Crystal chemical studies on some compounds in the $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$ system

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Abstract

There was a disagreement of chemical formulae between the formula derived from structure determination (CuBi_5S_8) [Ohmasa, M. and Nowacki, W. (1973) *Zeits. Krist.*, 137, pp. 422-432] and the one from synthetic studies (CuBi_3S_5). In order to clarify the origin of the disagreement, the crystal structure of the compound has been reinvestigated. It was found that some of the Bi atoms are partly substituted by Cu, and that the obtained chemical formula is $\text{Cu}_{1.57}\text{Bi}_{4.57}\text{S}_8$. When the number of S is fixed to five, the new formula can also be expressed as $\text{Cu}_{0.98}\text{Bi}_{2.86}\text{S}_5$, and is approximately identical with CuBi_3S_5 . The amount of substitution found in $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$ ($x=1.21$) [Ohmasa, M. (1973) *Neues Jahrb. Miner. Monatsh.*, pp. 227-233] was also reexamined for comparison.

Both structures consist of two kinds of slabs, and the substitution between Bi and Cu was found in the slab II. Since these elements have quite different properties, the substitution found in these compounds is quite unique. The chemical formulae of the fundamental structures, which are ideal structures having no substitution between Bi and Cu, are different from the apparent formulae given in the synthetic studies, and the discrepancies are compensated by substitution, Cu for Bi. The formula CuBi_5S_8 obtained in the previous study corresponds to that of the fundamental structure.

Introduction

A number of structural studies on sulfides and sulfosalts, which contain copper, have so far revealed that these compounds have the following striking crystal chemical features. The distances between atoms, copper and sulfur, vary in a rather wide range (Ohmasa, Suzuki and Takeuchi, 1977). The occupancies of copper atoms in some compounds are lower than 100% at an elevated temperature or even at room temperature, that is, copper atoms are statistically distributed at the several equi-points. The substitution between two kinds of atoms of different sizes and chemical properties, e.g., Cu for Bi, was found in $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$ ($x=1.21$) and cuprobismutite of $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$ join (Ohmasa, 1973, Ozawa and Nowacki, 1975). The last feature is the subject of this paper.

The first systematic studies on the phase relations of Cu_2S - Bi_2S_3 join were carried out by Sugaki and Shima (1971, 1972) and by Buhlmann (1971). Their phase diagrams are almost identical except the phase region between Cu_2S and Cu_3BiS_5 , in which Sugaki and Shima recognized an independent phase, Cu_9BiS_6 , but Buhlmann found a broad solid solution range of Cu_2S instead. In both diagrams, Bi_2S_3 (bismuthinite), CuBi_3S_5 , $\text{Cu}_3\text{Bi}_5\text{S}_9$, CuBiS_2 (emphlectite), CuBiS_2^* (cuprobismutite), Cu_3BiS_3 (wittichenite), Cu_2S (chalcocite) were described as stable phases. Of these phases, Ohmasa and Nowacki (1973) determined the crystal structure of CuBi_3S_5 , using the sample synthesized by Sugaki and Shima, and proposed a new formula, CuBi_5S_8 , for this compound. On the basis of an electron probe micro analysis, Sugaki and Shima reported that the formula should be CuBi_3S_5 (private communication). Recently, Chang and Hoda (1977) studied the phase relations in PbS - Cu_2S - Bi_2S_3 system and confirmed the stability of CuBi_3S_5 at 400°C and 500°C .

If the formula CuBi_3S_5 is correct, and if the structure of CuBi_5S_8 is also essentially correct, a part of Bi atoms in the latter should be substituted by Cu atoms. The present studies were undertaken in order to clarify such substitution, if any, in CuBi_3S_5 . The amount of substitution in $\text{Cu}_3\text{Bi}_5\text{S}_9^{**}$ was also reexamined for comparison with that in CuBi_3S_5 . In the following section, CuBi_3S_5 will be denoted as CB-135 and $\text{Cu}_3\text{Bi}_5\text{S}_9$ as CB-359 for brevity. Different notation of the atoms have been used for these compounds in the previous studies, but a new notation is adopted for the convenience of comparison in this study.

Experimental and reinvestigation of the structure

The specimen of CB-135, kindly supplied by Dr. Kitakaze, was hydrothermally synthesized at 241°C and 230 kg/cm^2 . An acicular crystal ($0.08 \times 0.04 \times 0.16\text{ mm}$) was selected for determination of the lattice parameters and intensities. A four-circle diffractometer (Syntex P2₁) with $\text{MoK}\alpha$ radiation, monochromatized by a graphite monochromator, was employed for the measurements of intensities. However, intensities less than 2σ were excluded as unobserved data. A total of 922 independent reflections was finally obtained. The intensity data, thus determined, were corrected for Lorentz and polarization factors. Absorption effects ($\mu=627.8\text{ cm}^{-1}$) were also corrected with a program ACACA

* Sugaki *et al.* and Buhlmann reported that cuprobismutite should contain more Cu_2S component.

** The formula of this compound was previously expressed as $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$ ($x=1.21$) by one (M.O., 1973) of us.

written by Prewitt (Wuensch and Prewitt, 1965).

For the refinement of the structure of CB-359, the same data as those used for the previous studies (Ohmasa, 1973) were employed again, because the error of the measurement was estimated to be very low. Marked satellite reflections are observed on X-ray photographs of CB-359, as was described in the previous studies. These reflections were excluded in this study. Chang and Hoda did not find this phase at 500°C , although Schenck (1937), Nuffield (1947), Sugaki and Shima, Buhlmann and one of us (M.O.) could synthesize the phase. Since

FIG. 1. Idealized powder diffraction patterns of CB-135 and CB-359 calculated with the parameters determined in the present studies.

the powder diffraction diagrams of CB-135 and CB-359, calculated with the structural data, resemble closely as shown in Fig. 1, it might be possible that Chang and Hoda could not find the difference. The crystal data of both materials are listed in Table 1.

TABLE 1. Crystal data.

CB-135 (present study)	CB-359 (Ohmasa, 1973)
Monoclinic, $C2/m$	Monoclinic, $C2/m$
$a=13.217\pm0.002\text{ \AA}$	$a=13.207\pm0.005\text{ \AA}^*$
$b=4.0327\pm0.0005$	$b=3.993\pm0.005$
$c=14.076\pm0.004$	$c=14.812\pm0.005$
$\beta=115.53^\circ\pm0.02^\circ$	$\beta=100.2^\circ\pm0.08^\circ$
$Z=2$	$Z=2$

* These values correspond to the subcell.

Difference Fourier maps of CB-135 were first calculated with the coordinates and the temperature factors of CuBi_5S_8 . In the maps, some positive peaks were found around the Cu site. Some negative peaks were found at the Bi positions in the galena-like slab and some positive peaks around the negative peaks. These facts suggest that the complex distribution of the Cu atoms is similar to that of the corresponding sites in the structure of CB-359, and that the Bi atoms in the galena-like slab are partly replaced by Cu. The coordinates and the temperature factors of all atoms together with the occupancies of the Cu and the Bi atoms were then refined by a least squares method. The occupancies of Cu4 and Cu5 in the galena-like slab were assigned to the following relations: $M(\text{Cu})=100\%-M(\text{Bi})$, where $M(\text{Bi})$ is the occupancy of the Bi atom refined by the least squares calculation and $M(\text{Cu})$ the occupancy of the Cu atom. The discrepancy index $R=\sum||F_o|-|F_c||/\sum|F_o|$ was reduced to 7.8%. Four new copper sites were found in the process of the refinement.

The structure of CB-359 was also refined by difference Fourier syntheses and by a least squares method. The difference Fourier maps revealed two anomalous peaks. One of them is at about (0.46, 0.0, 0.09) and the other at (0.5, 0.15, 0.5). Least squares calculations, varying the atomic coordinates, the temperature factors and the occupancies of the Cu and the Bi atoms, reduced R to 5.9%.

The refinement was carried out with versions of the full matrix least squares programs ORFLS (Busing, Martin and Levy, 1962) and LINUS (Coppens and Hamilton, 1970). Scattering factors for neutral atoms from International Tables for X-ray Crystallography (1968) were used. Corrections for anomalous

TABLE 2. Atomic coordinates, temperature factors in the expression $\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$, isotropic temperature factors and occupancies, M of CB-135 and CB-359. Their estimated standard errors are given in parentheses in the unit of last digit.

Atomic parameters of CB-135

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{13}	B	M
Bi1	0.2106(2)	0.5	0.3593(1)	0.0037(1)	0.0283(10)	0.0013(1)	-0.0002(1)	0.8	100.0
Bi2	0.0	0.0	0.0	0.0013(1)	0.0131(14)	0.0011(1)	0.0006(1)	0.8	80.2(7)
Bi3	0.3441(1)	0.0	0.1492(1)	0.0019(1)	0.0137(9)	0.0011(1)	0.0004(1)	0.9	88.4(4)
Cu1	0.5	0.184(6)	0.5	0.0034(10)	0.10(12)	0.0034(9)	0.0006(7)	3.7	40.1(18)
Cu2	0.030(5)	0.5	0.470(5)	0.001(3)	0.04(5)	0.001(3)	0.0003(28)	1.2	7.8(15)
Cu3	0.037(6)	0.0	0.565(5)	0.001(3)	0.16(13)	0.002(3)	0.0013(29)	4.0	9.1(18)
Cu4	0.072(14)	0.0	0.011(8)	0.027(18)	0.04(6)	0.002(4)	0.005(8)	6.5	19.8
Cu5	0.423(15)	0.0	0.155(11)	0.023(18)	0.11(13)	0.008(8)	0.008(10)	8.3	11.6
S1	0.1648(9)	0.5	0.0753(8)	0.0024(6)	0.023(5)	0.0023(5)	0.0010(5)	1.5	100.0
S2	0.4969(9)	0.5	0.1968(8)	0.0027(6)	0.030(6)	0.0012(5)	0.0002(5)	1.6	100.0
S3	0.1282(9)	0.0	0.4523(7)	0.0031(6)	0.023(6)	0.0008(4)	0.0006(4)	1.3	100.0
S4	0.3548(8)	0.0	0.3432(7)	0.0030(6)	0.024(6)	0.0010(5)	0.0010(5)	1.3	100.0

Atomic parameters of CB-359

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{13}	<i>B</i>	<i>M</i>
Bi1	0.2479 (1)	0.0	0.6246 (1)	0.0063 (1)	0.0374 (8)	0.0043 (1)	-0.0027 (1)	3.4	100.0
Bi2	0.1508 (1)	0.0	0.0679 (1)	0.0023 (1)	0.0797 (14)	0.0019 (1)	0.0005 (1)	2.8	74.2 (3)
Bi3	0.4475 (1)	0.0	0.1897 (1)	0.0023 (1)	0.0469 (12)	0.0020 (1)	0.0003 (1)	2.1	65.5 (3)
Cu1	0.5	0.1351 (70)	0.5	0.0044 (10)	0.158 (39)	0.0044 (9)	-0.0015 (7)	5.6	24.4 (11)
Cu2	0.4516 (11)	0.0	0.5455 (12)	0.0029 (8)	0.047 (13)	0.0052 (9)	-0.0007 (7)	3.1	25.6 (10)
Cu3	0.0225 (9)	0.0	0.5736 (12)	0.0020 (6)	0.0258 (10)	0.0075 (10)	0.0005 (6)	3.1	25.6 (10)
Cu4	0.2298 (23)	0.0	0.1684 (22)	0.0147 (25)	0.034 (14)	0.0114 (20)	0.0090 (20)	7.3	25.8
Cu5	0.5124 (9)	0.0	0.2510 (11)	0.0033 (7)	0.067 (12)	0.0070 (9)	0.0015 (6)	4.1	34.5
Cu6	0.4628 (29)	0.5	0.0934 (30)	0.0025 (20)	0.222 (89)	0.0036 (21)	-0.0015 (16)	6.3	10.4 (12)
S1	0.5	0.0	0.0	0.0026 (4)	0.0577 (74)	0.0021 (3)	0.0002 (3)	2.4	100.0
S2	0.0905 (4)	0.0	0.2299 (3)	0.0028 (3)	0.0251 (38)	0.0021 (2)	0.0002 (2)	1.8	100.0
S3	0.1412 (4)	0.0	0.4591 (3)	0.0025 (3)	0.0212 (38)	0.0024 (2)	0.0005 (2)	1.7	100.0
S4	0.4001 (4)	0.0	0.3567 (4)	0.0026 (3)	0.0213 (38)	0.0035 (3)	0.0005 (2)	2.0	100.0
S5	0.2073 (4)	0.0	0.8725 (4)	0.0025 (3)	0.0220 (40)	0.0036 (3)	0.0002 (2)	2.0	100.0

dispersion were employed for all atoms using the values by Cromer (1965). Individual weights, $1/\sigma^2(F_o)$, based on counting statistics, were used during the course of the refinements. The final parameters are listed in Table 2. After the refinements, the anomaly in the difference Fourier maps of the both materials disappeared.

Discussion

The structures of CB-135 and CB-359 projected along the b -axis are shown in Fig. 2 and in Fig. 3. The interatomic distances and the bond angles are tabulated in Table 3. Both structures consist of two kinds of slabs, I and II. Slab I is characterized by double chains and slab II by a closed packed arrangement of Bi and S atoms analogous to that of Pb and S atoms in galena.

In slab I, the bismuth atoms (Bi1) make a double chain Bi_2S_4 on a plane parallel to (001) along the b -axis. Two sets of S3 and S4 in the adjacent double chains form a channel along the b -axis, in which Cu atoms are statistically distributed on three different equi-points (Fig. 4). The positions of the Cu atoms in the channel are almost the same in both compounds. That is, Cu1, being on the two fold axis (b -axis), is situated at about the middle of the two mirror planes, and the others (Cu2 and Cu3), about 0.7 Å apart from the two-fold axis, are on the mirror planes (Fig. 5). The distribution of Cu atoms onto the three sites of CB-135 is markedly different from that onto the corresponding sites of CB-359. In CB-135, the occupancy of the Cu atom on the two-fold axis is 40% and that on the mirror planes is 17%. However, the corresponding occupancies of the Cu atom in CB-359 are 25% and 51%, respectively. These complex distributions in the channels (Fig. 5) suggest that the copper atoms may flow along the b -axis at an elevated temperature, that is, these two compounds may be one-dimensional ionic conductors at high temperatures. Similar statistical distribution of Cu atoms is also found in the structure of β -chalcocite (Sadanaga, Ohmasa and Morimoto, 1965), an ionic conductor (Hirahara, 1951).

In the arrangement of atoms in slab II, the Bi atoms are surrounded by six sulfur atoms octahedrally and are partly substituted by Cu atoms. These Cu atoms don't occupy the centers of the octahedra, but are located near the centers of triangles on the surfaces of the octahedra. In CB-135, 20% of Bi2 and 12% of Bi3 are substituted by Cu, while 25% of Bi2 and 35% of Bi3 are substituted in CB-359. In CB-359, a tetrahedral site, Cu6, is also occupied by small amount of copper (about 10%). The chemical formula of CB-135 determined from the refined crystal structure is $\text{Cu}_{1.57}\text{Bi}_{4.57}\text{S}_8$, in contrast to the

FIG. 2. The crystal structure of CB-135 projected along the b -axis. Thick circles indicate the atoms at $y=0$ and thin circles the atoms at $y=1/2$. Regions of slab I and slab II are denoted at the left end of the figure.

FIG. 3. Projection of the crystal structure of CB-359 parallel to the b -axis. Thickness difference of the circles indicates the different levels of the atoms as shown in Fig. 2.

TABLE 3. Interatomic distances and bond angles of CB-135 and CB-359. The values in parentheses indicate estimated standard errors.

Interatomic distances of CB-135

	S1	S2	S3	S4
Bi1			2.593(2) 2.861(1)	2.839(1)
Bi2	2.8190(3)	2.7821(6)		
Bi3	2.937(1) 3.094(2)	2.719(1)		2.664(2)
Cu1			2.435(14)	2.355(9)
Cu2			2.47(3)	2.25(5) 2.43(5)
Cu3			2.08(6) 2.37(6)	2.51(4)
Cu4	2.33(7)	2.64(7)		
Cu5	2.92(11)	2.21(6)		

Bond angles of CB-135

S3 - Bi1 - S3'	83.07(3)°	S3'' - Cu1 - S4	153.2(07)°
S4 - Bi1 - S3'	86.34(1)	S3 - Cu1 - S4''	92.2(1)
S3' - Bi1 - S3''	80.78(4)	S4' - Cu1 - S4''	60.1(03)
S3' - Bi1 - S4	78.74(4)		
S4 - Bi1 - S4'	90.48(5)	S3 - Cu2 - S3'	109.4(22)
		S3 - Cu2 - S4	89.6(15)
S1 - Bi2 - S1'	91.31(1)	S3 - Cu2 - S4'	109.2(15)
S1 - Bi2 - S1''	88.69(1)	S4' - Cu2 - S4''	145.9(28)
S2 - Bi2 - S1'''	88.62(1)		
S2 - Bi2 - S1	91.38(1)	S3 - Cu3 - S3'	137.3(30)
		S3 - Cu3 - S4	89.9(16)
S1 - Bi3 - S1'	86.70(4)	S3' - Cu3 - S4	113.8(16)
S2 - Bi3 - S1	88.55(1)	S4'' - Cu3 - S4'	107.1(24)
S2 - Bi3 - S2'	95.71(5)		
S1 - Bi3 - S4	92.45(4)	S1 - Cu4 - S1'	119.5(65)
S2 - Bi3 - S4	92.85(4)	S1 - Cu4 - S2	107.1(26)
S1 - Bi3 - S1''	87.78(4)		
		S2 - Cu5 - S2'	132.1(80)
S3 - Cu1 - S3'	116.8(10)	S2 - Cu5 - S1	101.9(30)

Atomic distances of CB-359

	S1	S2	S3	S4	S5
Bi1			2.602(6) 2.884(4)	2.842(4)	
Bi2	2.873(2)	2.659(5)			2.774(4) 3.113(6)
Bi3	3.011(2)	2.741(4)		2.656(6)	2.889(4)
Cu1			2.524(17)	2.354(9)	
Cu2			2.338(9)	2.756(19) 2.220(15)	
Cu3			2.507(17) 2.129(13)	2.392(9)	
Cu4		2.191(23)			2.286(11)
Cu5		2.295(7)		2.337(15)	
Cu6	2.524(29)	2.397(37)			2.387(43)

Bond angles of CB-359

S3 - Bi1 - S5	79.9(1)°	S3' - Cu1 - S3	109.4(11)°
S5 Bi1 S5'	89.3(2)		
S3 Bi1 S3'	80.0(1)	S3 - Cu2 - S3'	117.3(7)
S3' Bi1 S3''	87.6(2)	S3 Cu2 S5	86.4(4)
		S5 Cu2 S5'	133.9(8)
S2 - Bi2 - S4	90.3(2)	S3 Cu2 S5'	114.6(4)
S4 Bi2 S4'	92.1(2)		
S2 Bi2 S1	90.9(1)	S5 - Cu3 - S3'	116.0(4)
S1 Bi2 S1'	88.0(1)	S5 Cu3 S5'	113.2(6)
S4 Bi2 S4''	92.1(1)	S3 Cu3 S5	91.2(4)
S1 Bi2 S4''	86.6(1)	S3 Cu3 S3'	125.2(8)
S2 - Bi3 - S5	93.7(1)	S2 - Cu4 - S4	118.8(5)
S2 Bi3 S2'	93.5(2)	S4 Cu4 S4'	121.7(10)
S4 Bi3 S5	91.6(2)		
S4 Bi3 S4'	87.4(2)	S2 - Cu5 - S5	116.5(4)
S1 Bi3 S2	86.5(1)	S2 Cu5 S2'	120.9(5)
S1 Bi3 S4	88.2(1)		
		S1 - Cu6 - S1'	104.5(17)
S5 - Cu1 - S5'	153.6(14)	S1 Cu6 S2	106.6(10)
S5 Cu1 S3	91.7(3)	S1 Cu6 S4	113.5(10)
S5 Cu1 S3'	103.6(4)	S2 Cu6 S4	111.6(19)

FIG. 4. Projections of electron density and arrangement of the atoms in slab I of CB-359. Contours of electron density are drawn at arbitrary intervals.

previously reported CuBi_5S_8 . The new formula can also be expressed as $\text{Cu}_{0.98}\text{Bi}_{2.86}\text{S}_5$, when the number of S atoms is fixed to five. This is approximately identical with CuBi_3S_5 , given in the synthetic studies. The new expression of CB-359, being $\text{Cu}_{2.93}\text{Bi}_{4.89}\text{S}_9$, coincides well with the formula, $\text{Cu}_3\text{Bi}_5\text{S}_9$.

The same mode of substitution between Bi and Cu was also found in the structure of cuprobismutite (Ozawa and Nowacki, 1975). The substitution between two kinds of atoms in a crystal structure is empirically recognized only when the atoms have similar radii, electronegativities and same electric charges. The apparent electric charges of Bi, Cu and S atoms in sulfosalts are usually known to be +3, +1 and -2. Since the valences of Bi and Cu are quite different and the difference of atomic radii is fairly large ($\sim 20\%$), the substitution between Bi and Cu atoms found in the above compounds is quite unique. The existence of such substitution may be interpreted as follows. In the struc-

FIG. 5. Arrangement of Cu1, Cu2 and Cu3 in a channel of slab I. An equivalent set of Cu2 and Cu3 related by the two-fold axis is omitted to avoid complexity of the figure.

ture of galena, the electric charge of Pb atoms is regarded as +2, and the structure keeps the balance of charges. When Bi atoms occupy octahedral sites in cubic closest packing of S atoms analogous to Pb in galena, the electric charge of such structure deviates from neutrality. The substitution of Bi by monovalent Cu, found in the above compounds, should reduce the deviation from electric neutrality, and may stabilize the structures. As Cu atoms have tetrahedral or triangular coordination in most sulfides and sulfosalts, Cu atoms replacing Bi atoms should prefer rather triangular or tetrahedral sites to octahedral one.

The apparent chemical formulae of CB-135, CB-359 and cuprobismutite, and the formulae derived from their structures reveal a common feature as shown in Table 4. The ratios of the elements, given in the last column, were calculated from the formulae of the derived structures. They coincide well with the ratios of the elements in the apparent formulae, given in the synthetic studies. The discrepancies between the formulae derived from the fundamental structures, ideal structures having no substitution between Bi and Cu, and the apparent ones, are compensated by the substitution between Bi and Cu. Hence, the formula CuBi_5S_8 , determined in the previous study, corresponds to the fundamental structure.

The X-ray photographs of CB-359 show distinct satellite reflections, and the anisotropic temperature factors of the atoms in the slab II have very high β_{22} components. Recent analyses of the satellite reflections revealed that waves of scattering amplitudes and of atomic positions exist along the b -axis of the structure, that is, a periodic clustering of Cu atoms exists in the structure (Ohmasa, Tomeoka and Sadanaga, 1979). While the X-ray photographs of CB-135 show no extra reflections and the atoms in the slab II have no remarkable anisotropy of the temperature factors. These facts

TABLE 4. Chemical formulae of CB-135, CB-359 and cuprobismutite.

compounds	formulae of the fundamental structure	formulae determined from the structure analyses	apparent formulae	ratios of elements calculated from the formulae of the second column
CB-135	$\text{Cu}_{1\sim 2}\text{Bi}_5\text{S}_8$	$\text{Cu}_{1.57}\text{Bi}_{4.57}\text{S}_8$	CuBi_3S_5	0.98:2.86:5
CB-359	$\text{Cu}_{1\sim 2}\text{Bi}_6\text{S}_9$	$\text{Cu}_{3.03}\text{Bi}_{4.79}\text{S}_9$	$\text{Cu}_3\text{Bi}_5\text{S}_9$	3.03:4.79:9
cuprobismutite	$\text{Cu}_4\text{Bi}_7\text{S}_{12}$	$\text{Cu}_{2.61}\text{Bi}_{3.14}\text{S}_6$	CuBiS_2^*	0.87:1.05:2

* The chemical analyses of the natural specimens by Taylor *et al.* (1973) indicate that the ratio Cu:Bi is not 1:1. Sugaki and Shima (1970, 1972) and Buhlmann (1971) noted the same fact in their synthetic studies.

suggest that no periodic clustering exists in CB-135. The content of Cu in CB-359 is about two times of that in CB-135. The channels of the slab I in the former contain 25% more Cu than those in the latter. The amount of Cu, substituting Bi in the slab II of the latter, is 14.3%, while 30.2%, of Bi in the slab II of the former is substituted by Cu. Besides, some amount of Cu atoms occupies also tetrahedral sites in the slab II of the former. Since the Cu-contents of the slab II in CB-359 are about three times of those in CB-135, a correlation among Cu atoms should be much stronger in CB-359 than in CB-135. Such strong correlation in the former may be the origin of the periodic clustering of Cu atoms in the structure.

Versions of the following computer programs were used in this work.

ACACA by C. T. Prewitt (Wuensch and Prewitt, 1965).

LINUS by P. Coppens and W. C. Hamilton (1970).

ORFFE by W. R. Busing, K. O. Martin and H. A. Levy (1964).

ORFLS by W. R. Busing, K. O. Martin and H. A. Levy (1962).

POWD5 by C. M. Clark, D. K. Smith and G. G. Johnson (1973).

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