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The crystal structure of, and the bismuth-copper distribution in synthetic cuprobismuthite

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Auszug

Die Kristallstruktur von synthetischem Cuprobismuthit wurde mittels dreidimensionaler Röntgendaten bestimmt. Die Raumgruppe ist $C2/m$ mit $a = 17{,}520(1)$, $b = 3{,}926(3)$, $c = 15{,}261(1)$ Å und $\beta = 100{,}18(1)°$. Die sich aus der Kristallstrukturanalyse ergebende chemische Formel kann als $(Cu_x, Bi_{\frac{1}{2}(1-x)})(Cu_y, Bi_{1-y})Cu_{xy}$, $Cu_2Bi_2S_6$ [$x = 0{,}32$, $y = 0{,}20$], $Z = 4$ dargestellt werden. Least-squares-Verfeinerungen mit anisotropen Temperaturfaktoren ergaben einen R-Wert von 0,049 für die 997 beobachteten Reflexe (0,054 für alle 1109 Reflexe).

Alle Atome liegen in den Spiegelebenen der Raumgruppe bei $y = 0$ und $\frac{1}{2}$. Die Struktur entspricht wesentlich einer Schicht von Hodrushit, (Pb ?, Ag ?, Fe, Bi) $Cu_4Bi_5S_{11}$. Zwei Bi-Lagen mit oktaedrischer Koordination gegenüber Schwefel sind teilweise durch Kupfer besetzt. Diese Substitutionen können durch die Valenzregel befriedigend erklärt werden. Die vorliegenden Ergebnisse scheinen nicht darauf hinzuweisen, daß Cuprobismuthit und Emplektit dimorphe Formen sind.

Abstract

The crystal structure of synthetic cuprobismuthite has been determined using three-dimensional x-ray diffraction data. The space group is $C2/m$ with $a = 17.520(1)$, $b = 3.926(3)$, $c = 15.261(1)$ Å and $\beta = 100.18(1)°$. The chemical formula derived from the crystal structure analysis is represented as $(Cu_x, Bi_{\frac{1}{2}(1-x)})(Cu_y, Bi_{1-y})Cu_{xy}$, $Cu_2Bi_2S_6$ ($x = 0.32$, $y = 0.20$), $Z = 4$. Least-squares refinement with anisotropic temperature factors resulted in a conven-

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tional R index of 0.049 for the observed 997 reflections (0.054 for all the 1109 reflections).

All atoms lie on mirror planes of the space group at $y = 0$ and $\frac{1}{2}$. The structure corresponds essentially to one layer in hodrushite, (Pb ?, Ag ?, Fe, Bi) $Cu_4Bi_5S_{11}$. Two bismuth sites in octahedral coordination with sulfur are partially substituted by copper atoms. These substitutions can be reasonably explained by the valence rule. The present results do not seem to indicate that cuprobismuthite is dimorphous with emplectite.

Introduction and brief summary of previous studies

The minerals of the system copper—bismuth—sulfur, which have been structurally investigated are wittichenite, $3Cu_2S \cdot Bi_2S_3$ (Matzat, 1972; Kocman and Nuffield, 1973) and emplectite, $Cu_2S \cdot Bi_2S_3$ (Hofmann, 1933; Kupčík, 1965; Portheine and Nowacki, 1975). Moreover, the validity of cuprobismuthite as a distinct species has been established by some workers.

Hillebrand (1884) reported cuprobismuthite from the Missouri mine, Halls Valley, Park County, Colorado as a probable new mineral and proposed the formula $3(Cu,Ag)_2S \cdot 4Bi_2S_3$. His data were listed in Dana's System of mineralogy (Dana, 1892). Later two mineralogists, Short (1931) and Palache (1940), much questioned the validity of this mineral based on studies of the specimen from the type locality. Nuffield (1952), however, reexamined the type specimen of cuprobismuthite which had been studied by Palache, by x-ray diffraction techniques. He found a crystal which gave a new diffraction pattern and confirmed that the crystal had a monoclinic cell with space group $C2/m$. Although his attempts to determine the exact composition of cuprobismuthite were not successful, he could synthesize a nearly homogeneous phase with proportion of Cu/Bi $\sim$ 1 whose x-ray powder pattern was identical with that of the natural cuprobismuthite specimen. In addition, he could measure the density of his product. The value was almost identical with that of emplectite. After all, he mentioned that it was not unreasonable to suggest that the chemical formula was $Cu_2S \cdot Bi_2S_3$ and that cuprobismuthite was therefore dimorphous with emplectite, from the intimate relations of the unit cell dimensions, cell volumes, densities and chemical composition between them. The final proof of the composition of cuprobismuthite was, however, left as a subject for future studies.

Recently some experimental investigations on the phase relations of Cu_2S–Bi_2S_3 system have been made. Godovikov and Fedorova (1969) analysed emplectite thermographically and obtained the result

that the chemical formula for cuprobismuthite was represented approximately as $3Cu_2S \cdot 4Bi_2S_3$ or $Cu_6Bi_8S_{15}$ which agreed with the formula proposed by HILLEBRAND (1884). GODOVIKOV and PTITSIN (1969), on the other hand, suggested on the basis of their synthetic studies that the formula for cuprobismuthite was close to $Cu_{10}Bi_{12}S_{23}$. Both formulae proposed by SUGAKI and SHIMA (1970, 1972), $Cu_{24}Bi_{26}S_{51}$, and by BUHLMANN (1971) were also deficient in copper content as compared with emplectite. TAYLOR, RADTKE and CHRIST (1973) reported similar data on the composition of cuprobismuthite from Tunnel Extension Number Two Mine, Ohio mining district, Utah. From the results of their electron microprobe analyses they concluded that the chemical formula for unsubstituted cuprobismuthite is $5Cu_2S \cdot 6Bi_2S_3$ or $Cu_{10}Bi_{12}S_{23}$ which agreed closely with the experimental results of GODOVIKOV and PTITSIN (1969). In spite of the excellent agreement between the calculated density and measured one of their specimens, a unit-cell content of 23 sulfur atoms was not compatible with the requirements of the possible space groups, $C2/m$, Cm and $C2$, as indicated by them. On the other hand, CHEN and CHANG (1974) described that cuprobismuthite had a solid solution ranging from 52 to 47 mol % Cu_2S and 51 to 48 mol % Cu_2S along the join Cu_2S—Bi_2S_3 at 454° and 300 °C, respectively. Their results suggest that cuprobismuthite is stable at higher temperatures and dimorphous with emplectite.

The stability range of cuprobismuthite varies according to authors. For example, the lower temperature limit of stability is 383 °C according tho GODOVIKOV and FEDOROVA (1969), but 290 °C according to BUHLMANN (1971).

The crystal structur eof cuprobismuthite was presumed from that of hodrushite, $(Pb?, Ag?, Fe, Bi)Cu_4Bi_5S_{11}$ (KUPČÍK and MAKOVICKÝ, 1968; KODĚRA, KUPČÍK and MAKOVICKÝ, 1970; MAKOVICKÝ and MACLEAN, 1972). The structure of hodrushite consists of two distinct layers, one of which has the unit-cell dimensions of cuprobismuthite. KODĚRA *et al.* (1970) suggested that the layer of hodrushite must correspond to the structure of cuprobismuthite. Present study confirmed the suggestion to be correct in principle. The proposed structure using powder data (MARIOLACOS, KUPČÍK, OHMASA and MIEHE, 1975) was also essentially correct.

The present structure determination was undertaken in order to elucidate the chemical composition and the relationship with emplectite and hodrushite.

Experimental

Synthetic crystals of cuprobismuthite were kindly supplied by Dr. A. A. GODOVIKOV for the present investigation. A zero-level back-reflection Weissenberg photograph about [010] (camera radius 57.3mm) with copper radiation, taken for precise determination of the unit-cell dimensions, was calibrated by the superposition of a powder pattern of silicon. Least-squares methods (T. ITO, unpublished) using 21 measured $h0l$ reflections with θ between 63° and 79° gave the following monoclinic cell dimensions (a, c and β). The b axis was determined with the aid of a Weissenberg diffractometer:

$a = 17.520(1)$, $b = 3.926(3)$, $c = 15.261(1)$ Å, $\beta = 101.18(1)°$. Systematic absences of hkl for $h+k$ odd and $00l$ for l odd indicate that the possible space groups are $C2/m$, Cm and $C2$. Crystals are usually of a slender thin prismatic shape. The longest dimension is along [010], and (001) is the most developed face as described by NUFFIELD (1952). One crystal with dimensions $0.056 \times 0.18 \times 0.020$mm was selected and mounted for rotation about the [010] axis. A total of 1109 independent reflections were collected on a Supper-Pace single-crystal automatic diffractometer by ω-scan methods using Ni-filtered Cu$K\alpha$ radiation. The intensities were corrected for Lorentz, polarization and absorption effects using the programme of ACACA (WUENSCH and PREWITT, 1965), but not for extinction effect. Based on the counting statistics, a weight was assigned to each reflection.

Table 1. *Crystal data for cuprobismuthite*

(Estimated standard deviations are given in parentheses)

composition $Cu_{2.58}Bi_{3.14}S_6$

space group $C2/m$, $Z = 4$, $F(000) = 1657$

$\mu(CuK\alpha) = 1240$ cm^{-1}

	Missouri mine (NUFFIELD, 1952)	Tunnel Extension Number Two mine (TAYLOR *et al.*, 1973)	present work
a	17.65 Å	17.628 ± 0.01 Å	17.520(1) Å
b	3.93	3.911 ± 0.002	3.926(3)
c	15.24	15.190 ± 0.01	15.261(1)
β	100.5°	100°16′	100.18(1)°
ϱ_o		6.36 g · cm^{-3}	
ϱ_c			6.53 g · cm^{-3}
V	1039 Å^3	1027 Å^3	1031 Å^3

Reflections with I less than $2.33\sigma(I)$ were considered to be unobserved. The final data list contained 102 unobserved reflections. Some crystal data are given in Table 1.

Structure determination and refinement

The statistics of the normalized structure amplitudes, Table 2, suggests the presence of a center of symmetry. Therefore the centric space group $C2/m$ was adopetd as the correct one. The intensity distribution of $h0l$ reflections is similar to those of $h2l$ and $h4l$ reflections. This characteristic applies also to the relation between $h1l$ and $h3l$ reflections. These phenomena suggest that almost all atoms should be on planes perpendicular to the b axis with $y = 0$ and $y = \frac{1}{2}$.

The Patterson map was calculated and solved. The assumption that cuprobismuthite might have a part of the structure of hodrushite was very usuful for the solution. The approximate coordinates of copper and bismuth atoms exept Cu(3), Cu(4) and Cu(5) were thus located. A trial of symbolic addition procedures provided us the same result. A structure-factor and a three-dimensional Fourier synthesis were then calculated with the coordinates of the metal atoms, assuming that all these sites were fully occupied. A block-diagonal least-squares programme and a Fourier programme written by Dr. T. Ito were used. The sulfur atoms were found from the Fourier map. A few cycles of three-dimentional least-squares refinement for positional parameters and isotropic temperature factors reduced the R index to 13%. At this stage, the deficiencies of Bi(1) and Bi(2) sites and an additional peak near Bi(1) site were found on a Fourier map. This peak was assigned to Cu(3), judging from the coordination

Table 2. *Distribution of E values*

	cuprobismuthite	theoretical*	
		centric	acentric
$<E^2>$	1.000	1.000	1.000
$<\|E^2-1\|>$	0.941	0.968	0.736
$<\|E\|>$	0.816	0.798	0.886
$\|E\| > 1.0$	32.0%	32.0%	36.8%
$\|E\| > 2.0$	4.2%	5.0%	1.8%
$\|E\| > 3.0$	0.1%	0.3%	0.01%

* G. H. Stout and L. H. Jensen (1968): *X-ray structure determination*, p. 321. Macmillan, New York.

Table 3. *Atomic coordinates and site occupancies*

(Estimated standard deviations are given in parentheses in terms of the last digit)

Atom	x	y	z	Site occupancy*
Cu(1)	0.1598(4)	0	0.1432(3)	
Cu(2)	0.0868(2)	0	0.4772(3)	
Cu(3)	0.0460(9)	0.5	0.0857(10)	0.34(2)
Cu(4)	0.2962(14)	0.5	0.1532(14)	0.20(2)
Cu(5)	0.378(6)	0	0.070(4)	0.07(2)
Bi(1)	0	0.5	0	0.679(8)
Bi(2)	0.33342(7)	0.5	0.09025(7)	0.803(6)
Bi(3)	0.49227(5)	0	0.28075(5)	
Bi(4)	0.24447(5)	0.5	0.37089(5)	
S(1)	0.1639(3)	0.5	0.0610(3)	
S(2)	0.4873(4)	0.5	0.1245(3)	
S(3)	0.3404(3)	0	0.2175(3)	
S(4)	0.1528(3)	0	0.2887(3)	
S(5)	0.4649(3)	0.5	0.3867(3)	
S(6)	0.1612(3)	0.5	0.4931(3)	

* All the occupancies were refined independently. Therefore the sum of Cu(3) and Bi(1), and that of Cu(4) and Bi(2) showed a slight deviation from 1.

Table 4. *Thermal parameters in the expression*

$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$; $\beta_{12} = 0$, $\beta_{23} = 0$

(Estimated standard deviations are given in parentheses in terms of the last digit)

Atom	β_{11}	β_{22}	β_{33}	β_{13}
Cu(1)	0.0055(3)	0.038(3)	0.0024(1)	0.0014(2)
Cu(2)	17(1)	33(3)	32(1)	4(1)
Cu(3)	26(6)	44(11)	45(7)	6(5)
Cu(4)	24(8)	30(16)	35(9)	−4(7)
Cu(5)	0.007(5)	−0.01(3)	0.005(3)	0.002(3)
Bi(1)	0.0017(1)	0.038(2)	0.0017(1)	0.0000(1)
Bi(2)	12(1)	33(1)	21(1)	1(1)
Bi(3)	14(1)	20(1)	17(1)	3(1)
Bi(4)	11(1)	19(1)	15(1)	3(1)
S(1)	19(2)	15(3)	20(2)	5(2)
S(2)	20(2)	22(4)	19(2)	5(1)
S(3)	12(2)	19(3)	20(2)	3(1)
S(4)	12(2)	14(3)	15(2)	3(1)
S(5)	14(2)	25(3)	13(1)	2(1)
S(6)	12(2)	27(4)	15(2)	2(1)

Table 5. *Interatomic distances in cuprobismuthite*
(Estimated standard deviations are given in parentheses in terms of the last digit)

Cu(1)—S(1)	2.338(4) Å	2×	Bi(3)—S(3)	2.649(6) Å	
—S(4)	2.246(6)		—S(5)	2.645(3)	2×
—S(2″)	2.981(9)		—S(2)	3.077(4)	2×
—S(3)	3.147(8)		—S(4″)	3.413(4)	2×
Cu(2)—S(5″)	2.308(7) Å		Bi(4)—S(4)	2.688(4) Å	2×
—S(5‴)	2.422(6)		—S(6)	2.581(5)	
—S(6)	2.342(4)	2×	—S(6″)	3.092(4)	2×
Cu(3)—S(1)	2.17(2) Å		—S(3)	3.699(4)	2×
—S(2″)	2.35(1)	2×	Cu(1)—Cu(3)	2.82(1) Å	2×
Cu(4)—S(1)	2.47(2) Å		—Cu(4)	3.07(2)	2×
—S(3)	2.26(1)	2×	Cu(3)—Cu(3′)	2.79(3)	
Cu(5)—S(1″)	2.00(7) Å		Cu(4)—Cu(5)	2.87(6)	2×
—S(2)	2.75(7)	2×	Cu(5)—Cu(3″)	2.91(10)	
—S(3)	2.46(7)		—Cu(3‴)	2.95(7)	
Bi(1)—S(1)	2.842(6) Å	2×			
—S(2″)	2.771(4)	4×			
Bi(2)—S(2)	2.644(6) Å				
—S(3)	2.747(4)	2×			
—S(1)	2.916(6)				
—S(1″)	3.037(4)	2×			

and the interatomic distances. The site occupancies of Bi(1) and Bi(2), which were calculated with a programme written by Dr. T. Ito (unpublished), converged to 0.68 and 0.80 respectively. The occupancy of Cu(3) site was assigned to [1 minus occupancy of Bi(1)], *i.e.* 0.32, because the Cu(3) and Bi(1) atoms were presumed to be statistically distributed as observed in the structure of $Cu_{2+x}Bi_{6-x}S_9$ ($x = 1.21$) (Ohmasa, 1973). A few additional cycles of least-squares refinement reduced R to 9% (Ozawa and Nowacki, 1975). The subsequent refinement with anisotropic temperature factors using the programme ORFLS (Busing, Martin and Levy, 1962) and the associated difference Fourier synthesis using the programme GSFFR written by Dr. M. Ohmasa revealed the existence of Cu(4) and Cu(5) sites. At the final stage, all the site occupancies of Cu(3), Cu(4), Cu(5), Bi(1) and Bi(2) atoms were independently refined, but they converged to very

Table 6. *Interatomic angles in cuprobismuthite*
(Estimated standard deviations are given in parentheses in terms of the last digit)

S(1)—Cu(1)—S(1′)		114.2(3)°	S(3)—Bi(3)—S(5)		86.3(1)°
S(1)	S(4)	122.9(1)	S(5)	S(5′)	95.8(2)
S(1)	S(2″)	94.8(2)	S(3)	S(2)	80.9(1)
S(1)	S(3)	93.4(2)	S(5)	S(4″)	78.3(1)
S(4)	S(2″)	81.2(2)	S(5)	S(4‴)	130.6(1)
S(4)	S(3)	83.6(2)	S(5)	S(2)	91.1(1)
			S(2)	S(2′)	79.3(1)
S(5″)—Cu(2)—S(5‴)		93.2(2)°	S(2)	S(4″)	63.9(1)
S(5″)	S(6)	119.6(1)	S(2)	S(4‴)	107.1(1)
S(5‴)	S(6)	101.8(2)	S(4″)	S(4‴)	70.2(1)
S(6)	S(6′)	113.9(3)			
			S(4)—Bi(4)—S(4′)		93.8(2)°
S(1)—Cu(3)—S(2″)		121.5(3)°	S(4)	S(6)	88.1(1)
S(2″)	S(2‴)	113.7(7)	S(4)	S(3)	67.7(1)
			S(4)	S(3′)	113.3(1)
S(1)—Cu(4)—S(3)		116.8(6)°	S(4)	S(6″)	92.5(1)
S(3)	S(3′)	120.4(9)	S(6)	S(6″)	79.5(1)
			S(3)	S(3′)	64.1(1)
S(1″)—Cu(5)—S(3)		144(5)°	S(3)	S(6″)	80.7(1)
S(1″)	S(2)	114(2)	S(3)	S(6‴)	120.8(1)
S(3)	S(2)	91(2)	S(6″)	S(6‴)	78.8(1)
S(2)	S(2′)	91(3)			
S(1)—Bi(1)—S(2″)		89.2(1)°			
S(1)	S(2⁗)	90.8(1)			
S(2″)	S(2‴)	90.2(2)			
S(2″)	S(2⁗)	89.8(2)			
S(2)—Bi(2)—S(3)		87.5(1)°			
S(3)	S(3′)	91.2(2)			
S(2)	S(1″)	89.1(1)			
S(3)	S(1)	90.7(1)			
S(3)	S(1″)	94.0(1)			
S(1)	S(1″)	92.8(1)			
S(1″)	S(1‴)	80.5(1)			

reasonable values. The final R index was 0.049 for the observed 997 reflections (0.054 for all the 1109 reflections). Neutral-atom form factors given in *International tables*, Vol. 3, p. 202, 210 and 212 (1968) were used. The effect of anomalous dispersion was considered (CROMER, 1965).

The final atomic coordinates and the anisotropic temperature factors are listed in Tables 3 and 4, respectively. Interatomic distances

Table 7. *Observed and calculated structure amplitudes*

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
2 0 0	14*	10	-6 0 5	458	478	-2 0 10	146	147	-4 0 17	28	21	-19 1 5	55	50	-5 1 10	52	54			
4	397	392	-4	327	342	0	215	221	-2	189	197	-17	149	153	-3	387	407			
6	510	502	-2	233	238	2	161	163	0	65	63	-15	155	154	-1	183	195			
8	383	366	0	333	323	4	34	28	2	55	56	-13	20*	15	1	312	323			
10	137	137	2	145	146	6	229	222	4	53	56	-11	42	1	3	41	34			
12	619	645	4	67	73	8	105	110	-10 0 18	44	47	-9	349	332	5	78	83			
14	56	34	6	384	392	10	20*	37	-8	137	146	-7	197	196	7	18*	9			
16	76	71	8	173	170	12	16*	8	-6	113	119	-5	380	394	9	260	252			
18	119	119	10	56	46	14	64	58	-4	47	49	-3	219	232	11	186	176			
20	137	142	12	194	188	-18 0 11	44	24	-2	204	218	-1	104	109	13	102	100			
-20 0 1	225	236	14	23*	6	-16	138	134	0	55	55	1	150	136	15	31	30			
-18	162	163	16	49	52	-14	23*	44	3 1 0	477	463	3	444	460	-17 1 11	143	134			
-16	157	164	18	63	60	-12	224	197	5	318	284	5	287	293	-15	58	39			
-14	20*	13	-20 0 6	107	99	-10	46	45	7	170	167	7	215	215	-13	118	104			
-12	181	183	-18	112	108	-8	117	114	9	414	406	9	23*	11	-11	23*	9			
-10	52	50	-16	68	51	-6	35	20	11	43	38	11	23*	23	-9	450	435			
-8	383	372	-14	209	186	-4	300	308	13	171	176	13	241	239	-7	23*	8			
-6	429	420	-12	22*	17	-2	19*	23	15	159	161	15	151	155	-5	260	266			
-4	255	247	-10	254	237	0	374	392	17	181	195	17	182	188	-3	232	241			
-2	52	49	-8	86	76	2	17*	5	19			16*	24	-19 1 6	51	44	-1	173	177	
0	86*	42	-6	86	85	4	306	311	-19 1 1	76	86	-17	223	234	1	124	118			
2	141	141	-4	22*	32	6	121	122	-17	122	127	-15	134	131	3	423	440			
4	166	160	-2	95	91	8	333	324	-15	78	82	-13	265	254	5	47	44			
6	579	611	0	110	111	10	44	39	-13	19*	20	-11	93	85	7	122	116			
8	19*	24	2	105	79	12	315	308	-11	157	162	-9	130	127	9	232	228			
10	93	86	4	75	76	14	17	18	-9	172	162	-7	77	74	11	68	63			
12	215	211	6	332	332	-18 0 12	102	98	-7	257	245	-5	347	367	13	56	58			
14	168	165	8	90	90	-16	166	155	-5	15	21	-3	253	260	-17 1 12	159	159			
16	39	35	10	74	68	-14	104	99	-3	45	35	-1	301	290	-15	28	22			
18	237	248	12	110	101	-12	168	152	-1	191	208	1	275	266	-13	84	70			
20	91	97	14	55	54	-10	157	140	1	158	164	3	23*	17	-11	215	187			
-20 0 2	48	53	16	56	58	-8	379	362	3	488	512	5	139	164	-9	78	49			
-18	58	57	18	269	264	-6	169	163	5	369	363	7	231	226	-7	95	87			
-16	47	48	-20 0 7	139	143	-4	214	211	7	73	56	9	340	335	-5	139	140			
-14	264	265	-18	61	59	-2	107	104	9	67	56	11	106	105	-3	44	38			
-12	113	107	-16	118	111	0	179	167	11	207	195	13	131	126	-1	69	73			
-10	18*	3	-14	466	464	2	143	138	13	158	161	15	72	75	1	139	139			
-8	180	167	-12	22*	21	4	276	279	15	314	341	17	91	84	3	107	105			
-6	139	123	-10	326	306	6	128	127	17	80	79	-19 1 7	120	130	5	59	51			
-4	31	22	-8	394	364	8	132	133	19	88	96	-17	88	84	7	54	49			
-2	263	270	-6	396	381	10	14*	11	-19 1 2	177	195	-15	228	235	9	35	26			
0	49*	7	-4	168	158	12	12*	8	-17	165	170	-13	111	108	11	85	84			
2	20*	3	-2	733	748	-18 0 13	16	11	-15	183	174	-11	469	450	-17 1 13	89	90			
4	421	447	0	47	42	-16	159	159	-13	118	98	-9	127	113	-15	169	164			
6	136	130	2	328	322	-14	159	150	-11	65	51	-7	209	205	-13	17*	14			
8	246	240	4	237	229	-12	197	180	-9	333	309	-5	97	89	-11	19*	15			
10	166	158	6	331	323	-10	67	54	-7	332	307	-3	394	406	-9	39	47			
12	82	78	8	26*	5	-8	79	77	-5	438	425	-1	44	24	-7	207	215			
14	62	55	10	491	481	-6	18*	24	-3	124	120	1	445	455	-5	289	297			
16	206	217	12	142	127	-4	173	175	-1	294	325	3	316	293	-3	172	172			
18	61	60	14	184	180	-2	212	216	1	95	96	5	265	255	-1	84	88			
20	61	64	16	92	88	0	135	128	3	396	433	7	159	156	1	65	70			
-20 0 3	81	90	18	100	103	2	37	33	5	239	231	9	253	244	3	93	92			
-18	79	82	-20 0 8	148	151	4	172	167	7	424	415	11	125	121	5	175	173			
-16	302	312	-18	188	196	6	60	57	9	104	89	13	208	190	7	281	284			
-14	50	40	-16	37	31	8	29	23	11	255	255	15	94	82	9	75	72			
-12	154	145	-14	67	55	10	164	159	13	72	79	17	66	65	11	69	67			
-10	163	162	-12	76	70	12	51	52	15	176	185	-19 1 8	149	148	-15 1 14	49	44			
-8	288	277	-10	324	311	-16 0 14	118	128	17	76	78	-17	88	96	-13	284	278			
-6	18*	18	-8	447	446	-14	75	75	19	181	189	-15	62	69	-11	15*	10			
-4	570	684	-6	259	259	-12	208	206	-19 1 3	69	71	-13	47	58	-9	227	227			
-2	21*	12	-4	26*	15	-10	206	203	-17	152	148	-11	85	72	-7	70	68			
0	259	223	-2	105	87	-8	97	95	-15	70	70	-9	66	73	-5	272	281			
2	114	120	0	348	362	-6	245	257	-13	482	505	-7	176	175	-3	76	72			
4	359	373	2	200	201	-4	218	230	-11	19*	10	-5	202	192	-1	372	387			
6	83	88	4	587	584	-2	71	67	-9	536	545	-3	24*	41	1	14*	4			
8	497	487	6	27*	12	0	279	284	-7	322	310	-1	199	202	3	238	237			
10	174	160	8	99	94	2	176	166	-5	242	245	1	187	185	5	61	60			
12	149	138	10	142	130	4	54	51	-3	69	76	3	49	47	7	157	157			
14	22*	52	12	285	261	6	128	128	-1	642	763	5	24*	19	9	24	16			
16	113	118	14	89	80	8	231	236	1	121	121	7	197	181	-15 1 15	20	15			
18	114	116	16	251	241	10	105	109	3	271	291	9	232	212	-13	66	69			
20	145	144	-20 0 9	90	80	-16 0 15	8*	3	5	194	197	11	96	81	-11	68	66			
-20 0 4	60	62	-18	102	102	-14	51	53	7	101	93	13	282	258	-9	142	143			
-18	47	48	-16	189	185	-12	102	104	9	55	38	15	14*	19	-7	131	130			
-16	46	45	-14	215	200	-10	190	195	11	345	332	-19 1 9	117	111	-5	34	39			
-14	219	215	-12	191	173	-8	64	69	13	105	105	-17	18*	35	-3	14*	8			
-12	122	117	-10	95	81	-6	107	107	15	21*	40	-15	85	79	-1	14*	12			
-10	501	484	-8	139	136	-4	66	58	17	117	118	-13	114	108	1	107	103			
-8	57	41	-6	26*	9	-2	208	215	19	88	91	-11	107	96	3	42	23			
-6	278	276	-4	380	362	0	77	65	-19 1 4	191	199	-9	108	97	5	161	160			
-4	54	49	-2	184	183	2	251	254	-17	73	75	-7	360	362	7	73	69			
-2	404	447	0	271	277	4	79	75	-15	19*	9	-5	113	97	-13 1 16	28	25			
0	146	145	2	225	225	6	133	133	-13	205	194	-3	274	276	-11	11*	6			
2	549	641	4	52	51	8	40	37	-11	34	30	-1	102	113	-9	174	174			
4	90	89	6	22*	7	-14 0 16	153	169	-9	106	97	1	129	137	-7	12*	2			
6	278	293	8	220	200	-12	28	18	-7	535	530	3	135	137	-5	46	53			
8	112	103	10	121	108	-10	100	108	-5	244	249	5	409	400	-3	150	149			
10	344	338	12	55	48	-8	59	64	-3	107	106	7	110	90	-1	69	61			
12	95	93	14	143	143	-6	235	244	-1	577	629	9	262	236	1	11*	3			
14	405	424	16	48	47	-4	116	116	1	194	186	11	105	94	3	261	263			
16	21*	5	-20 0 10	136	132	-2	172	179	3	101	108	13	130	124	5	10*	6			
18	185	194	-18	151	151	0	41	41	5	498	544	15	64	66	-11 1 17	9*	10			
-20 0 5	33	34	-16	19*	38	2	62	61	7	349	356	-19 1 10	148	147	-9	103	101			
-18	295	296	-14	43	38	4	78	82	9	38	33	-17	104	96	-7	23	31			
-16	166	167	-12	299	273	6	164	172	11	443	442	-15	367	362	-5	184	186			
-14	232	232	-10	78	66	-12 0 17	23	26	13	41	35	-13	45	51	-3	115	114			
-12	152	144	-8	188	170	-10	162	170	15	117	127	-11	383	362	-1	174	177			
-10	193	178	-6	315	299	-8	101	101	17	173	176	-9	24*	22	1	40	34			
-8	59	47	-4	47	20	-6	48	47	19	168	166	-7	158	151	3	69	66			

Table 7. *(Continued)*

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
-7 1 18	201	197	14 2 4	328	350	8 2 9	189	167	3 3 0	283	269	-11 3 6	75	69	-5 3 13	211	212
-5	79	77	16	16*	2	10	93	85	5	196	179	-9	104	93	-3	115	116
-3	102	99	-18 2 5	241	254	12	47	46	7	100	108	-7	65	63	-1	74	72
-1	22	23	-16	131	135	14	114	119	9	256	261	-5	226	234	1	51	44
2 2 0	27	1	-14	191	199	-16 2 10	34	34	11	34	33	-3	180	181	3	81	82
4	316	308	-12	121	117	-14	31	31	13	125	132	-1	181	185	-5 3 14	209	211
6	370	356	-10	160	156	-12	249	229	15	97	103	1	178	177	-3	40	41
8	305	297	-8	37	37	-10	71	55	-15 3 1	64	71	3	22*	2	-1	269	274
10	112	111	-6	365	381	-8	147	133	-13	16*	15	5	136	125	2 4 0	13*	6
12	486	525	-4	230	241	-6	262	245	-11	118	116	7	152	142	4	200	184
14	19*	29	-2	191	192	-4	18*	21	-9	101	92	9	259	241	6	197	193
16	53	63	0	234	231	-2	112	115	-7	163	157	11	75	70	8	176	186
18	95	97	2	117	121	0	173	177	-5	16*	15	13	102	100	10	65	72
-18 2 1	123	134	4	44	56	2	131	133	-3	13*	8	-15 3 7	172	176	-10 4 1	31	31
-16	132	143	6	306	313	4	17*	12	1	111	119	-13	85	81	-8	180	181
-14	19*	9	8	131	123	6	187	182	3	292	293	-11	309	304	-6	158	157
-12	149	155	10	37	42	8	90	88	5	224	218	-9	90	71	-4	128	122
-10	40	44	12	160	154	10	30	29	7	57	54	-7	153	142	-2	13*	22
-8	302	298	14	42	8	12	12*	1	9	19*	19	-5	55	55	2	67	68
-6	309	309	16	42	42	-16 2 11	119	114	11	133	132	-3	200	277	4	86	78
-4	192	188	-18 2 6	92	95	-14	36	39	13	113	116	-1	17*	14	6	244	239
-2	36	34	-16	17	42	-12	177	162	15	217	240	1	285	292	8	15*	5
2	104	113	-14	154	153	-10	52	38	-15 3 2	117	122	3	195	189	10	45	55
4	141	132	-12	59	12	-8	112	99	-13	71	74	5	189	177	-10 4 2	14*	18
6	451	448	-10	194	185	-6	19*	14	-11	18*	30	7	102	98	-8	91	85
8	19*	15	-8	61	56	-4	239	252	-9	211	214	9	202	177	-6	66	63
10	73	75	-6	68	68	-2	16*	14	-7	189	190	11	92	85	-4	15*	20
12	163	171	-4	57	26	0	301	322	-5	301	294	-13 3 8	44	40	-2	120	130
14	131	138	-2	90	62	2	16*	2	-3	69	70	-11	35	37	0	35	34
16	17*	29	0	82	91	4	254	262	-1	192	210	-9	61	51	2	14*	16
18	195	207	2	65	49	6	99	98	1	56	55	-7	119	113	4	196	191
-18 2 2	49	51	4	62	58	8	269	274	3	255	280	-5	113	111	6	60	65
-16	35	40	6	272	269	10	33	31	5	144	140	-3	18*	19	8	115	117
-14	216	222	8	68	71	12	252	263	7	292	286	-1	125	129	-10 4 3	58	60
-12	82	82	10	79	63	-16 2 12	133	135	9	59	51	1	113	116	-8	123	130
-10	17*	7	12	97	88	-14	83	81	11	172	182	3	40	37	-6	16*	7
-8	141	136	14	67	53	-12	146	136	13	49	51	5	18*	10	-4	255	261
-6	109	99	16	54	47	-10	125	116	15	140	146	7	116	109	-2	15*	15
-4	30	23	-18 2 7	54	50	-8	305	305	-15 3 3	53	54	9	156	145	0	126	125
-2	198	212	-16	95	92	-6	126	128	-13	323	349	11	65	57	2	38	35
0	28*	20	-14	378	385	-4	179	182	-11	19*	16	-13 3 9	77	72	4	161	160
2	27	6	-12	20*	16	-2	84	81	-9	366	369	-11	96	86	6	49	48
4	323	336	-10	275	256	0	146	151	-7	195	186	-9	69	62	8	221	217
6	103	100	-8	293	289	2	108	110	-5	158	160	-7	258	248	-10 4 4	198	203
8	199	190	-6	297	302	4	238	236	-3	41	44	-5	56	55	-8	39	26
10	134	128	-4	124	120	6	110	103	-1	405	448	-3	187	193	-6	151	142
12	82	75	-2	565	583	8	115	117	1	83	83	-1	69	68	-4	44	45
14	40	41	0	49	34	10	16	6	3	177	189	1	118	120	-2	187	200
16	178	183	2	267	266	-14 2 13	140	129	5	117	122	3	86	81	0	63	57
18	49	48	4	195	179	-12	161	151	7	52	56	5	289	282	2	261	257
-18 2 3	64	69	6	268	260	-10	58	49	9	21*	27	7	55	56	4	45	39
-16	241	256	8	23*	1	-8	55	60	11	221	225	9	183	182	6	173	167
-14	38	35	10	403	397	-6	37	27	13	79	83	-13 3 10	45	42	8	27	25
-12	125	125	12	120	108	-4	138	141	-15 3 4	14*	7	-11	298	261	-8 4 5	16*	22
-10	134	124	14	164	155	-2	176	183	-13	127	125	-9	19*	15	-6	247	234
-8	221	219	-18 2 8	160	172	0	100	101	-11	19*	25	-7	123	111	-4	113	114
-6	17*	19	-16	28	22	2	39	32	-9	70	61	-5	30	25	-2	120	117
-4	459	503	-14	72	53	4	141	139	-7	332	325	-3	265	281	0	121	122
-2	16*	11	-12	63	54	6	56	53	-5	141	147	-1	139	141	2	96	88
0	208	190	-10	269	258	8	11*	15	-3	62	71	1	214	218	4	30	33
2	84	86	-8	353	355	-12 2 14	174	176	-1	362	368	3	27	28	6	200	189
4	269	276	-6	211	215	-10	175	169	1	126	118	5	61	62	-8 4 6	16*	22
6	73	72	-4	23*	23	-8	82	81	3	85	89	7	12*	11	-6	37	40
8	386	383	-2	58	60	-6	207	214	5	318	334	9	177	176	-4	40	15
10	139	133	0	273	282	-4	186	191	7	236	232	-11 3 11	14*	10	-2	40	39
12	115	117	2	164	165	-2	54	55	9	34	27	-9	324	305	0	59	60
14	44	50	4	460	468	0	238	239	11	296	305	-7	15*	15	2	13*	16
16	95	100	6	23*	6	2	137	135	13	27	23	-5	187	195	4	32	27
18	103	103	8	98	84	4	45	44	-15 3 5	104	109	-3	162	167	6	179	165
-18 2 4	42	43	10	113	104	6	105	107	-13	16*	22	-1	119	120	-8 4 7	177	167
-16	52	45	12	238	220	-12 2 15	91	91	-11	19*	8	1	77	80	-6	185	179
-14	183	186	14	69	69	-10	166	165	-9	251	238	3	297	307	-4	74	68
-12	101	100	-18 2 9	86	86	-8	60	61	-7	116	114	5	21	24	-2	324	340
-10	383	377	-16	158	159	-6	94	92	-5	247	254	7	87	87	0	27	24
-8	43	38	-14	165	161	-4	50	44	-3	132	139	-11 3 12	131	131	2	168	170
-6	227	223	-12	158	150	-2	177	181	-1	100	94	-9	50	42	4	97	98
-4	33	32	-10	68	59	0	55	58	1	84	83	-7	69	68	-6 4 8	152	140
-2	314	341	-8	125	121	2	212	216	3	288	302	-5	93	95	-4	32	31
0	111	106	-6	24*	9	4	67	65	5	178	182	-3	12*	11	-2	12*	26
2	463	491	-4	299	292	-8 2 16	53	50	7	157	148	-1	44	40	0	160	159
4	63	65	-2	135	135	-6	206	210	9	49	16	1	97	96	2	102	103
6	235	246	0	220	230	-4	99	97	11	19*	8	3	73	69	-4 4 9	158	174
8	80	74	2	176	176	-2	157	159	13	171	167	5	47	45	-2	59	62
10	282	278	4	57	52	0	31	33	-15 3 6	95	97	-9 3 13	28	22	0	133	152
12	79	77	6	51	2	2	56	57	-13	178	176	-7	145	148			

and angles, Tables 5 and 6, were calculated with the programme ORFFE (BUSING, MARTIN and LEVY, 1964). A list of the final observed and calculated structure amplitudes is given in Table 7. The atomic arrangement projected along the *b* axis is shown in Fig. 1.

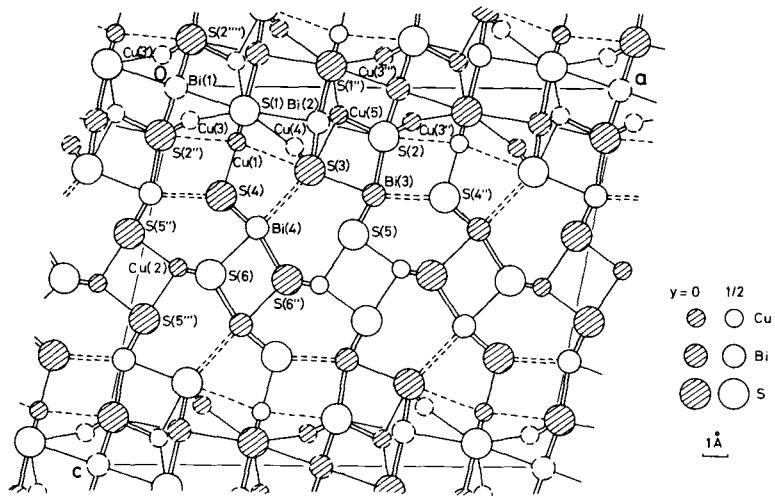

Fig. 1. The structure of cuprobismuthite projected along *b* axis. The broken circles indicate the statistically distributed atoms

Discussion of the structure and composition

There are four independent bismuth atom sites in the structure of cuprobismuthite. Bi(2) has a coordination of three plus three, forming two trigonal pyramids, together a distorted octahedron. Similar coordinations have been also found in the structures of hodrushite (Kupčík and Makovický, 1968), $Cu_4Bi_4S_9$ (Ozawa and Takéuchi, 1972), $CuBi_5S_8$ (Ohmasa and Nowacki, 1973), $Cu_{2+x}Bi_{6-x}S_9[x = 1.21]$ (Ohmasa, 1973) and cosalite (Srikrishnan and Nowacki, 1974). On the other hand, three sulfur atoms around Bi(3) form a trigonal pyramid; together with the two next neighbours they complete a square pyramid. The same applies to the coordination of sulfur atoms around Bi(4). The coordination of Bi(1), unusual in bismuth-bearing sulfosalts, has been found for Me(1) and Me(2) atoms in hodrushite and for Bi(1) in $CuBi_5S_8$. Each of these bismuth atoms lie on a center of symmetry. Instead of three sulfur neighbours, which approach usually within 2.5_5—2.8 Å to the associated bismuth atom, forming a trigonal pyramid with the bismuth, these above-mentioned bismuth atoms are coordinated to six sulfur atoms at fairy uniform distance of about 2.8 Å, so that the sulfur atoms may compose an approximately regular octahedron. Indeed the regularity is fairy strict, the bismuth-sulfur bond distances ranging from 2.77 to

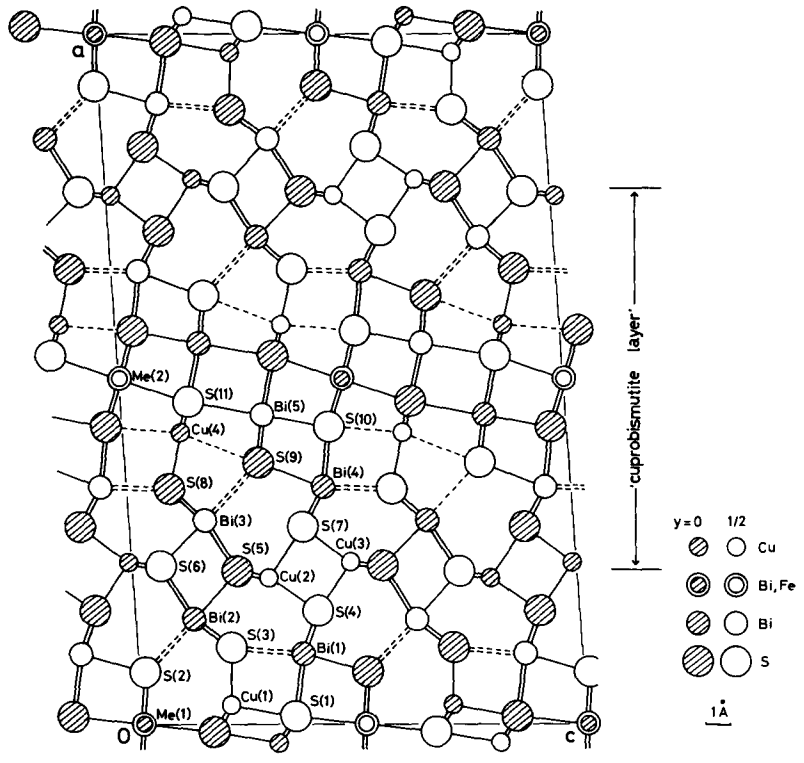

Fig. 2. The structure of hodrushite projected along b axis. Hodrushite has the following unit-cell dimensions (KODĚRA *et al.*, 1970); $a = 27.205$, $b = 3.927$, $c = 17.575$ Å, $\beta = 92°9'$. "Cuprobismuthite layer", b and c of hodrushite correspond to $c \sin\beta$, b and a of cuprobismuthite, respectively. Me(1) and Me(2) sites are occupied mostly by bismuth atoms (KUPČÍK and MAKOVICKÝ, 1968; KODĚRA *et al.*, 1970)

2.84 Å and the sulfur-bismuth-sulfur bond angles diviating from the ideal 90° value by only ± 2°.

Five independent sites for copper atoms were found in the structure. The coordination of Cu(2) is normal, being surrounded tetrahedrally by four sulfur atoms. Two symmetry-related Cu(2) tetrahedra share an edge in such a way that an endless double-chain along the b axis is formed. A similar double chain of copper has been reported in the structure of $Cu_4Bi_4S_9$, but with a different type of sharing. Cu(1), Cu(3) and Cu(4) are in nearly trigonal planar coordination with sulfur atoms. Such a coordination has been also reported for some copper atoms in hodrushite, $Cu_4Bi_4S_9$, $Cu_{2+x}Bi_{6-x}S_9$ and wittichenite (MATZAT,

1972; KOCMAN and NUFFIELD, 1973). Cu(3) and Cu(4) are substituted for Bi(1) and Bi(2), respectively. These substitutions appear to be very reasonable, judging from the copper-sulfur and copper-copper distances as given in Table 5. On the other hand, the coordination of Cu(5) is strange. Cu(5)—S(1) bond distance is too short. However, the Cu(5)—S, Cu(5) to other copper distances and Cu(5)—Bi(3) distance (3.438 Å) as well appear to indicate that this cavity for Cu(5) would be favourable in general for a copper atom, though it could not be discussed in detail due to the large standard deviations of its positional parameters.

The prediction as to the structure of cuprobismuthite by KODĚRA *et al.* (1970) was correct in principle as is evident from Fig. 2. The comparison of the bond distances between cuprobismuthite and

Table 8. *Comparison of the interatomic distances between cuprobismuthite and "cuprobismuthite layer" in hodrushite*

cuprobismuthite			"cuprobismuthite layer" in hodrushite*		
Cu(1)—S	2.338 Å	2×	Cu(4)—S	2.34 Å	2×
	2.246			2.26	
	2.981			2.94	
	3.147			3.26	
Cu(2)—S	2.308		Cu(3)—S	2.30	
	2.422			2.35	
	2.342	2×		2.36	2×
Bi(1)—S	2.771	4×	Me(2)—S	2.80	4×
	2.842	2×		2.82	2×
Bi(2)—S	2.644		Bi(5)—S	2.65	
	2.747	2×		2.74	2×
	2.916			2.97	
	3.037	2×		3.08	2×
Bi(3)—S	2.649		Bi(4)—S	2.73	
	2.645	2×		2.67	2×
	3.077	2×		3.08	2×
	3.413	2×		3.34	2×
Bi(4)—S	2.688	2×	Bi(3)—S	2.71	2×
	2.581			2.55	
	3.092	2×		3.05	2×
	3.699	2×		3.67	2×

* The atom number of hodrushite corresponds to the number in Fig. 2.

"cuprobismuthite layer" in hodrushite is presented in Table 8. The maximum difference is only about 0.1 Å.

From the present results, we may reasonably draw the following conclusion. The crystal structure of cuprobismuthite corresponds essentially to the cuprobismuthite layer in hodrushite (composition $Cu_4Bi_7S_{12}$), but some substitutions of copper for bismuth arise so that the valence rule may be satisfied. As is described above and evident from Fig. 1, Cu(3) is substituted for some part of Bi(1). Although the sum of their calculated occupancies deviates slightly from the ideal value, because they were independently refined, the deviation is only within one σ. Considering the fact that the standard deviation for Bi(1) is much smaller than that for Cu(3), the value for Bi(1) must be more reliable. Then we assign the occupancies of 0.68 and 0.32 for Bi(1) and Cu(3) sites, respectively, in the following discussion. Furthermore, some part of Bi(2) is substituted by Cu(4) and Cu(5). The occupancy of Cu(4) reaches [1 minus occupancy of Bi(2)], while the value for Cu(5) is much smaller, about 1/3 of that for Cu(4). These phenomena can be easily explained. The close approach of Cu(5) to Bi(1), 2.570 Å, does not allow these two sites to be occupied at the same time. The cavity available for Cu(5) fits a copper atom, only when both Bi(1) and Bi(2) sites are vacant. Therefore the occupancy of Cu(5) would be expressed as [1 minus occupancy of Bi(1)] $\times$ [1 minus occupancy of Bi(2)]. The obtained value of about 7% agrees closely with the result expected from this formula.

After all, the chemical formula for cuprobismuthite could be expressed as $(Cu_x,Bi_{\frac{1}{2}(1-x)})$ $(Cu_y,Bi_{1-y})Cu_{xy}$ $Cu_2Bi_2S_6$ [$x = 0.32$, $y = 0.20$]. This expression leads to the actual formula, $Cu_{2.58}Bi_{3.14}S_6$, in which the ratio of copper to bismuth is approximately 5 to 6, in good accordance with the results from natural specimens by TAYLOR *et al.* (1973).

The present results provide us with another interesting conclusion. Since the discovery by HILLEBRAND (1884), the chemical composition of cuprobismuthite and its relation to emplectite have been the main subjects for studies of this mineral. However, so far as we assume only one type of substitution described above, the existence of cuprobismuthite with the same composition as emplectite which is expressed stoichiometrically as $Cu_3Bi_3S_6$, is rather difficult to be considered. The chemical composition of $Cu_3Bi_3S_6$ can be realized only when both the values of 1 for x and 0 for y in the above-mentioned expression are simultaneously satisfied, in other words, only when Bi(1) is perfectly

substituted by Cu(3), while the Bi(2) site is fully occupied. The range of solid solution for cuprobismuthite by CHEN and CHANG (1974) includes the stoichiometric composition of $Cu_3Bi_3S_6$, but it explains neither the data for the natural specimens by TAYLOR *et al.* nor the present results (45.1 mol % of Cu_2S). We believe that more careful experiments on this point will remove the disagreement between them.

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