

Refinement of the crystal structure of emplectite, CuBiS_2 *

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Auszug

Die Kristallstruktur des Emplektits, CuBiS_2 , wurde auf Grund von dreidimensionalen Röntgendaten verfeinert. Die Raumgruppe ist $Pnma$ und die Gitterkonstanten betragen: $a = 6,1426(3)$, $b = 3,9189(4)$ und $c = 14,5282(7)$ Å; $Z = 4$. Intensitäten wurden mit Hilfe eines Supper-Pace Autodiffraktometers unter Verwendung von $\text{CuK}\alpha$ -Strahlung gemessen. Für die 375 unabhängigen Reflexe ist der endgültige R -Wert gleich 0,063.

Die erhaltene Struktur stimmt mit derjenigen von HOFMANN (1933) und KUPČÍK (1965) überein. Die kürzesten (Bi—S)-Abstände [2,536(4) und 2 mal 2,653(2) Å] spannen eine trigonale Pyramide mit Bi als Spitze auf. Die BiS_3 -Pyramiden sind über gemeinsame Ecken zu endlosen Ketten verknüpft, welche die Zusammensetzung BiS_2 und die Periode b haben. Cu ist von vier S-Atomen [mit den Abständen 2,304(5), 2,317(5) und 2 mal 2,343(3) Å] in Form eines fast regulären Tetraeders koordiniert. Die BiS_2 -Ketten bilden zusammen mit den CuS_4 -Tetraederketten Schichten $\parallel (001)$. Wegen der endlosen BiS_2 -Ketten muß die Emplektitstruktur dem Typ IV.a₃ der Klassifikation von NOWACKI (1969) zugeordnet werden.

Die bekannten Strukturen der Cu,Bi-führenden Sulfosalze CuBi_5S_8 , $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$ ($x = 1,21$), Hodrushit, $\text{Cu}_4\text{Bi}_4\text{S}_9$ und Emplektit weisen gemeinsame strukturelle Einheiten, die als Doppelketten von viereckigen BiS_5 -Pyramiden beschrieben werden können, auf. Solch eine Pyramide wird von den fünf nächsten S-Nachbarn des Bi-Atoms gebildet, während das Bi-Atom selber dem Zentrum der Basisfläche naheliegt. Jede BiS_5 -Pyramide besitzt zwei gegenüberliegende Basiskanten, die mit angrenzenden Pyramiden gemeinsam sind, wodurch eine erste endlose Kette entsteht, und zwei Pyramidenkanten, die zu anderen angrenzenden Pyramiden gehören, welche eine zweite, mit der ersten parallele und äquivalente Kette bilden. Die Doppelkette hat eine Zusammensetzung von Bi_2S_4 und eine Periode von 4 Å, die mit der kleinsten Gitterkonstanten der genannten Strukturen übereinstimmt.

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Abstract

The crystal structure of emplectite, CuBiS_2 , has been refined with the aid of three-dimensional x-ray intensity data. The space group is $Pnma$ and the lattice dimensions are: $a = 6.1426(3)$, $b = 3.9189(4)$ and $c = 14.5282(7)$ Å; $Z = 4$. The intensities were measured by means of a Supper-Pace autodiffractometer using $\text{CuK}\alpha$ radiation. The final R value for the 375 independent reflections is 0.063.

The resulting structure corresponds to the structures of HOFMANN (1933) and KUPČÍK (1965). The three smallest Bi—S distances [2.536(4) and two of 2.653(2) Å] span a trigonal pyramid with Bi at the vertex. The BiS_3 pyramids are coupled by corner sharing to endless chains with composition BiS_2 and b as period. Cu is coordinated by four S atoms [at distances 2.304(5), 2.317(5) and two of 2.343(3) Å] in a nearly regular tetrahedron. The BiS_2 chains join with chains of CuS_4 tetrahedra to form sheets parallel to (001). Because of the endless BiS_2 chains emplectite belongs to type IV.a₃ of NOWACKI's (1969) classification.

The known structures of the Cu,Bi-bearing sulfosalts CuBi_5S_8 , $\text{Cu}_{2+x}\text{Bi}_{4-x}\text{S}_9$ ($x = 1.21$), hodrushite, $\text{Cu}_4\text{Bi}_4\text{S}_9$ and emplectite have in common structural units which can be described as double chains of BiS_5 square pyramids. Such a pyramid is formed by the five nearest S neighbours of the Bi atom, while the Bi itself lies near the center of the basal plane. Each BiS_5 pyramid shares two opposite edges of the basal plane with adjacent pyramids in one endless chain; two side edges are shared with pyramids belonging to the second chain, which is parallel and equivalent to the first chain. The double chain has a composition of Bi_2S_4 and a period of 4 Å corresponding to the shortest lattice dimension of the structures mentioned.

Introduction

The crystal structures of the sulfosalt minerals wolfsbergite CuSbS_2 and emplectite CuBiS_2 , which are isotopic, were determined by HOFMANN in 1933. His atomic coordinates were obtained by trial and error methods on the basis of photographic intensity data. KUPČÍK (1965) refined the emplectite structure, using photographic data, and showed that HOFMANN's (1933) structure is correct. At present a refinement of emplectite is reported in which diffractometer data are used. The resulting geometry is essentially the same as the previous ones, but more accurate.

Experimental

For this investigation a crystal was selected from a sample originating from Schwarzenberg in Germany. The crystal had the shape of a short needle with one naturally rounded-off end. It had an anthracite-like appearance and dimensions $0.085 \times 0.094 \times 0.127$ mm. The longest dimension was along the needle axis [010].

Because of the systematic absences $hk0$ for h odd and $0kl$ for $k + l$ odd the diffraction symbol is $mmmPn-a$. $Pnma$ (D_{2h}^{16}) and $Pn2_1a$

(C_{2v}^9) are the possible space groups. The centric space group was adopted and this proved satisfactory.

The lattice parameters were determined with the aid of zero-level Weissenberg photographs of the specimen rotated about [001] and [010]; the camera radius was 57.29 mm. Superposed Si powder lines were used for the calibration. The parameter values were calculated (T. ITO, unpublished) from 78 θ values between 50 and 80°. In Table 1 some diffraction data are given.

For the collection of the intensities the crystal was mounted on a Supper-Pace autodiffractometer for rotation around [010]. 1406 dependent reflections, comprising all accessible ones with this mounting, were measured with the ω -scan technique using Ni-filtered Cu radiation.

An ellipsoidal absorption correction according to JOHNSON (1963) was applied and structure amplitudes, F , were derived as mentioned earlier (PORTHEINE and NOWACKI, 1975). 375 independent¹ amplitudes, F_o , were obtained by averaging $F_o = (1/n) \sum_{i=1}^n F_i$, where n is the number of equivalent ones. 11 reflections were not significant at the 1⁰/₀ level.

The discrepancy between equivalent reflections $\left\langle \sum_{i=1}^n |F_i - F_o| / \sum_{i=1}^n F_i \right\rangle$, averaged over all, amounted to 0.073. This discrepancy is a measure for the inaccuracy of the absorption correction which implies rotational symmetry about [010]. The error in the average F_o due to absorption is probably smaller than 7.3⁰/₀.

Table 1. *Diffraction data of emplectite*

Composition CuBiS₂, $M = 336.6 \text{ g} \cdot \text{mole}^{-1}$,
space group $Pnma$, $Z = 4$, $F(000) = 576$ electrons,
 $\lambda = 1.54178 \text{ \AA}$, $\mu = 1125 \text{ cm}^{-1}$.

	HOFMANN (1933)	KUPČÍK ^I (1965)	present work ^{II}	DANA (1944)
a	6.14(1) Å (from kx)	6.15(1) Å	6.1426(3) Å	
b	3.90(1)	3.92(1)	3.9189(4)	
c	14.54(1)	14.55(2)	14.5282(7)	
ρ_c	6.43 g · cm ⁻³	6.37 g · cm ⁻³	6.393 g · cm ⁻³	6.38 g · cm ⁻³

^I KUPČÍK's unit cell has been transformed according to {100, 00 $\bar{1}$, 010} and the origin has been moved towards the equivalent centre at 0 $\frac{1}{2}$ 0.

^{II} Quoted errors are twice the calculated standard deviations.

¹ The number of possible independent reflections in the Cu sphere is 456.

The statistics of the normalized structure amplitudes, E , indicate the presence of a center of symmetry (see Table 2).

Refinement

The structure was refined by Fourier and least-squares methods using programs adapted for the IBM 370/155 by T. ITO². The quantity $\sum w(F_o) \cdot (F_o - |F_c|/k)^2$ was minimized, where $w(F_o)$ is the weight of F_o , $|F_c|$ the calculated structure amplitude and k the scale factor.

As a start atoms at HOFMANN's (1933) positions for wolfsbergite (Sb replaced by Bi) were refined isotropically in space group $Pnma$. Unit weights were used and all measured reflections were included. The scattering factors for neutral atoms of DOYLE and TURNER (1968) were employed and the anomalous dispersion terms were taken from CROMER and LIBERMAN (1970). In three cycles the conventional R value, $\sum |F_o - |F_c|/k| / \sum F_o$, dropped to 0.0793. A difference map at this stage indicated that the structure was correct. The only significant features were negative regions at the atomic sites (see below). There was also evidence for anisotropic vibration of the Bi atom with highest amplitude in the [100] direction.

The parameters varied in this refinement were: k and for each of the four atoms the isotropic temperature factor and the positional parameters x and z . One could have accepted the results of a subsequent refinement in $Pn2_1a$ at a 0.005 significance level if R had dropped below $0.0793/\mathfrak{R}_{4,358,0.005} = 0.0777^3$. On the basis of the resulting value of 0.0790 however, the centric space group was retained.

Analysis of $|F_o - |F_c|/k|$ as a function of F_o prompted us to consider the weighting scheme: $w(F_o \leq 49.52) = (3.94 \cdot 10^{-2} \times F_o + 2.198)^{-2}$ and $w(F_o > 49.52) = (9.65 \cdot 10^{-4} \times F_o^2 + 4.61 \cdot 10^{-2} \times F_o$

Table 2. *Distribution of normalized structure amplitudes observed for emplectite compared with the theoretical distribution for the centric case*

	theor.	obs.		theor.	obs.
$\langle E^2 \rangle$	1.000	1.002	$E > 1$	32.0%	28.9%
$\langle E^2 - 1 \rangle$	0.968	1.018	$E > 2$	5.0	6.0
$\langle E \rangle$	0.798	0.789	$E > 3$	0.3	0.0

² Now in Tokyo.

³ In this case: the indices of \mathfrak{R} are the number of additional parameters varied in $Pn2_1a$ (y 's of the four atoms), the number of degrees of freedom in the refinement and the significance level.

$-0.50)^{-2}$, which effected independence of $w(F_o)$. $(F_o - |F_c|/k)^2$ on F_o over most of the F_o range. After two cycles of refinement with this weighting scheme R and $R_w = [\sum w(F_o) \cdot (F_o - |F_c|/k)^2 / \sum w(F_o) \cdot F_o^2]^{1/2}$ both amounted to 0.095.

Introduction of anisotropic thermal parameters lowered the values of R and R_w to 0.067 and 0.071 respectively. Comparison of the R_w values of the isotropic and the anisotropic refinements shows that the results of the latter are significantly better ($\mathfrak{R}_{12, 350, 0.005} = 1.030$).

In the subsequent difference map the regions at the atomic sites proved to have virtually the same minima as before: -18 , -10 , -3.6 and $-3.2 \text{ e} \cdot \text{\AA}^{-3}$ for Bi, Cu, S(1) and S(2) respectively. In addition it was found that for the strong reflections $|F_c|$ was systematically larger than $k \cdot F_o$. From the ratios $\langle |F_c|/kF_o \rangle$, averaged for different groups of F_o , a value of $2.34 \cdot 10^{-6}$ was derived for the extinction parameter g in the relation of STOUT and JENSEN (1968): $|F_c| = kF_o \cdot (1 + gLp|F_c|^2)$, where L and p are the Lorentz and polarization factors, respectively. Corrected structure amplitudes were obtained from the above expression after replacing $|F_c|/k$ by $F_o(\text{corr})$.

Further refinement with the aid of the $F_o(\text{corr})$ values resulted in the final parameters of Tables 3 and 4. The parameter shifts were less

Table 3. *Positional coordinates for emplectite in fractions of the cell edges σ in terms of the last digit is added in parentheses*

	x		y	z	
	KUPČÍK	this work		KUPČÍK	this work
Bi	0.2299	0.23156(11)	$\frac{1}{4}$	0.0636	0.06304(4)
Cu	0.7495	0.7509(4)	$\frac{3}{4}$	0.1692	0.1719(2)
S(1)	0.6367	0.6362(6)	$\frac{1}{4}$	0.0970	0.0980(2)
S(2)	0.1235	0.1258(6)	$\frac{3}{4}$	0.1786	0.1777(2)

Table 4. *Thermal parameters and associated σ 's for emplectite*

The Debye-Waller factor is defined as:

$$\exp \{-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{13}hla^*c^*)\}$$

	U_{11}	U_{22}	U_{33}	U_{13}	B^1
Bi	0.0259(4) \AA^2	0.0223(5) \AA^2	0.0141(4) \AA^2	-0.0010(2) \AA^2	1.64 \AA^2
Cu	0.0329(14)	0.0331(18)	0.0209(14)	-0.0006(9)	2.29
S(1)	0.0255(18)	0.0226(18)	0.0132(16)	-0.0014(13)	1.61
S(2)	0.0277(19)	0.0222(18)	0.0134(15)	0.0010(14)	1.66

¹ The equivalent isotropic temperature factor, B .

Table 5. Final list of structure amplitudes for *emplectite*.
 F_c is the calculated structure amplitude on twice absolute scale and F_o is equal to $2 \times 1.2064 F_{o, corr}$,
 where 1.2064 is the final value of the scale factor

h	F _o	F _c	h	F _o	F _c	h	F _o	F _c	h	F _o	F _c	h	F _o	F _c	h	F _o	F _c	h	F _o	F _c	h	F _o	F _c	h	F _o	F _c
h 0 0			h 0 6			h 0 12			h 1 2	5 177 185	3 75 75	5 267 283	2 52 50	4 145 148	2 170 167											
h 0 0			h 0 6	0 216 201	0 151 153	h 1 2	1 77 68	h 1 8	h 1 8	6 33 31	h 1 15	h 2 5	h 2 12	1 46 48	1 65 61											
2 868 694	1 339 359	1 344 365	2 157 150	2 196 188	2 83 83	3 14 12	1 17 16	0 17 18	1 54 56	h 2 5	h 2 5	h 2 12	0 110 118	2 25 25	2 6 3											
4 279 315	3 192 195	3 274 282	4 101 110	4 125 129	4 11 10	5 131 146	3 17 18	2 52 53	3 25 26	1 285 296	3 92 93	h 3 4	3 92 93	h 3 15	h 3 15											
6 193 210	5 106 109	5 178 171	6 61 64	h 0 1	5 106 109	5 178 171	6 61 64	4 120 123	5 11 11	h 1 16	5 84 83	3 235 232	5 93 88	0 231 221	1 103 100											
1 57 29	6 59 59	h 0 13	7 134 123	5 114 112	7 89 80	h 0 13	7 134 123	5 11 11	6 154 150	1 35 36	h 2 6	h 2 13	h 3 5	1 103 100												
3 68 71	h 0 7	1 21 9	h 1 3	4 68 71	h 0 7	2 31 31	0 785 620	h 1 9	2 10 7	h 2 6	h 2 13	0 337 365	h 4 0	h 4 0												
5 137 149	1 27 27	3 33 34	1 118 108	6 12 7	2 35 36	4 78 78	2 430 442	1 408 443	0 127 135	h 1 17	0 168 170	1 8 7	1 60 63	2 244 250												
6 12 7	2 35 36	4 78 78	2 430 442	7 135 130	5 98 96	5 54 50	3 32 33	2 115 119	0 75 78	2 159 161	3 30 28	4 68 65	4 186 183	1 16 15												
7 135 130	4 33 33	h 0 14	5 26 23	h 0 2	5 132 137	6 38 38	0 85 82	6 159 141	5 205 211	h 2 0	5 94 91	h 2 14	h 3 6	3 47 48												
0 334 206	6 38 38	0 85 82	6 159 141	1 272 232	h 0 8	1 237 248	7 35 31	6 37 36	2 478 502	6 58 53	0 73 72	h 3 72	h 4 2	h 4 2												
1 272 232	h 0 8	2 134 139	h 1 4	2 293 262	h 0 8	3 167 168	h 1 5	h 1 10	4 217 241	h 2 7	1 205 202	1 24 25	0 139 123	0 139 123												
2 293 262	0 565 583	3 167 168	h 1 4	4 174 186	1 30 26	4 195 159	1 86 80	1 16 14	6 174 169	h 2 7	3 144 138	3 60 60	1 109 115	1 109 115												
4 174 186	1 30 26	4 195 159	1 86 80	5 113 125	2 426 465	h 0 15	3 137 144	3 36 36	h 2 1	2 28 29	h 2 15	4 79 75	2 118 121	2 118 121												
5 113 125	2 426 465	h 0 15	3 137 144	6 87 89	3 117 122	1 42 41	4 15 15	4 63 65	2 125 126	4 28 27	1 34 34	h 3 7	h 4 3	h 4 3												
6 87 89	3 117 122	1 42 41	4 15 15	h 0 3	6 175 176	3 87 89	6 12 12	6 95 88	4 53 57	6 33 32	h 2 16	0 50 49	1 9 9	1 9 9												
7 67 62	4 263 285	3 87 89	6 12 12	1 38 31	h 0 9	4 20 21	7 126 115	h 1 11	5 117 122	h 2 8	h 2 8	1 215 224	2 68 68	2 68 68												
h 0 3	6 175 176	4 20 21	7 126 115	2 181 171	h 0 9	h 0 16	h 1 5	0 216 225	6 7 6	h 2 8	0 198 188	2 33 32	3 10 8	3 10 8												
1 38 31	h 0 9	h 0 16	h 1 5	3 25 18	1 112 111	0 228 232	0 661 624	1 119 123	h 2 2	0 411 449	h 3 0	3 195 195	h 4 4	h 4 4												
2 181 171	h 0 9	h 0 16	h 1 5	4 149 161	2 112 112	0 228 232	0 661 624	1 119 123	h 2 2	0 411 449	h 3 0	3 195 195	h 4 4	h 4 4												
3 25 18	1 112 111	0 228 232	0 661 624	5 72 78	3 155 165	1 50 50	1 81 78	2 226 234	0 221 213	2 340 363	2 64 68	0 57 55	0 57 55	0 57 55												
4 149 161	2 112 112	0 228 232	0 661 624	6 104 108	4 62 65	2 213 217	2 468 486	3 17 15	1 185 186	3 91 92	4 107 112	1 208 211	1 208 211	1 208 211												
5 72 78	3 155 165	1 50 50	1 81 78	7 58 55	5 82 82	3 60 59	3 72 75	4 192 197	2 197 207	4 223 228	h 3 1	1 11 10	2 22 20	2 22 20												
6 104 108	4 62 65	2 213 217	2 468 486	h 0 4	6 17 17	h 0 17	4 260 288	5 25 21	3 143 151	5 74 71	h 2 16	2 15 14	3 237 231	3 237 231												
7 58 55	5 82 82	3 60 59	3 72 75	0 206 185	h 0 10	1 59 60	6 174 175	h 1 12	4 143 155	h 2 9	2 51 53	4 89 84	h 4 5	h 4 5												
h 0 4	6 17 17	h 0 17	4 260 288	1 655 580	0 214 213	2 11 3	7 30 27	1 89 91	6 81 77	1 88 88	3 242 288	h 3 9	1 32 30	1 32 30												
0 206 185	h 0 10	1 59 60	6 174 175	2 75 73	1 208 210	h 1 0	h 1 6	2 5 4	h 2 3	2 93 91	4 47 48	2 26 23	2 26 23	2 26 23												
1 655 580	0 214 213	2 11 3	7 30 27	3 331 371	2 238 243	2 119 112	1 37 40	3 139 143	4 14 15	3 135 135	5 197 194	0 92 93	3 18 15	3 18 15												
2 75 73	1 208 210	h 1 0	h 1 6	4 16 15	3 124 107	2 119 112	1 37 40	4 14 15	1 19 17	4 135 134	h 3 2	2 86 83	h 4 6	h 4 6												
3 331 371	2 238 243	2 119 112	1 37 40	5 299 352	4 210 225	4 148 169	2 183 186	5 79 76	2 123 126	5 73 68	h 3 2	2 86 83	h 4 6	h 4 6												
4 16 15	3 124 107	2 119 112	1 37 40	6 8 8	5 67 68	6 137 142	3 89 91	h 1 13	3 14 15	h 2 10	1 32 33	3 236 227	0 110 110	0 110 110												
5 299 352	4 210 225	4 148 169	2 183 186	7 132 123	6 121 114	h 1 1	4 108 111	h 1 13	4 123 129	h 2 10	2 86 90	4 58 55	2 107 104	2 107 104												
6 8 8	5 67 68	6 137 142	3 89 91	h 0 5	h 0 11	0 33 27	6 40 39	0 312 334	1 141 146	1 174 180	4 72 73	h 3 10	h 4 7	h 4 7												
7 132 123	6 121 114	h 1 1	4 108 111	1 89 82	1 15 7	1 624 480	h 1 7	0 281 294	6 96 90	2 195 195	5 104 100	1 11 10	h 4 7	h 4 7												
h 0 5	h 0 11	0 33 27	6 40 39	2 58 53	2 64 61	2 62 55	h 1 7	3 85 87	h 2 4	3 97 95	h 3 3	2 14 5	1 12 12	1 12 12												
1 89 82	1 15 7	1 624 480	h 1 7	3 35 34	3 30 33	3 416 465	0 104 107	4 215 216	0 117 119	4 189 185	h 3 3	3 26 24	2 18 16	2 18 16												
2 58 53	2 64 61	2 62 55	h 1 7	4 130 139	4 102 101	4 49 54	1 329 341	h 1 14	1 416 428	5 63 61	0 343 359	h 3 11	h 4 8	h 4 8												
3 35 34	3 30 33	3 416 465	0 104 107	5 94 100	5 45 44	5 247 291	2 31 27	h 2 11	2 49 49	h 2 11	2 251 273	0 162 159	h 4 8	h 4 8												
4 130 139	4 102 101	4 49 54	1 329 341	6 143 145		6 18 16	3 271 286	1 41 43	3 391 413	h 2 11	2 251 273	0 162 159	h 4 8	h 4 8												
5 94 100	5 45 44	5 247 291	2 31 27	7 94 88		7 118 106	4 111 115	2 59 57	4 18 16	1 6 5	3 14 12	1 96 93	1 3 4	1 3 4												

than $\frac{1}{2} \sigma$, the estimated standard deviation. The final list of structure amplitudes is given in Table 5. Corresponding R values are $R = 0.063$ and $R_w = 0.067$.

The most pronounced minima in the final difference map are at the Bi and Cu positions, amounting to -4.0 and $-2.4 \text{ e} \cdot \text{\AA}^{-3}$ respectively. The largest maxima (about 4 and $2 \text{ e} \cdot \text{\AA}^{-3}$) occur as positive spherical shells around these positions. Since the crystal in question had strong reflections even at the edge of the limiting sphere, which is demonstrated by the fact that only 11 reflections were not significant, these extremes may be due to the effect of series termination.

Discussion of the structure

It can be seen from Table 3 that our structure of *emplectite* corresponds to that of KUPČÍK (1965), but there are differences in parameter values. The distances between the atomic positions in the two

Table 6. *Interatomic distances and associated σ 's in emplectite*

Bi—S(1)	2.536(4) Å	S(1)—Cu } —Cu'' }	2.343(3) Å
—S(2) } —S(2)'	2.653(2)	—Bi	2.536(4)
Average	2.614	—Bi' } —Bi'' }	3.158(3)
Bi—S(1)' } —S(1)'' }	3.158(3)	—Bi'''	3.692(4)
—S(1)'''	3.692(4)	S(1)—S(2)''	3.772(5) 2 ×
Bi—Cu'	3.415(3)	—S(2)'''	3.804(4) 2 ×
—Cu'''	3.881(2)		
—Cu ^{IV}	4.322(3) 2 ×		
Cu—S(2)''	2.304(5)	S(2)—Cu'''	2.304(5)
—S(2)'''	2.317(5)	—Cu ^{IV}	2.317(5)
—S(1) ^{IV} } —S(1) }	2.343(3)	—Bi } —Bi ^{IV} }	2.653(2)
Average	2.327		
Cu—Cu ^{IV}	3.819(4) 2 ×	S(2)—S(2)'''	3.721(5) 2 ×

Table 7. *Interatomic angles and associated σ 's in emplectite*

S(1)—Bi—S(2)	96.57(10)° 2 ×	Bi'''—S(1)—Cu	76.41(11)° 2 ×
—S(1)'	84.03(9) 2 ×	Bi'''—S(1)—Bi'	69.10(7) 2 ×
—S(1)'''	160.57(9)	—Bi	160.57(13)
S(1)'—Bi—S(2)	94.00(7) 2 ×	Bi'—S(1)—Cu	75.12(8) 2 ×
—S(1)''	76.71(6)	Bi'—S(1)—Bi''	76.71(8)
—S(1)'''	110.90(8) 2 ×	—Bi	95.97(9) 2 ×
S(2)—Bi—S(1)'''	70.80(9) 2 ×	Cu—S(1)—Bi	112.73(11) 2 ×
—S(2)'	95.24(8)	Cu—S(1)—Cu''	113.50(17)
S(2)''—Cu—S(1)	108.50(12) 2 ×	Cu ^{IV} —S(2)—Bi	120.74(10) 2 ×
—S(2)'''	107.28(17)	Cu ^{IV} —S(2)—Cu ^{III}	111.47(18)
S(1) ^{IV} —Cu—S(1)	113.50(16)	Bi—S(2)—Bi ^{IV}	95.24(11)
—S(2)'''	109.43(12) 2 ×	Bi—S(2)—Cu'''	102.82(12) 2 ×

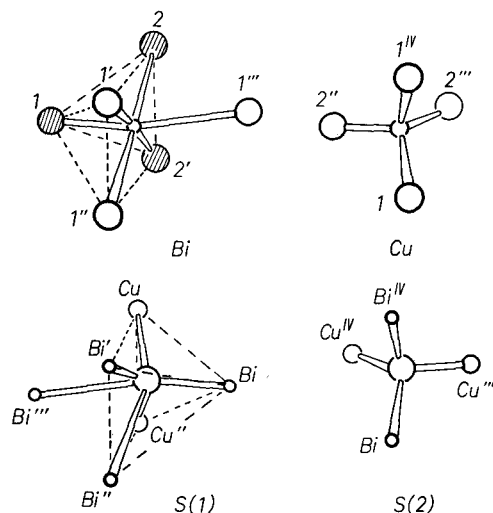


Fig. 1. Atomic coordinations in emplectite. For Bi and S(1) the square pyramids are indicated with broken lines. The three nearest S neighbours of Bi are marked by hatching

structures are 0.013, 0.036, 0.015 and 0.022 Å for Bi, Cu, S(1) and S(2) respectively.

The interatomic distances (Table 6) and angles (Table 7) are calculated with the aid of the program BDS (P. ENGEL, unpublished). Numerals of equivalent atoms are illustrated in Fig. 1 in which the coordinations of the atoms are drawn. In Fig. 2a the (010) projection of the structure is given.

Usually the Bi atom in sulfosalts has three S neighbours at approximately orthogonal distances smaller than 2.85 Å, spanning a trigonal pyramid⁴. This is also the case in emplectite and the average Bi—S distance of 2.614 Å lies near the lower limit of the range of averages 2.59–2.79 Å, observed in other sulfosalts. Each BiS₃ group shares corners with two adjacent groups in such a way that endless chains are formed running along *b*, having *b* as period and BiS₂ · $\frac{1}{2}$ + 1 = BiS₂ as composition.

The Cu atom is surrounded by four S atoms in a nearly regular tetrahedron. The average Cu—S distance of 2.327 Å lies well in the

⁴ Exceptions to this rule are the atoms Bi(1) in cosalite (Pb₂Bi₂S₅, WEITZ und HELLNER, 1960 and SRIKRISHNAN and NOWACKI, 1974) and in CuBi₅S₈ (OHMASA and NOWACKI, 1973). In cosalite Bi(1) has five S atoms nearer than 2.86 Å forming a square pyramid and in CuBi₅S₈ Bi(1) is coordinated octahedrally by six S atoms within this distance.

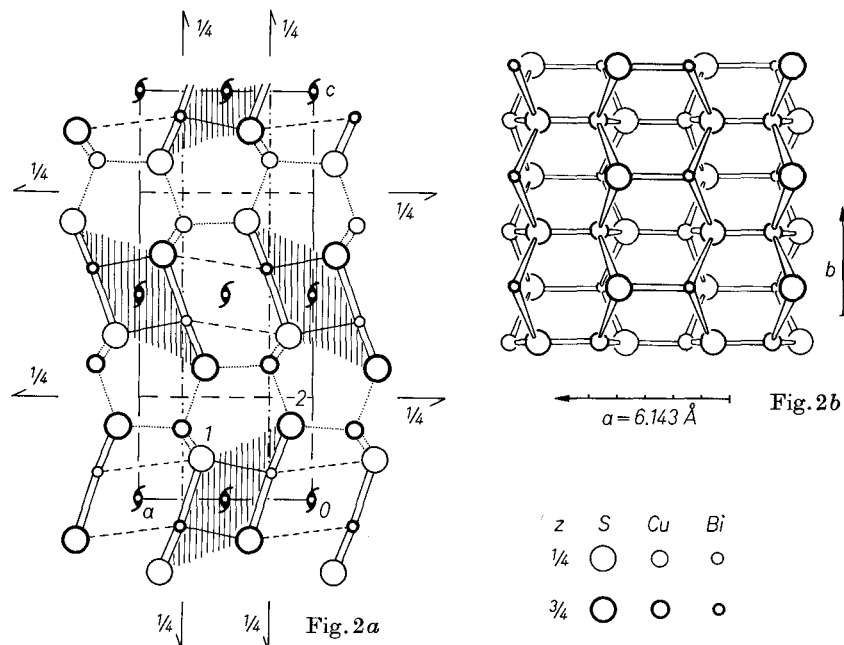


Fig. 2a. (010) projection of the emplectite structure. Bi—S distances inside the BiS_5 pyramids are fully drawn while those outside are broken. Cu—S distances are dotted. Double distances represent different distance vectors which are projected above each other. Hatched areas indicate the Bi_2S_4 double chains

Fig. 2b. Sheet of composition CuBiS_2 in emplectite perpendicular to c

range of 2.304–2.365 Å for Cu in tetrahedral coordinations not strongly distorted⁵. In the same way as the BiS_3 pyramids the CuS_4 tetrahedra are joint together into endless chains along b ; they have the composition $\text{CuS}_2 \cdot \frac{1}{2} + 2 = \text{CuS}_3$.

By means of corner sharing between the elementary tetrahedra and pyramids the two kinds of chains are joint in sheets perpendicular to c with a thickness of $\frac{1}{2}c$. The composition of these sheets as seen in Fig. 2b is CuBiS_2 . The sheet representation of the emplectite structure is in accordance with the principal cleavage along (001).

Within a distance of 3.2 Å the coordination of S(1) consists of three Bi and two Cu atoms in the form of a square pyramid. The farther Bi''' atom (see Fig. 1) completes a distorted octahedral coordination similar to that of Bi. The thermal parameters of Bi and S(1)

⁵ Coordinations with S—Cu—S angles of more than 115° are excluded.

are virtually equal which is consistent with this similarity. The thermal parameters of Cu and S(2) show the same trend, specifically $U_{\beta}(\text{Cu}) \sim 1.4 U_{\beta}\{\text{S}(2)\}$, but in view of the high symmetry of the coordinations involved it is not clear why in each case $U_{33} < U_{11} \sim U_{22}$.

Emplectite belongs to class IV in NOWACKI's (1969) classification since the atomic S/Bi ratio is equal to 2. The complete specification is IV.a₃ because of the endless chains of BiS₃ pyramids (of composition BiS₂).

Comparison of the structures of Cu,Bi-bearing sulfosalts

The structures of emplectite and the other Cu,Bi-bearing sulfosalts: CuBi₅S₈ (OHMASA and NOWACKI, 1973), Cu_{2+x}Bi_{6-x}S₉ ($x = 1.21$, OHMASA, 1973), hodrushite (Cu₃Bi₁₂S₂₂⁶, KUPČÍK and MAKOVICKÝ, (1968 and KODĚRA, KUPČÍK and MAKOVICKÝ, 1970) and Cu₄Bi₄S₉ (OZAWA and TAKÉUCHI, 1972) have in common Bi-containing structural units which are easily visualized if one takes into account neighbours more distant from Bi than the three nearest S atoms.

The five nearest S neighbours of Bi in sulfosalts are arranged in a square pyramid⁷ with Bi near the centre of the basal plane⁸. Distances towards the fourth and fifth nearest S atoms range between 2.86 and 3.16 Å.

Two types of Bi coordinations can be distinguished when further S neighbours are considered. Either there is one additional S at a distance between 2.99 and 3.45 Å completing an octahedron (type α) or there are two additional ones comprising a split vertex of an octa-

⁶ This is an idealized composition. The one resulting from microprobe analysis (KODĚRA *et al.*, 1970) is Cu_{8.12}Bi_{11.54}Fe_{0.29}S_{22.00}.

⁷ There are four examples where the square pyramid is not formed by the five nearest S atoms. The square pyramids of Bi(1) in bismuthinite (Bi₂S₃, KUPČÍK and VESELÁ-NOVÁKOVÁ, 1970), Bi(1) in Cu₄Bi₄S₉ and Bi(5) in hodrushite are formed by the three nearest S atoms together with the fifth and sixth nearest. For Bi(2) in galenobismuthite (IITAKA and NOWACKI, 1962) the square pyramid is realized within the six nearest S atoms if the third is omitted [see Fig. 3d].

⁸ The "square pyramid" for Bi in wittichenite Cu₃BiS₃ (KOCMAN and NUFFIELD, 1973) has an exceptional form. The three nearest S neighbours are arranged at virtually equal distances (2.57, 2.60 and 2.61 Å) and constitute a side face which is nearly perpendicular to the "basal plane". The fourth and fifth S atoms lie at unusual large distances 3.43 and 3.56 Å (normal value = 3.0 ± 0.15 Å). The BiS₃ pyramids occur as isolated units in the structure and consequently wittichenite, with its atomic S/Bi ratio of 3, belongs to type II.a₁ of NOWACKI's (1969) classification.

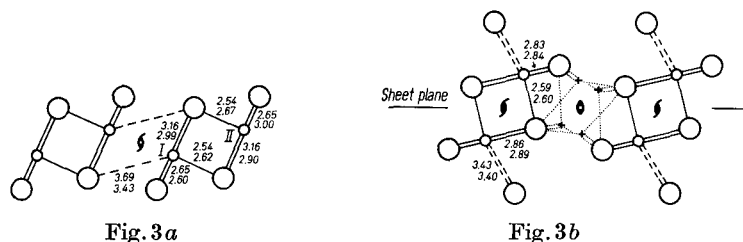


Fig. 3a

Fig. 3b

Fig. 3a. Schematic projection of two adjacent Bi_2S_4 chains in emplectite. In nuffieldite (KOHATSU and WUENSCH, 1973) a similar constellation of two chains is found. In the latter case M(4) (= Bi) corresponds to Bi(I) in the figure and M(1) (= Pb + Bi) to Bi(II). Distances are given in Å; upper values apply to emplectite

Fig. 3b. Fragment of the sheet which contains the type- β Bi atoms in CuBi_5S_8 and $\text{Cu}_{2+x}\text{Bi}_{6-y}\text{S}_9$. The square (on the twofold axis) and the crosses are the projections of the Cu atoms in the two structures respectively. Distances are given in Å

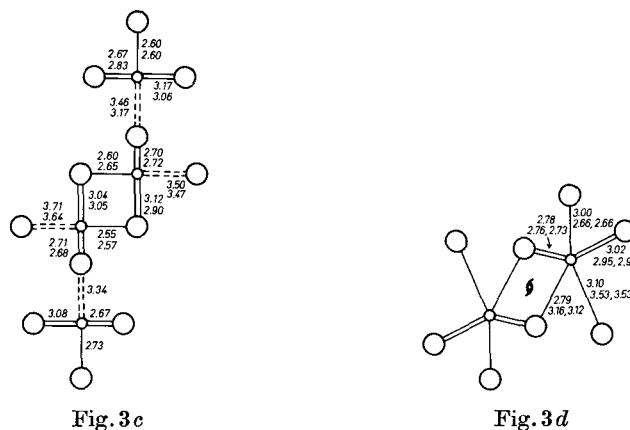


Fig. 3c

Fig. 3d

Fig. 3c. Schematic projection of the four-membered chain in hodrushite. Distances with two values indicate the three-membered subchain in $\text{Cu}_4\text{Bi}_4\text{S}_9$

Fig. 3d. Projections of the Bi_2S_8 chain in galenobismuthite (ITAKA and NOWACKI, 1962) and aikinite. The lower distance values correspond to aikinite (left: OHMASA and NOWACKI, 1970; right: KOHATSU and WUENSCH, 1971)

hedral coordination (type β). The octahedral coordination of Bi in emplectite will be characterized as type β , with one atom of the split vertex missing, because of the large deviation from regularity. The same coordination is found for M(4) (= Bi) in nuffieldite (KOHATSU and WUENSCH, 1973; see Fig. 3a).

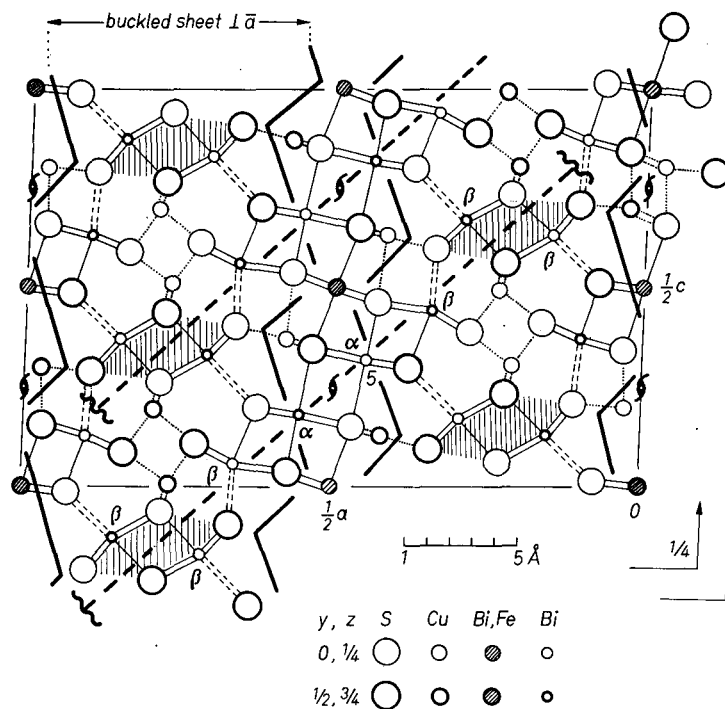


Fig. 4 (a)

Fig. 4. Projections of the structures of (a) hodrushite and (b) $\text{Cu}_4\text{Bi}_4\text{S}_9$ on the plane perpendicular to the axis of 4 \AA . Thick lines are the boundaries of the buckled sheets which consist of Bi atoms with type- β coordinations and CuS_4 tetrahedra. Broken lines with wavy ends mark the eight-membered chain which the two structures have in common. See also legend of Fig. 2a

The emplectite structure can now be described in another way. The basal planes of the BiS_5 pyramids, which are parallel to \mathbf{b} , share edges perpendicular to \mathbf{b} , thus forming endless chains with \mathbf{b} as period and $\text{BiS}_4 \cdot \frac{1}{2} + 1 = \text{BiS}_3$ as composition. Two of these chains are joint to a double chain, Bi_2S_4 , with the same period, by side-edge sharing of the elementary pyramids. The two single chains are related by an internal 2_1 axis (see Fig. 2a). The chains of CuS_4 tetrahedra, already mentioned, link the double chains in a three-dimensional structure by means of edge and corner sharing. Additionally there are Bi-S interactions of the sixth-nearest-neighbour type between the double chains (Fig. 3a).

Similar Bi_2S_4 double chains are found in the structures of CuBi_5S_8 , $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$, hodrushite and $\text{Cu}_4\text{Bi}_4\text{S}_9$. In all cases the chain periods

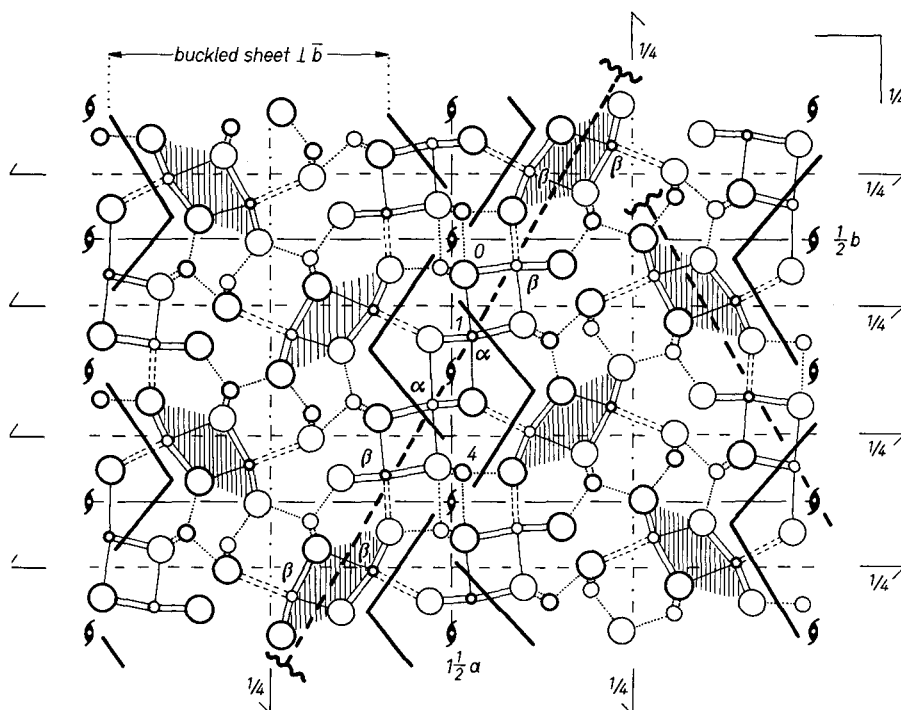


Fig. 4 (b)

correspond to the shortest lattice periods which are equal to 4.025, 3.993, 3.93 and 3.95 Å respectively. As in emplectite the Bi atoms in these chains have coordinations belonging to type β . The structures of hodrushite (KUPČÍK und MAKOVICKÝ, 1968) and $\text{Cu}_4\text{Bi}_4\text{S}_9$ (OZAWA and TAKÉUCHI, 1972) are given in Fig. 4 as projections on the plane perpendicular to the lattice translation of 4 Å.

In CuBi_5S_8 and $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$ the double chains are connected by parallel chains of distorted CuS_4 tetrahedra⁹ in sheets (Fig. 3b) with compositions of CuBi_2S_4 and $\text{Cu}_2\text{Bi}_2\text{S}_4$. The sheets are packed together alternatingly with parallel layers having a structure similar to PbS (OHMASA, 1973). In these layers there are only type- α -coordinated Bi atoms.

⁹ The chains in CuBi_5S_8 consist of tetrahedra which share edges perpendicular to an internal twofold axis. The tetrahedra are far from regular because of a compression of 0.7 Å along the chain axis. In $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$ there are two interwoven double chains of CuS_4 tetrahedra, with Cu occupancies of $\frac{1}{2}$, in between consecutive Bi_2S_4 chains. The CuS_4 tetrahedra share corners within a single chain and a double chain is formed by edge sharing.

The Bi_2S_4 chains in $\text{Cu}_4\text{Bi}_4\text{S}_9$ (along *c*) have attached to them a parallel single chain of Bi atoms which have a type- β coordination as well. The resulting three-membered chains (Fig. 3*c*) form, together with parallel chains of corner-sharing CuS_4 tetrahedra and CuS_3 triangles, buckled sheets perpendicular to *b*. In the structure these sheets are stacked anti-parallel to each other with double chains of BiS_6 octahedra and CuS_4 tetrahedra in between them.

The Bi atoms with type- β coordinations in hodrushite are found in four-membered chains (Fig. 3*c*), which consist of a central Bi_2S_4 double chain and two flanking single chains. Together with double chains of CuS_4 tetrahedra these four-membered chains form buckled sheets [parallel to (100)] similar to those in $\text{Cu}_4\text{Bi}_4\text{S}_9$. In the structure PbS-like layers with type- α Bi¹⁰ atoms are sandwiched by pairs of such sheets and the resulting triple layers are stacked parallel to each other with double chains of CuS_4 tetrahedra¹¹ and single chains of BiS_6 octahedra¹² in between them.

There is another similarity between the structures of $\text{Cu}_4\text{Bi}_4\text{S}_9$ and hodrushite which will be pointed out now. All Bi atoms in $\text{Cu}_4\text{Bi}_4\text{S}_9$ are found in eight-membered chains with internal distances smaller than 3.2 Å and a composition of Bi_8S_{16} . These eight-membered chains consist of two of the three-membered chains already mentioned at opposite sides of a double chain of octahedrally coordinated Bi atoms. The chains are stacked in a zig-zag way in the structure. In hodrushite these chains are found as subunits of sheets parallel to (302), which corresponds to the best developed crystal face (KODĚRA, KUPČÍK and MAKOVIČKÝ, 1970).

For CuBi_5S_8 , $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$, hodrushite, $\text{Cu}_4\text{Bi}_4\text{S}_9$ and emplectite the ratio of Bi atoms with type- β coordinations and the total number of Bi atoms increases monotonously as follows: 0.40, 0.42, 0.69, 0.75 and 1.00. The given order corresponds to an increase¹³ of the atomic

¹⁰ One third of the corresponding atomic positions is occupied for about $\frac{1}{2}$ by Bi and contains possibly the additional Fe in the structure (KODĚRA, KUPČÍK and MAKOVIČKÝ, 1970).

¹¹ The four independent Cu atoms in the structure have four S neighbours within 3.0 Å, which form a distorted tetrahedron in such a way that the Cu is near the centre of a side face. A similar coordination is found for one of the Cu atoms in $\text{Cu}_4\text{Bi}_4\text{S}_9$.

¹² The central atoms have the partial occupancies mentioned in footnote ¹⁰.

¹³ The Cu content of $\text{Cu}_4\text{Bi}_4\text{S}_9$ is probably a little lower than the formula indicates. OZAWA and TAKÉUCHI (1972) mention as a possible explanation for the high temperature factor ($B = 7.2 \text{ \AA}^2$) of Cu(4) a partial occupancy of this atoms.

ratio $\text{Cu}/(\text{Cu} + \text{Bi})$ ¹⁴. In the same order the distortions of constituent CuS_4 tetrahedra or the percentage of distorted ones decreases until in emplectite a near regularity is reached.

It seems that the geometries of the two Bi coordinations are incompatible. In all structures discussed there are endless chains consisting of Bi atoms with the same coordination type. The type- β Bi chains are joint together in multimembered chains with up to four chain units while the type- α Bi chains tend to form layers with a PbS-like structure. Together with single or double chains of CuS_4 tetrahedra the multimembered chains form sheets which in CuBi_5S_8 and $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$ occupy about 45% of the cell volume and in hodrushite and $\text{Cu}_4\text{Bi}_4\text{S}_9$ about 80%. Emplectite is a three-dimensional array of type- β Bi (double) chains and CuS_4 chains and consequently its structure comprises the limiting case of the mentioned structures which contain sheets.

In the sulfosalt structures known thus far it appears that the Bi_2S_4 double chain is specific for the Cu,Bi-bearing sulfosalts. When additional Pb is present in the structure four-membered Pb,Bi-mixed chains occur (KOHATSU and WUENSCH, 1973) which are similar to the four-membered chains in bismuthinite. Just as in the case of the Bi_2S_4 double chains the end members of these four-membered chains are single chains of Bi atoms with type- β coordinations. In galenonbismuthite and aikinite (PbCuBiS_3 , OHMASA and NOWACKI, 1970; KOHATSU and WUENSCH, 1971) another type of double chain (Fig. 3d) is found which consists of Bi atoms with type- β coordinations. This chain has the composition Bi_2S_8 .

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¹⁴ For hodrushite the ratio $\text{Cu}/(\text{Cu} + \text{Bi} + \text{Fe})$ is taken.

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