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STUDIES OF THE SULFOSALTS OF COPPER. II. THE CRYSTALLOGRAPHY AND COMPOSITION OF SINNERITE, $Cu_6As_4S_9$.

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ABSTRACT

Synthetic sinnerite has the composition $Cu_6As_4S_9$; it is triclinic, space group $P1$, with cell dimensions $a = 9.06$ Å, $b = 9.83$ Å, $c = 9.08$ Å, $\alpha = 90°00'$, $\beta = 109°30'$, $\gamma = 107°48'$ and a pronounced pseudocubic F-centered subcell ($a = 5.25$ Å). The crystals are twinned so that each composite prism contains six individuals twinned on the planes (010) and (110). The other twin laws, the twin plane (410) and threefold axis parallel to [001], are secondary and derived by a multiple application of the two primary ones.

INTRODUCTION

Sinnerite was described as a new mineral by Marumo and Nowacki (1964) from a highly twinned crystal found in the Lengenbach Quarry, Binnenthal, Switzerland. The authors were able to establish a composition by electron microprobe analysis, the X-ray powder diffraction pattern, a possible symmetry, and a specific gravity of 5.2.

During a study of the phase relations of the system Cu–As–S, Maske and Skinner (1971) prepared a phase on the join Cu_2S–As_2S_3 which, on the basis of X-ray powder diffraction patterns and composition, they identified as sinnerite.

COMPOSITION

Marumo and Nowacki reported analyses of their crystal by two different electron microprobes without stating the uncertainties. Because the difference in copper contents between the two sets of data exceeds 2 percent by weight, we tend to accept the average of the elements present.

The analytical results are close to, but not identical with, the composition determined by Maske and Skinner (see Table 1). The synthetic composition was determined by complete reaction of carefully weighed charges of Cu + As + S, and is accurate to ±0.2 percent by weight of each element. Within the limits of weighing accuracy, the composition of the synthetic compound coincides exactly with $3Cu_2S \cdot 2As_2S_3$, or $Cu_6As_4S_9$. Thus, within the presumed uncertainties of Marumo and Nowackis' analyses, the composition of natural and synthetic phases are identical. Although no evidence was found in

Table 1. Composition of sinnerite in weight percent. Analyses of the Lengenbach crystal from Marumo and Nowacki (1964). Synthetic material from a sample prepared at 450°C by Maske and Skinner (1971). The formula derived from the synthetic sample is $Cu_6As_4S_9$.

Sample	Cu	As	S	Total
Lengenbach	41.3%	29.2%	29.8%	100.3
Lengenbach	39.1	29.7	28.7	97.5
Mean	40.2	29.5	29.3	99.0
Synthetic	39.33	30.93	29.74	100.00

synthetic samples to indicate a compositional variation for sinnerite, the possibility must still be entertained for natural samples.

STABILITY AND SYNTHESIS OF SINNERITE

Sinnerite was synthesized at a number of temperatures at and above 300°C by Maske and Skinner. The upper limit of thermal stability is 489°C, where it melts incongruently to the compound $Cu_{24}As_{12}S_{31}$ (a phase not known as a mineral) and an As–S liquid. Maske and Skinner did not establish a lower temperature of stability for sinnerite and 300°C only represents the lowest temperature at which reasonable reaction rates could be obtained for the method of synthesis employed. There is no evidence to suggest that sinnerite does decompose between 25°C and 300°C and we therefore believe that it is a stable phase from room temperature to 489°C.

The effect of pressure on the stability of sinnerite has not been systematically investigated. In an attempt to grow untwinned crystals for X-ray diffraction studies, we recrystallized a finely ground sinnerite powder in the presence of a 2 molar NH_4Cl solution at 450°C and 2000 atm. pressure, using a welded gold capsule and a temperature and pressure controlled cold seal bomb. The powder recrystallized to individual crystals as large as 1 mm across, unfortunately always twinned, establishing that sinnerite is still stable at the pressure and temperature of the run.

The stability observations suggest that suitable chemical environments, rather than temperature and pressure, are likely to be the limiting factors in the occurrence of sinnerite in nature.

Crystals of sinnerite for the present study were prepared by reacting appropriate amounts of spectrographically pure Cu, As, and S in sealed, evacuated silica glass tubes at 450°C for a period of three weeks. The crystals always grow in mutually parallel groups of composite prisms nucleated on a large sinnerite grain below. Cross-sections of the composite prisms range from roughly rectangular to hexagonal, but with re-entrant angles, reflecting the complexity of growth twins (Fig. 1). In polished sections twins have coarse, irregular and interlocking boundaries whereas no fine-scaled polysynthetic twinning has been observed. This, together with a lack of any thermal anomaly on a heating curve of sinnerite as well as with the complete optical and X-ray identity of sinnerite quenched from 300°C with the material quenched from temperatures just below the melting point, suggests that the twinning of sinnerite is a growth phenomenon.

X-RAY DIFFRACTION

Weissenberg photographs of the composite crystals reveal (1) a very strong sphalerite-type subcell (a feature also observed by Marumo and Nowacki) and (2) very weak additional spots arranged in mutually inconsistent rows and peculiar clusters (Figs. 2, 5). If sharp differences in the intensities of adjacent geometrically identical groups of spots are not taken into account, the reciprocal lattice of each

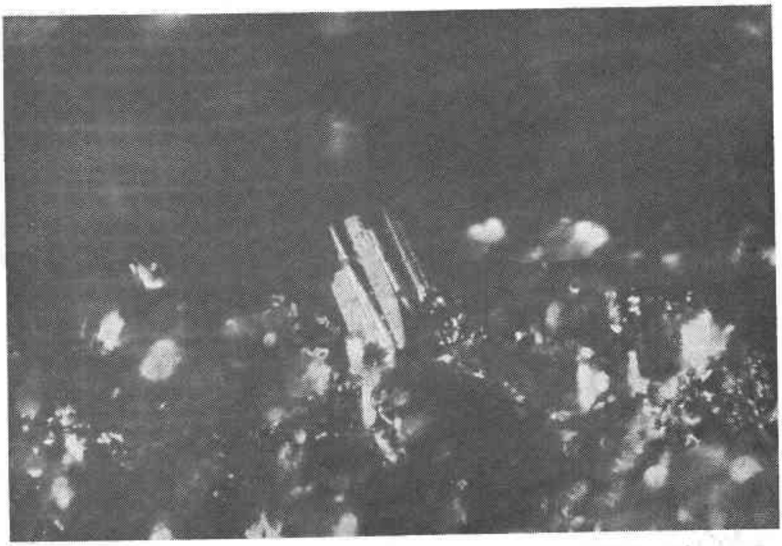

FIG. 1. Composite prism of synthetic sinnerite grown at 450°C with re-entrant angles. Length 0.1 mm.

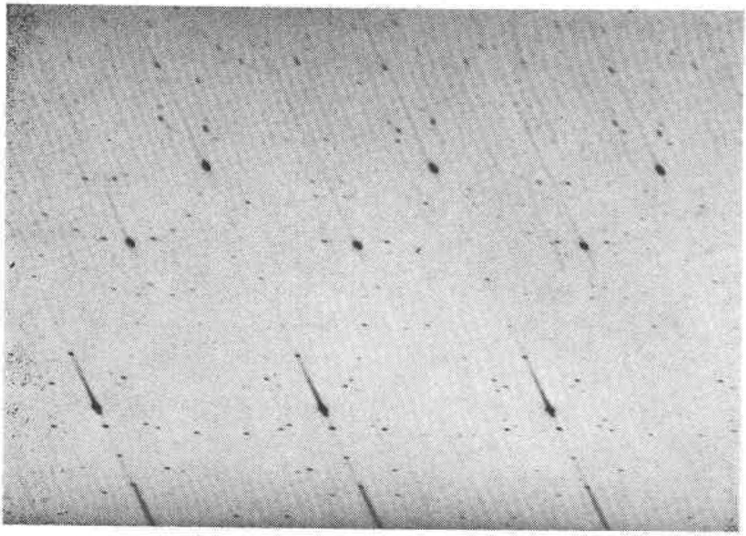

FIG. 2. Zero-level Weissenberg photograph of a sinnerite composite twin. Strong reflections belong to six closely overlapping pseudocubic subcells and weak reflections to six triclinic sinnerite lattices. The relationships may be traced with a help of Figure 3.

composite prism displays rhombohedral holohedry. The intensity of different clusters and of individual reflections in each cluster varies between different composite prismatic crystals. This suggests that each set of reflections connected by the rhombohedral symmetry represents the same reflection from six differently sized individuals in a composite twin. The multiple character of the strong subcell spots shows that they also represent several overlapping orientations of a slightly deformed sphalerite-type subcell.

Detailed tracing of the Weissenberg photographs reveals that sinnerite has a primitive triclinic lattice with a unit cell as follows:

$$
\begin{aligned}
a &= 9.064 \pm 0.008 \text{ Å} \\
b &= 9.830 \pm 0.008 \text{ Å} \\
c &= 9.078 \pm 0.008 \text{ Å} \\
\alpha &= 90°00' \pm 20' \\
\beta &= 109°30' \pm 20' \\
\gamma &= 107°48' \pm 20'
\end{aligned}
$$

The subcell indicates that the crystal structure of sinnerite is built on a sphalerite-type substructure and, consequently, that the noncentrosymmetric group $P1$ must be assumed for the mineral. The F-centered subcell is only slightly deformed against the ideal cubic situation:

$$\begin{array}{ll} a = 5.25\ \text{Å} & \alpha = 89°59' \\ b = 5.25\ \text{Å} & \beta = 89°45' \\ c = 5.23\ \text{Å} & \gamma = 90°29' \end{array}$$

The unit cell of sinnerite is given in terms of the F-centered subcell by the matrix

$$\begin{array}{ccc} -1 & -1 & 1 \\ 3/2 & -1 & -1/2 \\ 1 & 1 & 1 \end{array}$$

The a and c-axes of sinnerite are perpendicular to two different sets of sphalerite-type layers of tetrahedra, and their lengths are almost

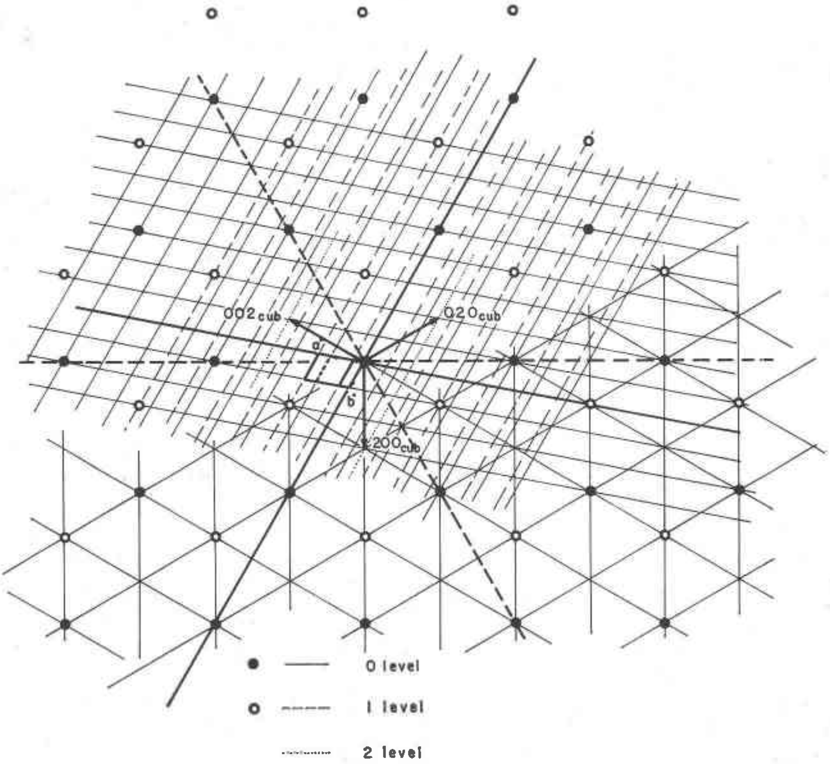

FIG. 3. Zero and first levels of the reciprocal lattice of sinnerite. Nodes of the cubic sublattice are denoted by circles. Reciprocal cell of sinnerite (in a projection on the $a^*\cdot b^*$ plane) and edges of the cubic reciprocal subcell are given in heavy outlines at the origin.

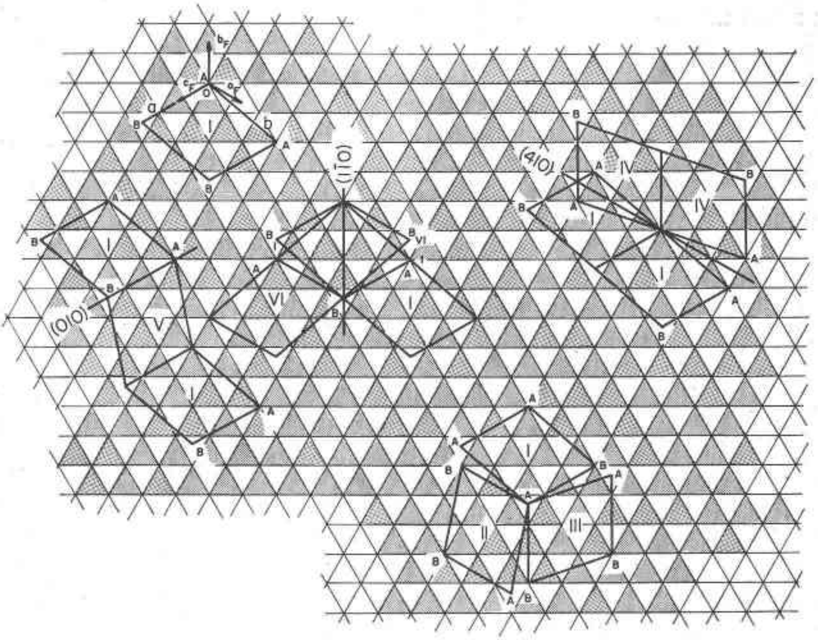

FIG. 4. Unit cell, edges of the *F*-centered cubic subcell and four observed twin laws of synthetic sinnerite on a background of the cubic substructure of sinnerite. Projection along the *c*-axis, perpendicular to the *ABC* layer stack of tetrahedra of the cubic sphalerite-like substructure with the tetrahedra of the *A* layer shaded. A and B indicate the position of the ends of the unit cell vectors with respect to the layers when the origin is situated in the *A* layer.

equal because they correspond to the height of 3 layers of tetrahedra. In this respect, sinnerite is similar to the 3 layer *c*-axis repeat in nowackiite, a Cu(Zn)–As sulfosalt also based on the sphalerite substructure (Marumo, 1967). The difference between sinnerite and nowackiite may best be illustrated by comparing the matrices relating their unit cells to the smallest hexagonal cell possible in the sphalerite-type substructure with the *c*-axis parallel to those of the two minerals:

$$\begin{array}{ccc} 1\ 1/3 & -1\ 1/3 & -1/3 \\ 2 & 3 & 0 \\ 0 & 0 & 1 \end{array}$$

for sinnerite, and

$$\begin{array}{ccc} 4 & 1 & 0 \\ -1 & 3 & 0 \\ 0 & 0 & 1 \end{array}$$

for nowackiite. The c-axis of sinnerite is parallel to the elongation of the prismatic twins and common to all individuals of a twin.

Three-dimensional considerations show that sinnerite contains 20 MeS tetrahedra of the sphalerite-type substructure in one unit cell. Total cell volume being 721.19 Å^3, the fraction of the cell volume per one tetrahedron is almost exactly the same as in an ideal sphalerite structure with dimensions reduced to fit the equation

$$[111]_{\text{cubic}} = [001]_{\text{sinnerite}} \text{ or } [001]_{\text{nowackiite}}$$

The empirical chemical formula of sinnerite recalculated for 20 metal atoms per unit cell is then almost exactly $Cu_6As_4S_9$ with $Z = 2$.

The pseudocubic subcell of sinnerite found by us is practically identical with that described by Marumo and Nowacki (1964). Their orthorhombic subcell as well as two of the three twinning planes suggested tentatively by them were not confirmed by our results and the same holds consequently for their tentative unit cell. Some of the submultiples in the sections of the reciprocal lattice of sinnerite given by Marumo and Nowacki indicate that the natural and synthetic material have the same reciprocal lattices and these authors used the reciprocal direction $[2\bar{1}2]$ of sinnerite as their c direction.

The powder diffraction pattern of sinnerite contains a very pronounced system of subcell reflections forming strong, broad lines (Table 2) which become finely split at high angles. True-cell reflec-

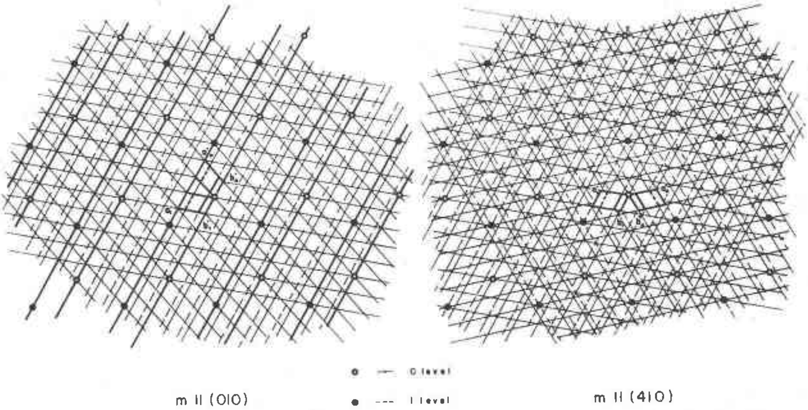

FIG. 5. Manifestation of the twinning on planes (010) and (410) in the reciprocal space. Zero and first levels of the reciprocal lattice of sinnerite are given. Subcell nodes denoted by circles, true-cell by the intersections of the reciprocal-lattice grid. Reciprocal unit cells of the two twin individuals (in projection on the $a^*\cdot b^*$ plane) and overlapping rows of the reciprocal lattices of them are indicated by heavy solid lines for both levels.

Table 2: X-ray powder diffraction data for synthetic sinnerite compared to natural sinnerite from Lengenbach after Marumo and Nowacki (1964). CuKα radiation (λ=1.5418Å) Ni filter. Relative intensities (I) estimated visually on a scale of 10. B indicates a broad line. Indices calculated from the single crystal data.

Present work		M & N	Indices in terms of the unit cell of Sinnerite	
d(Å)	I	d(Å)	Subcell reflections	The strongest true-cell reflections
3.343	2			$2\bar{1}1$
3.024	10	3.041	$121,1\bar{3}1,\bar{3}11,\bar{1}03$	
2.611	4	2.634	$2\bar{1}2,\bar{2}32,\bar{2}22$	013
2.538	0.5			$\bar{3}31,\bar{3}\bar{1}1,\bar{1}23,\bar{1}\bar{2}3$
2.237B	1			$2\bar{4}1,\bar{4}21$
2.177B	0.5			$\bar{1}14,\bar{3}\bar{2}1,\bar{1}33$
2.149B	0.5			$\bar{3}41,1\bar{4}2$
2.109	0.5			$\bar{1}42,\bar{3}33$
2.054	1			$320,\bar{1}\bar{4}0,132,3\bar{2}2,\bar{3}42,\bar{3}04,\bar{1}\bar{2}4$
1.915B	0.5			$\bar{2}43,2\bar{3}3,1\bar{5}1,141$
1.852	8	1.859	$4\bar{4}0,410,050,\bar{4}14,0\bar{3}4,024$	
1.667	0.5			$4\bar{5}0,420,0\bar{4}4,034$
1.640	0.5			$\bar{5}41,\bar{1}\bar{4}4,\bar{1}25$
1.614	0.5			$500,151,1\bar{6}1,\bar{2}61,1\bar{4}4$
1.581	7	1.584	$5\bar{2}1,\bar{3}\bar{4}1,\bar{3}61,313,\bar{1}53,\bar{5}43$ $\bar{3}35,\bar{3}\bar{2}5,1\bar{1}5$	$\bar{2}35$
1.556	2			$\bar{4}\bar{3}1,\bar{2}\bar{5}1,5\bar{3}1,\bar{4}53,\bar{4}\bar{1}5,1\bar{2}5,\bar{2}\bar{3}\bar{5},105$
1.514	0.5	1.516	$242,\bar{6}22,2\bar{6}2,\bar{2}06$	
1.329	0.5			$4\bar{7}0,440,6\bar{3}1,\bar{4}71,\bar{6}53,4\bar{5}3,3\bar{6}3,054$ $0\bar{6}4,1\bar{2}6$
1.312	2	1.313	$4\bar{2}4,\bar{4}64,\bar{4}\bar{4}4$	$106,\bar{3}\bar{3}6$
1.297	0.5			$4\bar{3}4,\bar{3}\bar{5}4$
1.288	0.5			$\bar{2}\bar{1}7,\bar{7}23,324,\bar{3}46,\bar{7}32$
1.205	3	1.206	$\bar{7}51,\bar{7}01,5\bar{7}1,531,171,1\bar{8}1$ $\bar{7}25,1\bar{6}5,145,\bar{5}17,\bar{1}\bar{3}7,\bar{1}27$	
1.172	0.5	1.174	$6\bar{5}2,602,\bar{6}72,\bar{6}\bar{3}2,\bar{2}82,2\bar{7}2$ $2\bar{4}6,\bar{6}46,216,\bar{6}\bar{1}6,\bar{2}56,\bar{2}\bar{5}6$	
1.072	2	1.073	$8\bar{3}0,460,\bar{4}90,434,4\bar{7}4,\bar{8}54$ $0\bar{8}4,074,\bar{8}04,\bar{4}28,0\bar{1}8,\bar{4}38$	$\bar{2}\bar{3}8,\bar{7}73$
1.060	0.5			$370,6\bar{7}2,5\bar{8}2,\bar{3}92,622,2\bar{6}6,236$
1.010B	1	1.010	$7\bar{3}3,\bar{9}33,5\bar{9}3,3\bar{9}3,363,\bar{5}\bar{6}3$ $5\bar{5}5,\bar{7}\bar{3}5,505,\bar{3}85,775,\bar{3}\bar{7}5$ $3\bar{2}7,\bar{5}\bar{4}7,\bar{5}67,\bar{3}09$	$2\bar{5}7$
			Subcell reflections only (CuKα_1 and α_2):	
0.928	0.5		$\bar{8}80,820,0.10.0,\bar{8}28,0\bar{6}8,048$	
0.887B	1		$9\bar{1}1,9\bar{6}1,\bar{7}.10.1,\bar{3}.11.1,\bar{3}\bar{9}1,\bar{7}\bar{5}1,\bar{9}\bar{2}3,723,7\bar{8}3,\bar{9}83,\bar{1}.\overline{10}.3,\bar{1}.10.3,$ $\bar{9}57,\bar{9}07,337,3\bar{7}7,\bar{1}\bar{8}7,\bar{1}77,119,1\bar{4}9,\bar{3}\bar{5}9,\bar{3}59,\bar{7}\bar{1}9,\bar{7}49$	
0.884 & α_2 0.887			$\overline{10}.6.2,\overline{10}.1.2,6.\overline{10}.2,652,2.\overline{11}.2,292,\overline{10}.3.6,6\bar{3}6,2\bar{9}6,\bar{6}96,\bar{6}\bar{6}6,$ 266	
0.830B	1		$8\bar{6}4,\bar{4}.11.4,\bar{8}.10.4,\bar{8}\bar{5}4,\bar{4}\bar{9}4,4\bar{5}8,408,\bar{8}78,\bar{4}\bar{7}8,\bar{8}\bar{3}8,\bar{4}88$	
0.802B	0.5		$1.\overline{11}.5,195,581,\bar{2}.2.10,\bar{6}.1.10,\bar{2}.\bar{3}.10$	
0.800 & α_2 0.802			$555,\overline{11}.6.5,\overline{11}.1.5,5.\overline{10}.5,5.\overline{12}.1,\overline{11}.4.1,\bar{6}\bar{8}2,10.\bar{4}.2,\bar{6}.12.2,$ $626,6\bar{8}6,\overline{10}.\bar{2}.6,\overline{10}.8.6,\bar{2}.\overline{10}.6,\bar{2}.10.6$	

Table 3. Detailed analysis of two subcell lines from the powder pattern of sinnerite

d meas (Å)	Components and their d-spacings (Å)	Contribution to the line width from the spread of d values $\Delta\theta = \theta_{max} - \theta_{min}$
1.205	$\bar{7}54$ (1.2003), $\bar{7}25$ (1.2012), $\bar{7}01$ (1.2017), $5\bar{7}1$ (1.2020), $\bar{5}17$ (1.2021), $\bar{1}37$ (1.2026), $\bar{1}27$ (1.2029), $1\bar{6}5$ (1.2034), 531 (1.2041), 145 (1.2045), $1\bar{8}1$ (1.2060), 171 (1.2069)	0.26°
1.072	$8\bar{3}0$ (1.0680), $\bar{8}54$ (1.0684), $\bar{8}04$ (1.0693), $4\bar{7}4$ (1.0695), $0\bar{1}8$ (1.0696), $\bar{4}38$ (1.0700), $\bar{4}\bar{2}8$ (1.0702), 434 (1.0710), $\bar{4}90$ (1.0714), $0\bar{8}4$ (1.0724), 074 (1.0730), 460 (1.0731) $\bar{2}\bar{3}8$ (1.0720), $\bar{7}73$ (1.0754)	0.29°

tions are weak and very few of them are measurable. Due to the small amount of material Marumo and Nowacki (1964) obtained only the lines of the strong subcell reflections. The presence in sinnerite of the typical subcell with dimensions and consequently *d*-spacings definitely different from the subcells of the other phases of the Cu–As–S system (Maske and Skinner, 1971) makes the identity of the natural and synthetic phases well established. We have indexed the powder pattern of sinnerite using the single-crystal data, both the interplanar distances and the X-ray intensities. The subcell lines which are always broad, clearly result from a sizable set of overlapping lines with slightly different *d*-values (Table 2, 3). The ratio of subcell to true-cell intensities from a single crystal is about 500:1 for the small values of θ. While this ratio drops to 10:1 for the reflections with the highest θ angles, the drop is offset by an increasing number of reflections contributing to a given line in this region. Multiplicity of reflections makes it impossible to index them by standard indexing procedures.

Table 4. Twinning of the lattice of synthetic sinnerite

Twin law	Note	Overlapping lattice spots
m//(010)	for the lattice: identical with 2 ⊥ (010)	$\underline{h} = 4n + \underline{\ell}$
m//($\bar{1}$10)	identical with 2 ⊥ ($\bar{1}$10)	$\underline{h} + \underline{k} = 5n - 2\underline{\ell}$
m//(410)	identical with 2 ⊥ (410)	subcell spots only
3//[001]	rotation of 120° and 240°	subcell spots only for both rotations

Table 5. Twin operations between the six lattice orientations of a sinnerite twin

		from twin individual number:					
		1	2	3	4	5	6
to twin individual number:	1	1	3	3^{-1}	m_{410}	m_{010}	$m_{\bar{1}10}$
	2	3^{-1}	1	3	$m_{\bar{1}10}$	m_{410}	m_{010}
	3	3	3^{-1}	1	m_{010}	$m_{\bar{1}10}$	m_{410}
	4	m_{410}	$m_{\bar{1}10}$	m_{010}	1	3	3^{-1}
	5	m_{010}	m_{410}	$m_{\bar{1}10}$	3^{-1}	1	3
	6	$m_{\bar{1}10}$	m_{010}	m_{410}	3	3^{-1}	1

Note: 3 is a positive rotation of 120° around [001]
3^{-1} is a positive rotation of 240° around [001]
m_{hkl} is a mirror parallel to (hkl)

TWINNING

Due to the small size and insufficient morphological quality of the crystals of synthetic sinnerite only the X-ray information on twinning is available. Every composite prism contains six lattice individuals with sizes varying from substantial to almost imperceptible in X-ray photograph. If we pick up anyone of them the remaining 5 individuals are related to it by the operations of symmetry given in Table 4. The overlapping of certain spots of the reciprocal lattice, resulting from the twinning, is perfect for the ideal cubic sublattice and but slightly imperfect for the real sublattice. All the twin operations completely restore the sphalerite-type sublattice, representing thus a twinning by reticular pseudomerohedry (Donnay, written communication, 1971) of a triclinic lattice based on a highly symmetrical pseudocubic sublattice (Fig. 4). In two cases overlapping goes beyond the strong sublattice spots and influences parallel rows of the sinnerite lattice (Table 4, Fig. 5). If the contact planes of the individuals of the twin follow the twin planes (010), ($\bar{1}10$), (410) the fit of the two individual lattices is perfect. The individuals related by the three-fold axis, however, have not only unit cells without a real contact but also the largest possible misfit of the lattices in any contact plane. Therefore, this twin law is only secondary to the preceeding laws in the Table 4, and has been generated by a subsequent application of several mirror operations to the first individual lattice (Table 5). The same apparently holds for the twinning on the (410) twin plane which fails to restore the nodes of the sinnerite lattice. Thus the twin planes (010) and ($\bar{1}10$) connect one individual with two others and each of these is again connected by such a reflection operation with another individual etc., finally resulting in an intergrowth of six lattices (Table 5). Needle-like composite crystals of sinnerite exhibited only the above described modes of twinning of all the modes which can be constructed from the cubic character of the sublattice. Angular imperfections of a random nature in the twin orientations were observed in some cases but they do not exceed the value of 30′. The crystal structure determination is in an advanced stage and will be reported separately.

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REFERENCES

MARUMO, F., AND W. NOWACKI (1964) The crystal structure of lautite and of sinnerite, a new mineral from the Lengenbach quarry. *Schweiz. Mineral. Petrogr. Mitt.* 44, 439–454.

MARUMO, F. (1967) The crystal structure of nowackiite, $Cu_6 Zn_3 As_4 S_{12}$. *Z. Kristallogr.* 124, 352–368.

MASKE, S., AND B. J. SKINNER (1971) Studies of the sulfosalts of copper I. Phases and phase relations in the system Cu–As–S. *Econ. Geol.* 66, 901–918.

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