876)	121(34)	9(7)
S10	2/3 Se + 1/3 S	.3762(6)	1/4	.1872(23)	5.0(0.8)	3(1)	980(801)	56(19)	3(4)
S11	2/3 Se + 1/3 S	.4421(8)	3/4	.2001(24)	6.0(0.9)	6(2)	1000(837)	57(20)	6(5)
S12	S	.1758(11)	1/4	.0433(48)	1.1(0.8)	3(3)	30(992)	56(40)	4(8)
S13	S	.0242(16)	1/4	.0506(61)	4.9(2.0)	4(3)	1600(1295)	38(47)	2(10)
S14	2/3 Se + 1/3 S	.0959(8)	1/4	.0595(39)	9.8(1.4)	5(2)	750(853)	176(42)	9(7)
S15	S	.2475(11)	1/4	.1417(39)	2.0(1.2)	3(2)	30(901)	46(33)	4(8)
S16	S	.4448(12)	1/4	.3792(70)	4.9(1.8)	1(2)	800(1157)	124(72)	3(10)
S17	S	.2946(7)	1/4	.3534(30)	.4(0.3)	4(1)	640(831)	60(24)	1(4)
S18	S	.3658(8)	1/4	.4009(31)	1.4(1.0)	4(2)	950(897)	28(21)	2(4)

* Anisotropic temperature factor expression: $\exp \{- (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hkl\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$ with $\beta_{12} = 0$ and $\beta_{23} = 0$ for all atoms. All β_{ij} values are multiplied by 10^4 . Estimated standard deviations are given in parenthesis in terms of the last digit.

2.79 Å and [1+2] shortest bonds, set apart from the remaining longer bonds; these are, therefore, most probably the Bi-atom sites. On the other hand *Me*(4), with no bond shorter than 3.02 Å and *Me*(13), with no bond shorter than 2.96 Å, are most probably the sites of two of the Pb atoms in the structure. Among the remaining positions, *Me*(3) has bond distances less than 2.80 Å and an octahedral coordination in which there are three shorter bonds set apart from three longer bonds. Although it does not have a usual [1+2] configuration, it most probably is Bi.

Me(1) has two relatively short bonds [2.80 Å] and four long bonds [2.86, 2.91, 3.01(2) Å], *Me*(9) has two shorter bonds [2.81(2) Å] and four long bonds [2.83(2), 2.87, 3.13 Å] and *Me*(10) has a configuration of three short and four long bonds, but with no bonds shorter than 2.82 Å. Except for *Me*(10), which has a fairly typical Pb coordination-configuration, these last three sites are more difficult to categorize. The fact that eight probable sites [*Me*(2), *Me*(5), *Me*(6), *Me*(7), *Me*(8), *Me*(12),

Me(14) more definite, *Me*(3) less definite] have been established for Bi indicates that *Me*(1), *Me*(9) and *Me*(10) may all be Pb.

However, because the *esds* of the bond lengths in this structure are appreciable, Pb-Bi ambiguity or statistical replacement in several of the above-mentioned sites must be acknowledged. For example, the *Me*(9)-S(16) bond of 2.87 (x1) Å, with *Me*(9)-S(13) equal to 2.81 (x2) Å, may be interpreted as indicating Pb, Bi disorder on that site. Similarly, the configurations of *Me*(10) (and its high *B*) and *Me*(2), together with the large thermal motion observed for S(7), may also be interpreted as resulting from Pb-Bi substitution in those two sites.

Selenium ordering

Additional difficulty in distinguishing the BiS_3 groups in this structure is due to selenium ordering. In weibullite, selenium replacement of up to two-thirds is indicated in S(4), S(5), S(6), S(7), S(8), S(9), S(10), S(11) and S(14). The ionic radius of Se^{2-} is 1.98 Å,

TABLE 1B. THERMAL AND DISORDER ELLIPSOIDS IN WEIBULLITE

Atom	r.m.s. displacement	Angle to			Atom	r.m.s. displacement	Angle to		
		a	b	c			a	b	c
Me1	.2182 (143)	168 (10)	90	78 (10)	S3	.1206 (754)	90	0	90
	.2600 (185)	90	0	90		.1699 (1154)	126 (21)	90	144 (21)
	.3029 (152)	102 (10)	90	168 (10)		.2512 (698)	36 (21)	90	126 (21)
Me2	.2279 (123)	171 (18)	90	99 (18)	S4	.2472 (701)	121 (14)	90	31 (14)
	.2757 (156)	81 (18)	90	171 (18)		.2806 (1309)	90	0	90
	.2806 (157)	90	0	90		.2916 (1011)	149 (14)	90	121 (14)
Me3	.2069 (93)	90	0	90	S5	.2518 (449)	4 (19)	90	94 (19)
	.2168 (95)	168 (21)	90	78 (21)		.2681 (788)	90	0	90
	.2705 (123)	102 (21)	90	168 (21)		.2776 (573)	94 (19)	90	176 (19)
Me4	.2315 (104)	173 (46)	90	83 (46)	S6	.2159 (831)	118 (16)	90	152 (16)
	.2322 (114)	90	0	90		.2933 (980)	152 (16)	90	62 (16)
	.2944 (153)	97 (46)	90	173 (46)		.3271 (562)	90	0	90
Me5	.1970 (83)	172 (17)	90	82 (17)	S7	.0827 (482)	90	0	90
	.2533 (101)	90	0	90		.1357 (593)	166 (22)	90	76 (22)
	.2725 (114)	98 (17)	90	172 (17)		.5368 (683)	104 (22)	90	166 (22)
Me6	.2086 (74)	173 (19)	90	97 (19)	S8	.2796 (802)	173 (19)	90	97 (19)
	.2478 (92)	97 (19)	90	173 (19)		.3096 (954)	90	0	90
	.2517 (143)	90	0	90		.4634 (955)	83 (19)	90	173 (19)
Me7	.1974 (49)	174 (11)	90	96 (11)	S9	.2617 (832)	90	0	90
	.2533 (148)	90	0	90		.2774 (1139)	152 (14)	90	62 (14)
	.2693 (157)	96 (11)	90	6 (11)		.4059 (902)	62 (14)	90	152 (14)
Me8	.2036 (78)	162 (19)	90	72 (19)	S10	.1894 (564)	156 (25)	90	66 (25)
	.2562 (154)	108 (19)	90	162 (19)		.2715 (958)	114 (25)	90	156 (25)
	.2697 (189)	90	0	90		.2896 (367)	90	0	90
Me9	.2102 (124)	152 (19)	90	118 (19)	S11	.2246 (478)	124 (23)	90	34 (23)
	.2641 (129)	118 (19)	90	28 (19)		.2925 (1112)	90	0	90
	.2969 (147)	90	0	90		.3272 (907)	146 (23)	90	124 (23)
Me10	.2482 (96)	90	0	90	S12	.0507 (301)	90	0	90
	.2736 (158)	170 (18)	90	100 (18)		.1930 (1111)	153 (18)	90	63 (18)
	.3286 (179)	100 (18)	90	10 (18)		.2744 (789)	117 (18)	90	153 (18)
Me11	.0877 (362)	90	0	90	S13	.2011 (582)	122 (20)	90	32 (20)
	.1708 (201)	166 (10)	90	104 (10)		.2433 (1219)	148 (20)	90	122 (20)
	.4405 (421)	104 (10)	90	14 (10)		.3700 (1011)	90	0	90
Me12	.2125 (99)	178 (18)	90	88 (18)	S14	.2533 (660)	90	0	90
	.2567 (124)	90	0	90		.2591 (1092)	166 (15)	90	76 (15)
	.2961 (156)	92 (18)	90	178 (18)		.4693 (1029)	104 (15)	90	166 (15)
Me13	.2122 (98)	176 (19)	90	86 (19)	S15	.0507 (399)	90	0	90
	.2617 (124)	90	0	90		.1687 (680)	151 (18)	90	61 (18)
	.2891 (117)	94 (19)	90	176 (19)		.2516 (499)	119 (18)	90	151 (18)
Me14	.2175 (118)	16 (18)	90	106 (18)	S16	.0874 (998)	175 (10)	90	85 (10)
	.2465 (159)	90	0	90		.2617 (890)	90	0	90
	.2821 (178)	106 (18)	90	164 (18)		.3874 (744)	95 (10)	90	175 (10)
S1	.1308 (536)	90	0	90	S17	.2314 (398)	171 (19)	90	81 (19)
	.1727 (982)	56 (15)	90	146 (15)		.2340 (861)	90	0	90
	.2550 (600)	146 (15)	90	124 (15)		.2693 (544)	81 (19)	90	9 (19)
S2	.1008 (581)	154 (19)	90	116 (19)	S18	.1755 (998)	109 (25)	90	19 (25)
	.2533 (1121)	90	0	90		.2415 (1154)	19 (25)	90	71 (25)
	.3696 (729)	64 (19)	90	154 (19)		.2851 (709)	90	0	90

compared with 1.84 Å for S²⁻ (Shannon & Prewitt 1969). The covalent-bond radius reported by Pauling (1960) also differs by about the same amount: Se²⁻ is 1.17 Å compared with 1.04 Å for S²⁻. The effect of the larger size of selenium is reflected in the bond lengths

observed in the selenides Bi₂Se₃ and PbSe. Atabaeva *et al.* (1973) reported that in bis-muthinite-type orthorhombic Bi₂Se₃, the Bi-Se bond distances for M(1) are 2.85, 2.92(x2), 3.26(x2), 3.13 and 3.54 Å, compared with 2.63, 2.62(x2), 3.06(x2), 3.05 and 3.47 Å in

TABLE 2. BOND LENGTHS AND ANGLES IN WEIBULLITE

Interatomic distances				Bond angles			
Me1-S5	2.86(4) × 1	Me8-S11	2.77(4) × 1	S(1)-Me(1)-S(5)	89.9	S(5)-Me(8)-S(11)	88.8
-S6	2.80(3) × 2	S5	2.83(3) × 2	S(6)-Me(1)-S(5)	96.2	S(1)-Me(8)-S(11)	90.3
-S1	3.01(5) × 2	S1	2.95(5) × 2	S(1)-Me(1)-S(2)	83.9	S(5)-Me(8)-S(1)	89.2
-S2	2.91(6) × 1	S1'	2.94(8) × 1	S(6)-Me(1)-S(2)	89.5	S(1)-Me(8)-S(1)''	88.5
				S(1)-Me(1)-S(1)'	86.3	S(5)-Me(8)-S(5)'	93.2
				S(6)-Me(1)-S(6)'	94.6	S(1)-Me(8)-S(1)'	89.0
				S(1)-Me(1)-S(6)	89.2	S(5)-Me(8)-S(1)	91.9
Me2-S6	2.78(4) × 1	Me9-S6	3.13(4) × 1	S(2)-Me(2)-S(6)	88.7	S(13)-Me(9)-S(6)	102.8
S2	2.98(5) × 2	S13	2.81(6) × 2	S(7)-Me(2)-S(6)	88.6	S(14)-Me(9)-S(6)	83.1
S7	2.84(4) × 2	S14	2.83(3) × 2	S(2)-Me(2)-S(3)	89.5	S(13)-Me(9)-S(16)	82.3
S3	2.95(5) × 1	S16	2.87(11) × 1	S(7)-Me(2)-S(3)	93.2	S(14)-Me(9)-S(16)	91.6
				S(2)-Me(2)-S(2)'	87.4	S(13)-Me(9)-S(13)'	94.1
				S(7)-Me(2)-S(7)'	92.7	S(14)-Me(9)-S(14)'	93.0
				S(2)-Me(2)-S(7)	89.9	S(13)-Me(9)-S(14)	86.1
Me3-S7	2.95(4) × 1	Me10-S18	2.82(5) × 1	S(3)-Me(3)-S(7)	90.5	S(14)-Me(10)-S(18)	79.0
S8	2.76(4) × 2	S14	3.14(4) × 2	S(8)-Me(3)-S(7)	89.9	S(12)-Me(10)-S(18)	82.0
S3	2.97(5) × 2	S12	2.89(4) × 2	S(3)-Me(3)-S(4)	87.9	S(14)-Me(10)-S(14)'	81.8
S4	2.99(4) × 1	S7	3.19(5) × 2	S(8)-Me(3)-S(4)	91.6	S(12)-Me(10)-S(12)'	90.5
				S(3)-Me(3)-S(3)'	87.7	S(12)-Me(10)-S(14)	90.8
				S(8)-Me(3)-S(8)'	96.1		
				S(3)-Me(3)-S(8)	88.1	S(12)-Me(11)-S(8)	71.5
Me4-S8	3.02(5) × 1	Me11-S8	3.22(7) × 1	S(4)-Me(4)-S(8)	81.6	S(15)-Me(11)-S(8)	69.4
S4	3.30(3) × 2	S12	3.12(5) × 2	S(15)-Me(4)-S(8)	72.7	S(12)-Me(11)-S(12)	82.3
S15	3.02(5) × 2	S15	3.06(5) × 2	S(4)-Me(4)-S(4)'	77.1	S(15)-Me(11)-S(15)'	84.3
S17	3.24(3) × 2	S4	3.11(4) × 1	S(15)-Me(4)-S(15)'	85.7	S(12)-Me(11)-S(15)	83.9
		S17	2.84(5) × 1	S(4)-Me(4)-S(15)	92.7		
Me5-S15	2.59(6) × 1	Me12-S12	2.77(8) × 1	S(9)-Me(5)-S(15)	94.2	S(17)-Me(12)-S(12)	90.1
S9	2.84(4) × 2	S17	2.76(3) × 2	S(4)-Me(5)-S(15)	91.1	S(18)-Me(12)-S(12)	82.3
S4	3.01(3) × 2	S18	2.92(3) × 2	S(9)-Me(5)-S(3)	87.4	S(17)-Me(12)-S(17)	96.4
S3	2.99(5) × 1	S9	3.27(5) × 1	S(4)-Me(5)-S(3)	87.3	S(18)-Me(12)-S(18)	89.6
		S10	4.26(3) × 2	S(9)-Me(5)-S(9)'	92.7	S(17)-Me(12)-S(18)	93.2
				S(4)-Me(5)-S(9)	90.3		
				S(4)-Me(5)-S(4)'	86.2	S(18)-Me(13)-S(14)	79.7
Me6-S9	2.77(5) × 1	Me13-S14	2.97(6) × 1	S(10)-Me(6)-S(9)	92.9	S(16)-Me(13)-S(14)	86.4
S10	2.87(3) × 2	S18	2.96(3) × 2	S(3)-Me(6)-S(9)	89.0	S(18)-Me(13)-S(18)	88.0
S3	2.98(5) × 2	S16	3.00(5) × 2	S(10)-Me(6)-S(2)	90.1	S(16)-Me(13)-S(16)'	86.4
S2	3.03(6) × 1	S10	3.76(3) × 2	S(3)-Me(6)-S(2)	87.9	S(18)-Me(13)-S(16)	91.1
		S11	3.27(4) × 1	S(10)-Me(6)-S(10)'	91.3	S(16)-Me(14)-S(13)	85.0
				S(10)-Me(6)-S(3)	90.7	S(13)-Me(14)-S(13)''	78.6
				S(3)-Me(6)-S(3)'	87.3	S(16)-Me(14)-S(16)'	89.0
Me7-S10	2.78(3) × 1	Me14-S13	2.59(9) × 1	S(11)-Me(7)-S(10)	93.8	S(13)-Me(14)-S(13)'	81.4
S11	2.83(3) × 2	S16	2.93(5) × 2	S(2)-Me(7)-S(10)	93.1	S(13)-Me(14)-S(16)	92.5
S2	2.97(5) × 2	S13'	3.15(7) × 2	S(11)-Me(7)-S(1)	89.0		
S1	2.95(8) × 1	S11	3.62(4) × 1	S(2)-Me(7)-S(1)	83.9		
		S5	3.44(3) × 1	S(11)-Me(7)-S(11)'	93.3		
				S(2)-Me(7)-S(2)'	87.5		
				S(11)-Me(7)-S(2)	89.2		

Estimated standard deviations for bond angles is 0.7° .

Bi_2S_3 (Kupčík & Veselá-Nováková 1970). For $M(2)$, the comparable bonds are 2.85, 2.84(x2), 2.95(x2) and 3.41(x2) Å in Bi_2Se_3 and 2.58, 2.74(x2), 2.95(x2) and 3.41(x2) Å in Bi_2S_3 . In PbSe , the Pb-Se bond distances are 3.07 Å compared with Pb-S bond distances of 2.87 Å in PbS . Significant increases in some of the metal-anion bonds must therefore be expected in weibullite because of the selenium ordering, and this also adds to the difficulty experienced in defining the metal ordering more accurately than is discussed above.

Ag substitution

$Me(11)$ had a significantly smaller maximum in the final Fourier synthesis than the other metal atoms. Isotropic refinement with full occupancy of an average (Bi,Pb) atom resulted in $Me(11)$ having a much higher isotropic temperature factor (7.17 \AA^2) than any of the other metals except $Me(10)$, which was 6.05 \AA^2 (Table 1). Isotropic refinement with $Me(11)$ containing 0.33 Ag + 0.67 (Bi,Pb) resulted in a reduction of its temperature factor to 5.40

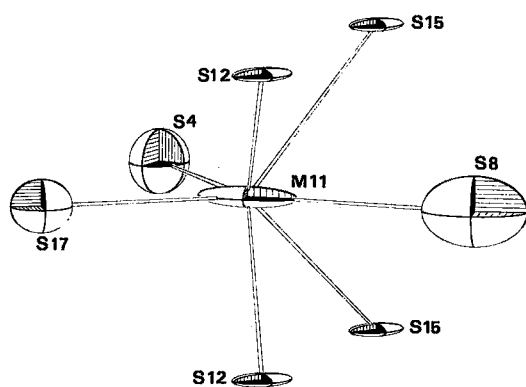


FIG. 2. The $Me(11)$ ($\frac{1}{3}Ag$, $\frac{2}{3}Pb + Bi$) metal-coordination polyhedra in the crystal structure of weibullite. The thermal vibration and disorder ellipsoids (see text) are drawn at the 50% probability level using ORTEP (Johnson 1965). View is along a .

\AA^2 , which is closer to the average, but with only a marginal improvement of the R value (0.124 to 0.120). The isotropic temperature-factor of $Me(10)$ remained about the same at 6.04\AA^2 . No peaks that would correspond to a Ag occupancy of interstitial sites in the structure were found in any of the Fourier syntheses or in a difference-Fourier map calculated at this stage. The results of the isotropic refinement, the overall chemical composition and the absence of interstitial Ag anywhere in the structure tend to support the idea that the Ag substitution is almost entirely incorporated in $Me(11)$.

The results of the anisotropic refinement (Table 1, Fig. 2) also seem consistent with Ag substitution in $Me(11)$. In contrast to all the other metal atoms, the thermal motion ellipsoid possessed by $Me(11)$ is extremely oblate, with its main axis almost parallel to a . This reflects a positional disorder of metal atoms consistent with a statistical occupancy of Ag and Pb (and possibly Bi). $S(8)$ also displays a large oblate ellipsoid with its long axis again almost parallel to a ; $S(4)$, $S(12)$, $S(16)$ and $S(17)$ all display more uniform thermal motion ellipsoids.

If the r.m.s. displacement of $Me(11)$, $S(8)$ and $S(15)$ is considered to contribute towards closer interactions between these atoms, the coordination of the deviated metal-atom would be a predominantly three-fold one, with distances of the order of 2.3\AA for $Me(11)$ - $S(8)$ and $2.7(x2) \text{\AA}$ for $Me(11)$ - $S(15)$ (av. $\sim 2.6 \text{\AA}$), consistent with three-fold pyramidal Ag . If the two longer bonds of 2.9\AA for

$Me(11)$ - $S(12)$ are included, the coordination of the deviated metal is five-fold pyramidal.

The metal atoms at r.m.s. displacement from the mean $Me(11)$ towards $S(4)$ and $S(17)$ would have distances of about 2.4 and 2.7\AA to the mean sulfur positions. These would be smaller (approximately 2.2 and 2.6\AA) if the sulfur displacements were also considered. This coordination is two-fold with a bond angle of only $\sim 100^\circ$, which is improbable because it is much lower than any previously observed for two-fold Ag .

As silver is the only element substituting in the structure of the weibullite from BSF 1753, the basic substitution mechanism must be by the valency accommodation $Ag + Bi \rightleftharpoons 2Pb$. The "best fit" structural formula derived by refinement, $Ag_{0.33}Pb_{5.33}Bi_{3.33}(S,Se)_{18}$, requires that some disorder of Pb and Bi occurs in the structure. The overall metal-ordering arrangement discussed above, the lengths of the mean $Me(11)$ -anion bonds (2.83 - 3.22\AA , which conform with normal Pb - S distances) and the coordinations of the r.m.s. deviated metal-sites suggest that, conceivably, such substitution occurs entirely in $Me(11)$. Also, because the $Me(11)$ site is so similar to the $Bi(2)$ site in galenobismutite (see later discussions), and in view of the r.m.s. shifts observed, the site must surely accommodate some Bi . On the other hand, a substitution in $Me(11)$ of only Ag (for Pb) requires that an additional replacement of Pb by Bi must occur in a site adjacent to $Me(11)$ in order to maintain the local valence-balance.

A general formula $Ag_xPb_yBi_z(S,Se)_{18}$ may be proposed for weibullite, in which the condition $z-x = 8$ must hold if the total number of metal atoms is 14, i.e., $Ag_xPb_{8-2x}Bi_{8+x}(S,Se)_{18}$. The formula, based on $(S + Se) = 18$, which was derived from our microprobe data, is in good agreement with $\Sigma Me = 14$, but the bismuth/silver ratio is slightly higher, and the Pb content slightly lower than is required by the above total metal/total sulfur + selenium ratio. These discrepancies probably reflect only the inaccuracy of the microprobe analysis.

Alternative interpretations of the chemical and structural results would include such formulae as $Ag_{0.45}Pb_{5.1}Bi_{8.45}(S,Se)_{18}$ and $Ag_{0.33}Pb_{5.33}Bi_{3.56}(S,Se)_{18}$. The first of these conforms to the requirements of the general formula described above but tends to weight the Pb and Bi analyses more favorably and to imply that the measured Ag content is low for the crystal analyzed. The second formula is an example

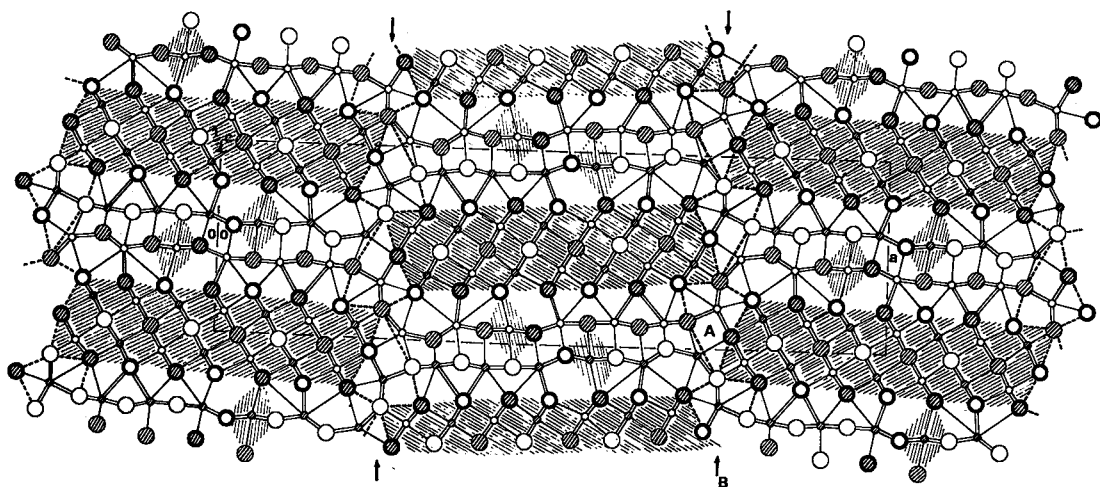


FIG. 3. The full crystal-structure of weibullite drawn as an assemblage of octahedra and other coordination polyhedra. The shaded portions indicate fragments of the regular (undeformed) PbS-type structure. Hatched circles are at $y = \frac{3}{4}$, open circles at $y = \frac{1}{4}$. Medium circles Pb, Bi; large circles S; significant Se replacement is in heavy outline. Projection onto (010). The distorted trigonal prisms (A) and glide/twin planes (B), discussed in the text, are indicated on the diagram.

of the result achieved if a charge balance is maintained without the restriction that $\Sigma Me = 14$ but only closely approaches it. It also agrees reasonably well with the analytical data but in this case implies some metal vacancies in the structure. The complexity of the structure, experimental errors and the negligible response of the R value to such modeling have made it impossible for us to differentiate between compositions as close together as these.

STRUCTURAL AND CHEMICAL RELATIONSHIPS OF WEIBULLITE

General structural features

The crystal structure of weibullite comprises two types of elongate blocks, both of which are parallel to (001). One of them is a block of little-deformed, regular galena-like structure, with all the metal atoms in octahedral coordination, such that $[110]_{\text{PbS}}$ corresponds with $[010]_{\text{weibullite}}$ and its long boundary is parallel to $(111)_{\text{PbS}}$. The other type contains Pb and Bi atoms in much more irregular coordinations. However, it may be regarded as a fragment of deformed galena-like structure, again with $[110]_{\text{PbS}}$ parallel to $[010]_{\text{weibullite}}$, but in this case its long boundary is parallel to $(100)_{\text{PbS}}$ (compare the orientation of the octahedra in both blocks, Fig. 3). Both blocks contain 14 metal atoms in 7×2 arrays, and because of their alignment and the action of

the n glides, the blocks regularly alternate with each other along both $[001]$ and $[100]$ (Fig. 3). The octahedral fragment has the overall composition $Me_{14}S_{24}$ and the other has the composition $Me_{14}S_{34}$, with 22 of the sulfur atoms in common between them. In the deformed galena fragment, only $Me(9)$ is octahedral; $Me(12)$, $Me(13)$, $Me(14)$ approach square pyramidal coordination, whereas $Me(4)$, $Me(10)$ and $Me(11)$ approach trigonal prismatic coordination.

Structural relationships with the lillianite homologues

Of the minerals with similar chemistry, weibullite does relate to cosalite in that they both contain large blocks of octahedral fragments (Weitz & Hellner 1960, Srikrishnan & Nowacki 1974). The octahedral fragments in cosalite are less extensive than those in weibullite; furthermore they are joined by single ribbons of octahedra. The most closely adjacent octahedral blocks in both structures are disoriented with respect to each other because of the action of the glide planes. In contrast, the copper-containing lead-bismuth seleniferous sulfosalts junonite (Mumme 1975) and proudite (Mumme 1976) have continuous ribbons of octahedra forming the basis of their structures, very similar to the members of the pavonite homologous series with low ^{35}P values (Makovicky *et al.* 1977), in which adjacent ribbons

(or slabs when wider) also have identical orientations.

However, the structure of weibullite is much more readily related to the structures of the lillianite homologous series (Makovicky & Karup-Møller 1977) but with the mirror twinning replaced by glide reflections (*cf.*, calcium ferrite CaFe_2O_4 , Hyde *et al.* 1974). In weibullite, $Me(4)$, a distorted, asymmetrical trigonal prism, occupies a position comparable with that occupied by the symmetrical trigonal prism in a lillianite homologue, ${}^N L$ or ${}^{N1,N2} L$, but in this case it resides between a regular, galena-like block and a dimensionally related, deformed galena block. With this representation (Fig. 3) the regular galena block is 7×2 , whereas the other is 6×2 . Because of the dimensions of the regular block, the skeleton of the crystal structure of weibullite obtained by leaving out the deformed galena block is best allied to the member of the lillianite homologous series, ${}^{14} L$, *i.e.*, the number with chain length 14 and with compositions $TM_{e14}S_{18}$ ($Z = 4$) for which the unsubstituted Pb-Bi end-member is $\text{Bi}_2\text{Pb}_{18}\text{S}_{18}$ and the maximum Ag-substituted end-member is $\text{Ag}_6\text{Bi}_8\text{PbS}_{18}$. Based on the average octahedral dimensions $l \sim 5.7$ and $w \sim 4.15$ Å in heyrovskyite and the unit-cell relationships in Makovicky (1977), $a = 13.69$ and $c = 55.29$ Å for the lillianite member ${}^{14} L$. If we take a

pavonite/benjaminite average dimension of $l \sim 5.3$ and $w \sim 4.075$ Å, then $a = 13.32$ and $c = 51.89$ Å (*cf.*, weibullite, $a = 53.68$ and $c = 15.40$ Å). Despite all approximations, $d_{(001)}$ of weibullite is therefore in quite good agreement with the mean calculated value of $d_{(100)}$ for ${}^{14} L$.

Approximate CaFe_2O_4 or galenobismutite homologues

The relationship between the structures of cosalite and galenobismutite and the structures typical of the lillianite series has been discussed by Makovicky (1977). He pointed out that cosalite fulfills the chemical requirements of the ${}^3 L$ member of the lillianite homologous series $\text{Pb}_{N-1}\text{Bi}_2\text{S}_{N+2}$ in the same way that galenobismutite PbBi_2S_4 corresponds with ${}^2 L$. However, although cosalite and galenobismutite both incorporate large units of the polyhedra comprising the lillianite structure (namely, trigonally prismatic coordinated lead atoms with adjacent BiS_6 pyramids and PbS_6 octahedra), the need to accommodate the long Bi-S interactions (lone pairs) of the more abundant Bi atoms, and other coordination properties of Pb and Bi discussed by Makovicky, leads instead to the formation of two new structure-types.

Weibullite forms in the chemical series (Fig. 4):

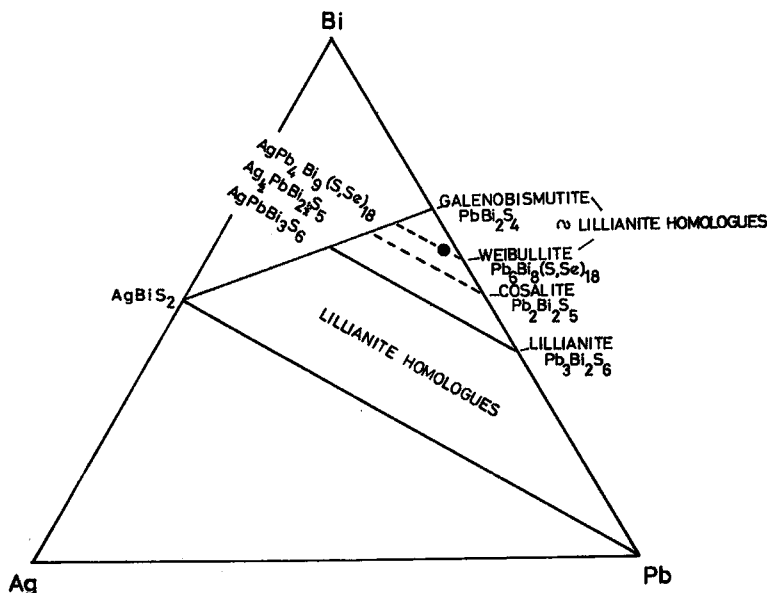


FIG. 4. The compositional plot Ag-Bi-Pb showing the field PbBi_2S_4 - AgBiS_2 - PbS and the relationship of weibullite (solid circle) to members of the lillianite homologous series. Unsubstituted and fully substituted end-members for weibullite, cosalite and lillianite are depicted.

	N	Mineral	End members
	2	galenobismutite	PbBi_2S_4
	$2\frac{1}{2}$	weibullite	$\text{Pb}_{1\frac{1}{2}}\text{Bi}_2(\text{S,Se})_{4\frac{1}{2}}$
	3	cosalite	$\text{Pb}_3\text{Bi}_2\text{S}_5$
lillianite homologues	4	lillianite	$\text{AgPbBi}_3\text{S}_6$
	5		$\text{Ag}_{1\frac{1}{2}}\text{PbBi}_{3\frac{1}{2}}\text{S}_7$
	<i>etc.</i>		

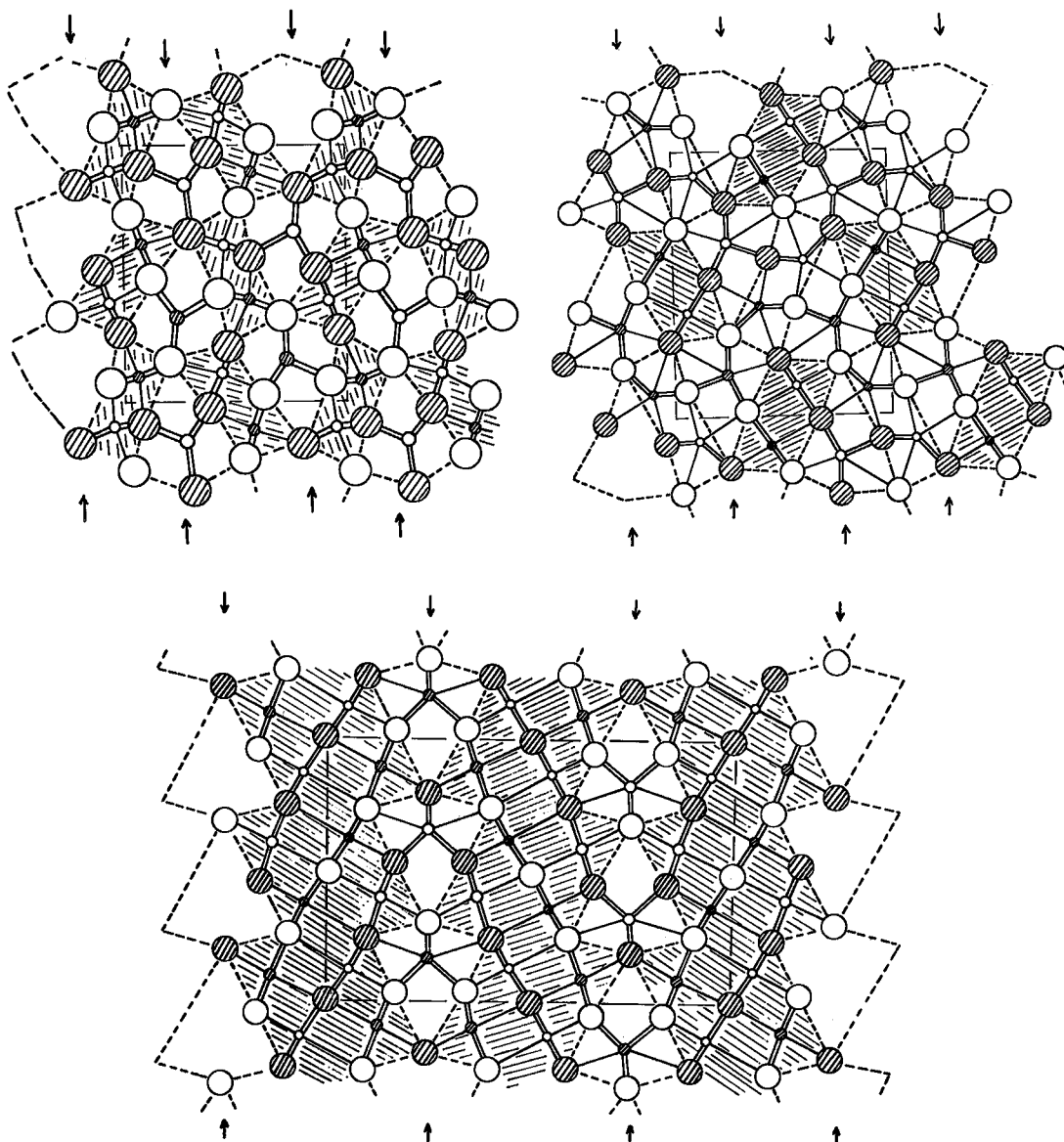


FIG. 5. The crystal structures of (a) calcium ferrite CaFe_2O_4 , (b) galenobismutite PbBi_2S_4 and (c) lillianite $\text{Pb}_3\text{Bi}_2\text{S}_5$, projected onto (010). Calcium ferrite and galenobismutite both have structural arrangements that are closely related to the linkage patterns in lillianite homologues. Weibullite (Fig. 3) is a higher CaFe_2O_4 or galenobismutite homologue; compare the position of trigonal prisms, glide planes and reflection planes.

Weibullite occupies the position intermediate between galenobismutite and cosalite and, similarly to them, does not represent a full homologue of lillianite. Instead, a close relationship exists between calcium ferrite (CaFe_2O_4) and the two lead-bismuth sulfosalts, galenobismutite and weibullite. In all three phases, the mirror plane characteristic of the lillianite series is replaced by a glide; the symmetrical trigonal prism in lillianite is replaced by an asymmetrical one, and two kinds of structural blocks occur in the structure. The relationship between the structures of the (approximate) CaFe_2O_4 or galenobismutite homologues thus formed and those of the lillianite series is illustrated in Figure 5. The calcium ferrite structure-type (CaFe_2O_4) and galenobismutite (PbBi_2S_4) are seen to be slightly different forms of an $\sim {}^2L$, both with (1 x 2) blocks on either side of the glides. Weibullite is clearly seen to be a progression from galenobismutite, which contains two differently sized blocks (7 x 2 and 6 x 2).

Whereas the structural trend from galenobismutite to weibullite is not sustained with the structure of cosalite, the formation of other phases intermediate to galenobismutite and weibullite (for example), which represent CaFe_2O_4 or galenobismutite homologues, will depend critically on two factors: (1) a structural balance between the lengths of a regular galena block and a deformed galena block which occur in galenobismutite and weibullite (*cf.*, also vernier structures, Hyde *et al.* 1974); (2) the requirement of attendant chemical compositions that conform with balanced charges.

Possible compositions of these intermediate phases may be derived from a consideration of the recent description and discussion of the cannizzarite structure by Matzat (1979). Two different statistical substructures of cannizzarite were determined by Matzat (1972). The composition of *A* was $(\text{Pb,Bi})_2\text{S}_2$ (*i.e.*, Me_2S_2); that of *B* was $(\text{Pb,Bi})_4\text{S}_6$ (*i.e.*, Me_4S_6). The cell dimensions of the sublattices are (*A*): a 4.31, b 4.09, c 15.48 Å, β 98.56° and (*B*): a 7.03, b 4.09, c 15.46 Å, β 98.00°, values which are very close to those originally derived by Graham *et al.* (1953). The structure of cannizzarite as determined by Matzat consists of two sets of alternating layers. One is a double octahedral layer (*B*) similar to the octahedral block in weibullite but which extends continuously, without disruption, in cannizzarite. The other, (*A*), a double layer of metal atoms with irregular coordinations, is similar to the deformed galena block in weibullite. Weibullite is composed of the critically sized segments of the cannizzarite

structure (those sandwiched between the glide planes) which were discussed above. The compositions of other possible (approximate) CaFe_2O_4 or galenobismutite homologues may be predicted from matches of the multiples of the *a* dimensions of the two cannizzarite subcells which may comprise such segments [that is, common multiples of $a_A = 4.13$ and $a_B = 7.03$ Å ($a_A/a_B \sim 1.7$)]. Weibullite itself results from the approximation $6A \sim 3\frac{1}{2}B$ and its composition is derived thus: $6A$ subcells + $3\frac{1}{2}B$ subcells + prism = $\text{Me}_{12}\text{S}_{12} + \text{Me}_{14}\text{S}_{21} + \text{Me}_2\text{S}_3 = \text{Me}_{28}\text{S}_{36} = \text{Pb}_{12}\text{Bi}_{16}\text{S}_{36}$. Other matches will result in the formation of structures that are built on the same principle as galenobismutite and weibullite, with suitably balanced layer segments between the glide planes.

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