The Crystal Structure of Lautite and of Sinnerite, a New Mineral from the Lengenbach Quarry[1])

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Summary

Lautite, CuAsS, is orthorhombic, space group *Pnma*, with four chemical units per unit cell of dimensions

$$a_0 = 11.356 \pm 0.008, \quad b_0 = 3.754 \pm 0.005, \quad c_0 = 5.453 \pm 0.005 \text{ Å}.$$

The crystal structure has been determined from a study of a *b*-axis projection and refined by means of threedimensional least square method. The structure is based on the diamond lattice and the atoms are arranged in such a way that each Cu is surrounded by 1 As + 3 S, each As by 1 Cu + 2 As + 1 S and each S by 3 Cu + 1 As. The bond length of As-As (2.498 Å) is equal to that of metalic As. The As-S (2.239 Å) and Cu-S (2.30 Å) bonds have normal values as in other arsenosulfides.

In the Lengenbach dolomite a small crystal of sinnerite, a new copper arsenosulfide mineral was found. The X-ray diffraction diagrams of sinnerite show a complicated superlattice structure pattern with a small subcell. The dimensions of the subcell are

$$a' = 3.72 \pm 0.01, \quad b' = 3.70 \pm 0.01, \quad c' = 5.24 \pm 0.01 \text{ Å}, \quad \alpha' = \beta' = \gamma' = 90°.$$

The symmetry of sinnerite is probably triclinic. Structurally sinnerite is closely related to binnite.

Introduction

In the course of the systematical study of the sulfosalt minerals from Lengenbach, Binnatal, a new mineral, a copper arsensulfide was found,

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which has some similarity to binnite and lautite in its unit cell dimensions and chemical composition. The mineral was named *sinnerite* in honour of the late RUDOLF VON SINNER, president of the Commission of the Naturhistorisches Museum Bern.

The crystal structure of binnite was determined by F. MACHATSCHKI (1928) and by L. PAULING and E. W. NEUMAN (1934). However, the details of the structure of lautite were not known, though two short notes on the structure were published by R. WEIL and R. HOCART (1939) and by S. KULPE (1961). The structure determination of lautite was, therefore, carried out to clarify the structural relationship between binnite, lautite and sinnerite. Since we could not get a single crystal of sinnerite (only twins), the precise structure of the mineral could not be determined, but some discussion on its structure is given in this paper.

A. The Crystal Structure of Lautite

1. Experimental

A crystal from the Grube Gabe Gottes near Sainte-Marie-aux-Mines was used in this investigation. The unit cell dimensions obtained from Weissenberg and oscillation photographs are

$$a_0 = 11.38 \pm 0.02, \quad b_0 = 3.77 \pm 0.01, \quad c_0 = 5.46 \pm 0.01 \text{ Å},$$

and the space group is *Pnma*. The values are in good agreement with those given by R. WEIL and R. HOCART (1939) and by S. KULPE (1961). However, since the measurement by S. KULPE seemed to be more accurate than ours, the values given by him, $a_0 = 11.356 \pm 0.008$ Å, $b_0 = 3.754 \pm 0.005$ Å, $c_0 = 5.453 \pm 0.005$ Å, were used throughout this study. An X-ray microanalysis gave the following chemical composition for this material,

$$Cu = 39.4\%, \quad As = 45.4\%, \quad S = 17.5\%.$$

The unit cell content calculated from these values, assuming 4.9 gcm^{-3} (DANA, 1944) for the density of this crystal, is $Cu_{4.25}As_{4.16}S_{3.74}$, which is identical with $4CuAsS$ within the experimental error. This idealized formula was used for the structure determination.

Since it was very difficult to make a small sphere with this material, a fragment with the dimension of about $0.07 \times 0.07 \times 0.06$ mm^3 was used for the intensity measurements. The integrated equiinclination Weissenberg photographs were taken with Cu Kα-radiation up to the third

layer, both around the b-axis and the c-axis. Intensities of about 400 threedimensional reflections were measured with a microdensitometer. The absorption corrections were made, assuming a spherical shape with the diameter of 0.065 mm of the crystal. The correction factors are ranged between 4.70 at $\theta = 0°$ and 3.25 at $\theta = 90°$. Since μr is not so large, the assumption of a spherical shape is sufficient for the present purpose.

2. Structure Determination

According to S. KULPE (1961) the crystal structure of lautite is based on the diamond lattice. All three kinds of atoms (Cu, As, S) occupy the equipoints of a diamond lattice in such a way that each Cu is surrounded by 1 As + 3 S, each As by 1 Cu + 2 As + 1 S and each S by 3 Cu + 1 As. Actually, there is a simple relationship between the lengths of the three axes, namely, $\sqrt{2/3}\,a_0 \doteqdot \sqrt{2}\,b_0 \doteqdot c_0 \doteqdot a_{\text{zincblende}}$. The number of atoms in the unit cell is 12, which is the same as the number of atoms in the corresponding volume of the zincblende structure.
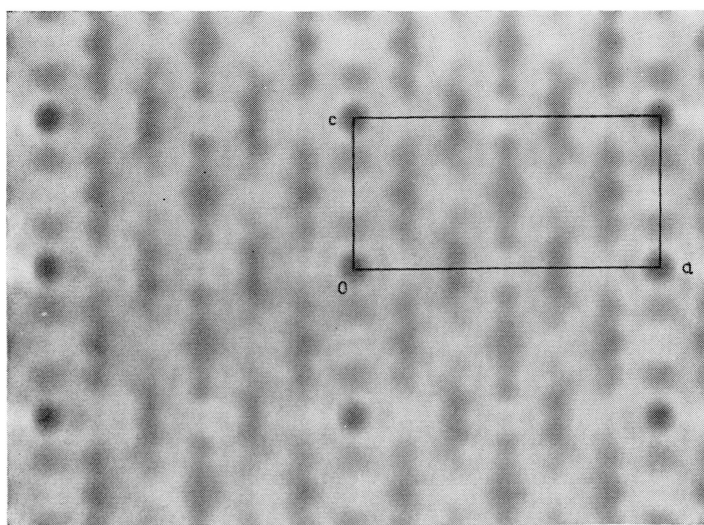
Fig. 1. Patterson projection along the b-axis.

The Patterson projektion $P(x,z)$ along the b-axis was prepared by von Eller's method (Fig. 1) to confirm the similarity to the diamond structure. If the structure is constructed on the diamond lattice, Patterson peaks must appear only at the positions of $(0,0)$, $(0,1/4)$, $(1/6,1/4)$, $(1/6,1/2)$, $(1/3,0)$, $(1/3,1/4)$, $(1/2,1/4)$, $(1/2,1/2)$, and the symmetrically related ones. The peaks in Fig. 1 obviously satisfy this condition, showing the existence of the similarity stated above. Since four chemical units of

CuAsS are contained in the unit cell, all the atoms must be at the four-fold position (c), namely on mirror planes, to form a diamond lattice. There is one independent atom in an asymmetric unit for each kind of atoms.

From the above information, we can deduce the approximate atomic positions as shown in Fig. 2, though it is still unknown which is occupied by a particular kind of atoms among the three independent positions in the figure. There are three different ways of assignment of atoms. One of them is the same arrangement as S. KULPE reported and most probable from the crystallochemical viewpoint. The $h0l$ structure amplitudes were
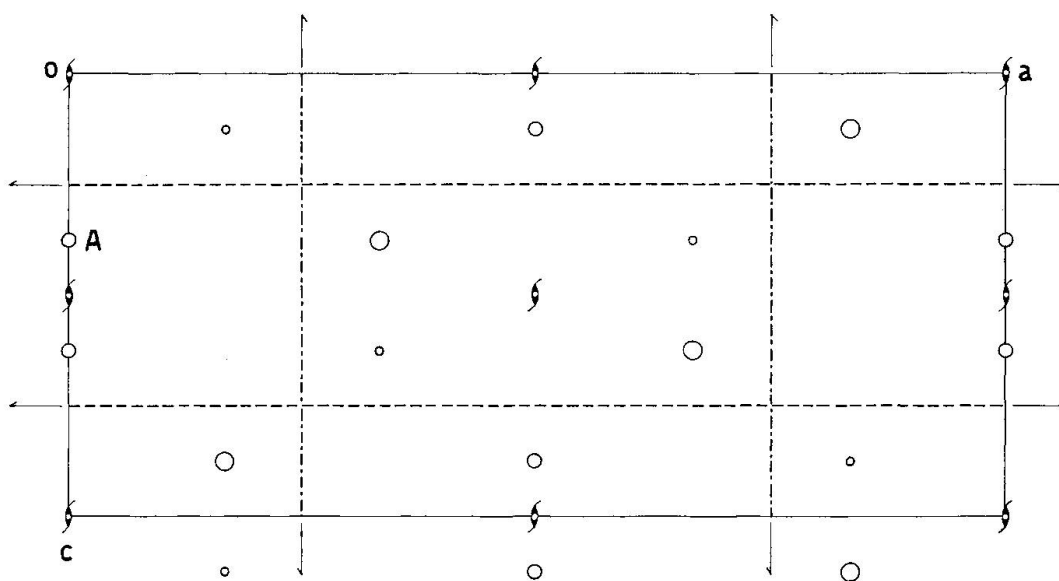
Fig. 2. An idealized atomic arrangement in the structure of lautite.

calculated for all of these atomic configurations, utilizing the atomic coordinates of the ideal diamond structure. However, no good agreement between the observed and the calculated structure factors was obtained, giving R-factors larger than 0.5. Several cycles of refinements, tried about each of these structures by means of the difference Fourier method, did not reduce the R-factors markedly. Probably the deviations of the atomic positions from the lattice points of the ideal diamond lattice are too large to be found by the refinement started from the diamond structure. Moreover, the high symmetry of the postulated structures makes it difficult to find the directions of the shifts of the atoms.

The following procedure was then tried, expecting to get a clue to find the relative directions of the shifts. At first the structure amplitudes

were calculated only with an atom which is at the position A in Fig. 2, but slightly shifted from the atomic sites in the diamond structure. There are four cases concerning the direction of the shift of this atom; namely, (1) $\varDelta x$ and $\varDelta z$ are positive, (2) $\varDelta x$ is positive, and $\varDelta z$ is negative, (3) $\varDelta x$ is negative and $\varDelta z$ is positive, (4) $\varDelta x$ and $\varDelta z$ are negative. However, these four cases are essentially identical for the present purpose, since we can choose arbitrarily the direction of the axes. In the actual calculation, the atomic position (x, z) was assumed as $(0.008, 0.360)$. Then a Fourier map was synthetized by von Eller's method with the signs obtained (Fig. 3). The peaks for two other atoms were clearly observed
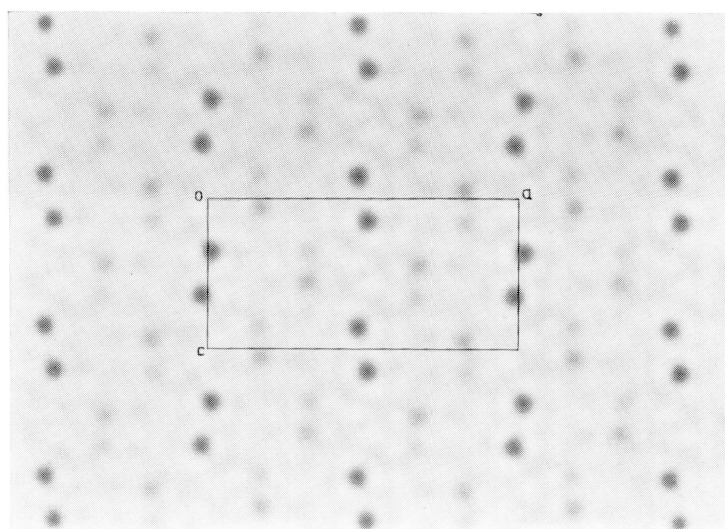
Fig. 3. Fourier projection along the b-axis, which was synthetized with the signs determined only with the atom A in Fig. 2.

near the expected positions in the map, and the kind of the atom at each position was also determined according to the peak hights. The new model gave an R-factor of 0.26 for the $h0l$ reflections, indicating that it is very near from the true structure. The structure was refined by the difference Fourier method still about the b-axis projection and the R-factor reduced to 0.12.

Since all the atoms are on mirror planes, the y-coordinates were easily determined. Three dimensional refinement was further carried out with least square method utilizing 395 reflections. The R-factor reduced to 0.09 without taking account of anisotropic temperature factors. The final atomic parameters are given in Table 1, the calculated and observed structure factors in Table 2. Fig. 4 shows the final electron map projected along b.

Table 1. *The atomic parameters and their standard deviations*

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	$B\ \text{Å}^2$	$\sigma(B)$
Cu	0.1752	0.00018	0.250	0	0.061	0.00034	2.1	0.031
As	0.0146	0.00009	0.250	0	0.352	0.00022	1.4	0.026
S	0.1651	0.00020	0.750	0	0.817	0.00055	1.0	0.041
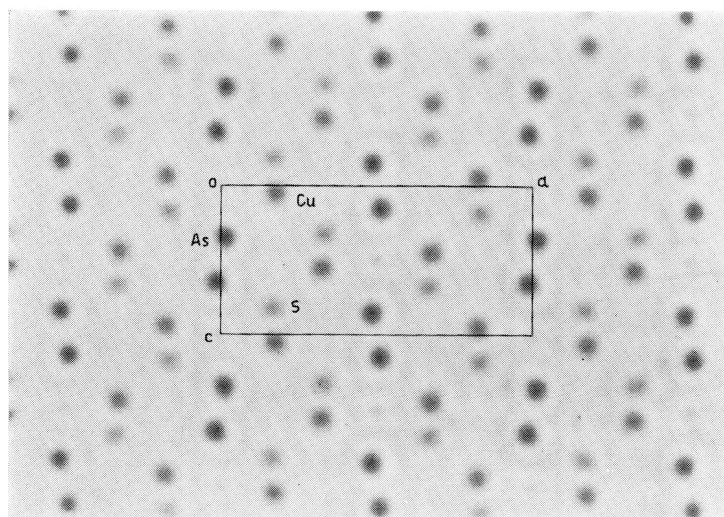
Fig. 4. Electron density projection along the *b*-axis.

Table 2. *Observed and calculated structure amplitudes*

h	k	l	$\lvert F_0 \rvert$	F_c	h	k	l	$\lvert F_0 \rvert$	F_c
2	0	0	27.8	29.7	13	0	1	9.6	− 7.3
4	0	0	42.5	45.4	14	0	1	14.4	12.8
6	0	0	145.8	172.5	0	0	2	0	7.2
8	0	0	0	− 3.6	1	0	2	14.7	−18.8
10	0	0	25.0	20.0	2	0	2	46.9	−50.0
12	0	0	65.8	62.2	3	0	2	34.4	−33.5
14	0	0	13.7	−16.0	4	0	2	27.9	−26.5
1	0	1	16.9	−15.7	5	0	2	44.0	−44.5
2	0	1	4.3	− 7.0	6	0	2	5.0	1.4
3	0	1	130.0	−164.6	7	0	2	24.9	−21.7
4	0	1	32.1	28.5	8	0	2	32.2	−32.0
5	0	1	9.1	8.9	9	0	2	53.2	−53.9
6	0	1	41.6	43.9	10	0	2	0	0.4
7	0	1	21.6	−20.8	11	0	2	33.2	−30.8
8	0	1	27.6	23.9	12	0	2	0	− 3.2
9	0	1	71.9	−71.1	13	0	2	27.1	−26.1
10	0	1	39.2	38.5	1	0	3	70.8	73.0
11	0	1	15.9	14.9	2	0	3	60.2	61.4
12	0	1	38.4	38.3	3	0	3	77.9	74.9

h	k	l	$|F_0|$	F_c	h	k	l	$|F_0|$	F_c
4	0	3	47.7	−48.4	14	1	0	19.6	20.4
5	0	3	59.9	61.2	0	1	1	131.0	−160.2
6	0	3	25.3	24.9	1	1	1	48.4	−54.9
7	0	3	35.5	33.8	2	1	1	42.0	−41.5
8	0	3	39.1	39.2	3	1	1	27.8	−28.2
9	0	3	46.5	40.9	4	1	1	41.5	−40.7
10	0	3	20.0	−19.4	5	1	1	50.9	−50.4
11	0	3	24.4	21.6	6	1	1	97.1	−102.1
12	0	3	22.4	21.9	7	1	1	14.7	13.9
13	0	3	3.7	0.2	8	1	1	16.1	−13.2
0	0	4	60.0	−57.6	9	1	1	44.8	−43.6
1	0	4	70.3	71.4	10	1	1	18.2	−12.9
2	0	4	53.8	−53.5	11	1	1	31.4	−27.9
3	0	4	0	2.8	12	1	1	45.9	−39.6
4	0	4	45.5	−46.5	13	1	1	7.5	− 5.2
5	0	4	38.0	−36.7	14	1	1	3.9	5.0
6	0	4	44.5	−39.9	1	1	2	49.3	48.4
7	0	4	65.1	68.3	2	1	2	59.5	59.7
8	0	4	29.7	−28.4	3	1	2	139.3	152.0
9	0	4	7.0	6.0	4	1	2	70.1	−71.2
10	0	4	18.5	−17.8	5	1	2	27.9	25.1
11	0	4	9.0	− 8.9	6	1	2	0	0.5
1	0	5	8.9	8.1	7	1	2	35.8	33.4
2	0	5	29.7	27.6	8	1	2	24.1	21.5
3	0	5	10.8	− 5.3	9	1	2	79.8	74.7
4	0	5	54.2	−55.6	10	1	2	47.1	−45.5
5	0	5	10.4	3.7	11	1	2	0	− 1.5
6	0	5	15.5	−14.8	12	1	2	0	− 0.8
7	0	5	8.1	10.0	13	1	2	8.8	6.4
8	0	5	0	− 3.7	0	1	3	73.2	−73.2
9	0	5	5.4	− 6.8	1	1	3	55.9	54.3
10	0	5	37.3	−47.8	2	1	3	5.6	1.8
0	0	6	31.3	29.4	3	1	3	16.6	15.7
1	0	6	11.0	9.8	4	1	3	11.8	−12.4
2	0	6	32.2	31.9	5	1	3	12.4	−10.1
3	0	6	5.5	3.5	6	1	3	50.8	−48.1
4	0	6	23.3	23.0	7	1	3	66.7	67.5
5	0	6	7.9	7.6	8	1	3	11.6	9.9
6	0	6	21.2	22.2	9	1	3	30.1	28.3
7	0	6	15.1	18.2	10	1	3	12.3	−12.7
2	1	0	44.4	−55.6	11	1	3	12.3	9.5
4	1	0	7.0	−11.1	12	1	3	16.5	−15.0
6	1	0	58.2	63.2	1	1	4	44.3	−41.4
8	1	0	49.0	47.0	2	1	4	7.9	− 5.5
10	1	0	28.4	25.1	3	1	4	19.3	−15.2
12	1	0	53.9	54.6	4	1	4	23.6	−21.1

h	k	l	$\|F_0\|$	F_c	h	k	l	$\|F_0\|$	F_c
5	1	4	45.5	−42.5	3	2	2	25.3	24.7
6	1	4	23.8	−22.1	4	2	2	21.4	18.7
7	1	4	18.9	−13.3	5	2	2	33.2	31.3
8	1	4	25.8	−21.7	6	2	2	5.8	2.9
9	1	4	14.8	−11.2	7	2	2	22.2	20.6
10	1	4	26.8	−26.1	8	2	2	26.2	23.9
11	1	4	19.4	−20.2	9	2	2	43.0	43.0
0	1	5	37.1	29.9	10	2	2	0	− 0.8
1	1	5	30.3	−26.7	11	2	2	25.7	24.2
2	1	5	61.7	60.9	12	2	2	4.9	3.6
3	1	5	0	2.0	1	2	3	57.2	−55.5
4	1	5	49.0	45.5	2	2	3	42.9	−44.7
5	1	5	26.4	23.6	3	2	3	62.9	−62.6
6	1	5	27.2	21.3	4	2	3	35.2	35.2
7	1	5	20.9	−19.9	5	2	3	47.3	−47.2
8	1	5	38.2	38.8	6	2	3	19.7	−19.1
9	1	5	4.1	3.3	7	2	3	29.4	−26.4
1	1	6	38.6	−38.1	8	2	3	32.2	−31.1
2	1	6	23.8	−20.6	9	2	3	38.2	−34.6
3	1	6	0	4.5	10	2	3	15.5	15.2
4	1	6	36.0	35.5	11	2	3	17.6	−17.1
5	1	6	31.0	−34.7	0	2	4	50.7	46.4
6	1	6	9.3	9.3	1	2	4	56.9	−55.7
0	2	0	154.3	−187.6	2	2	4	44.1	42.8
2	2	0	24.6	−25.1	3	2	4	0	− 2.7
4	2	0	36.7	−35.8	4	2	4	39.2	37.3
6	2	0	117.1	−129.9	5	2	4	30.4	29.3
8	2	0	0	0.6	6	2	4	37.6	32.4
10	2	0	20.5	−15.5	7	2	4	52.7	−55.0
12	2	0	48.4	−50.9	8	2	4	24.9	23.0
1	2	1	14.3	13.8	9	2	4	6.3	− 5.4
2	2	1	4.8	− 5.2	10	2	4	24.0	24.6
3	2	1	101.3	111.8	1	2	5	8.7	− 7.6
4	2	1	25.5	−24.0	2	2	5	24.0	−21.8
5	2	1	0	− 2.6	3	2	5	5.8	5.6
6	2	1	33.2	−33.9	4	2	5	43.9	44.5
7	2	1	18.8	16.8	5	2	5	4.5	− 3.6
8	2	1	19.3	−17.3	6	2	5	13.1	12.4
9	2	1	57.7	55.9	7	2	5	6.6	− 8.6
10	2	1	34.0	−32.6	8	2	5	3.1	3.1
11	2	1	11.3	−11.3	0	2	6	24.3	−25.2
12	2	1	29.5	−31.2	1	2	6	7.1	− 7.1
13	2	1	5.9	5.7	2	2	6	23.7	−25.5
0	2	2	6.5	− 0.3	3	2	6	3.6	− 3.0
1	2	2	9.9	− 9.6	4	2	6	15.7	−18.5
2	2	2	35.2	34.3	2	3	0	23.9	−23.0

h	k	l	$|F_0|$	F_c	h	k	l	$|F_0|$	F_c
4	3	0	5.5	− 3.9	1	3	4	27.7	24.3
6	3	0	36.4	−38.1	2	3	4	5.4	3.5
8	3	0	30.3	−26.3	3	3	4	18.7	14.9
10	3	0	20.5	−20.1	4	3	4	15.9	14.0
0	3	1	82.7	88.2	5	3	4	25.8	25.5
1	3	1	24.2	−22.9	6	3	4	15.1	14.7
2	3	1	27.3	26.0	7	3	4	10.5	7.7
3	3	1	16.3	15.5	0	3	5	24.6	−22.5
4	3	1	27.6	24.9	1	3	5	17.5	18.4
5	3	1	30.3	28.3	2	3	5	36.5	−39.0
6	3	1	64.7	65.2	3	3	5	0	− 1.2
7	3	1	4.7	− 3.9	4	3	5	25.0	−29.5
8	3	1	12.5	8.8	0	4	0	82.2	90.3
9	3	1	27.5	27.5	2	4	0	18.8	15.5
10	3	1	10.6	7.6	4	4	0	21.4	18.7
11	3	1	15.5	17.1	6	4	0	57.1	67.6
1	3	2	34.6	−31.6	8	4	0	3.9	0.8
2	3	2	34.8	−33.1	1	4	1	11.2	− 9.3
3	3	2	93.1	−91.2	2	4	1	0	− 1.8
4	3	2	43.3	41.6	3	4	1	51.3	−53.5
5	3	2	22.9	−18.1	4	4	1	17.2	16.7
6	3	2	0	0.8	5	4	1	4.9	− 1.1
7	3	2	24.7	−21.1	6	4	1	15.8	17.7
8	3	2	15.0	−14.1	7	4	1	9.7	− 8.9
9	3	2	48.2	−49.3	0	4	2	10.6	− 5.9
10	3	2	27.3	29.9	1	4	2	5.6	− 0.3
0	3	3	41.5	40.1	2	4	2	15.7	−14.8
1	3	3	35.2	−34.4	3	4	2	12.8	−12.5
2	3	3	4.9	2.3	4	4	2	10.0	− 8.0
3	3	3	11.9	−10.5	5	4	2	13.2	−13.2
4	3	3	10.3	9.7	6	4	2	5.9	− 5.2
5	3	3	8.1	7.3	1	4	3	25.4	27.5
6	3	3	28.7	28.0	2	4	3	18.4	21.8
7	3	3	43.9	−44.8	3	4	3	31.9	37.2
8	3	3	4.6	− 4.8	4	4	3	12.6	−16.9
9	3	3	16.8	19.3	5	4	3	17.6	23.8

3. Discussion of the Structure

The projection of the structure along the b-axis is shown in Fig. 5. The structure is essentially identical with the diamond structure. The directions of the a-, b- and c-axis of lautite correspond to the [110], [$\bar{1}$10] and [001] directions of diamond respectively. Each kind of atom is arranged in the same way as reported by S. KULPE: the Cu atom is surrounded by 3S and 1As, the As atom is surrounded by 2As, 1Cu and
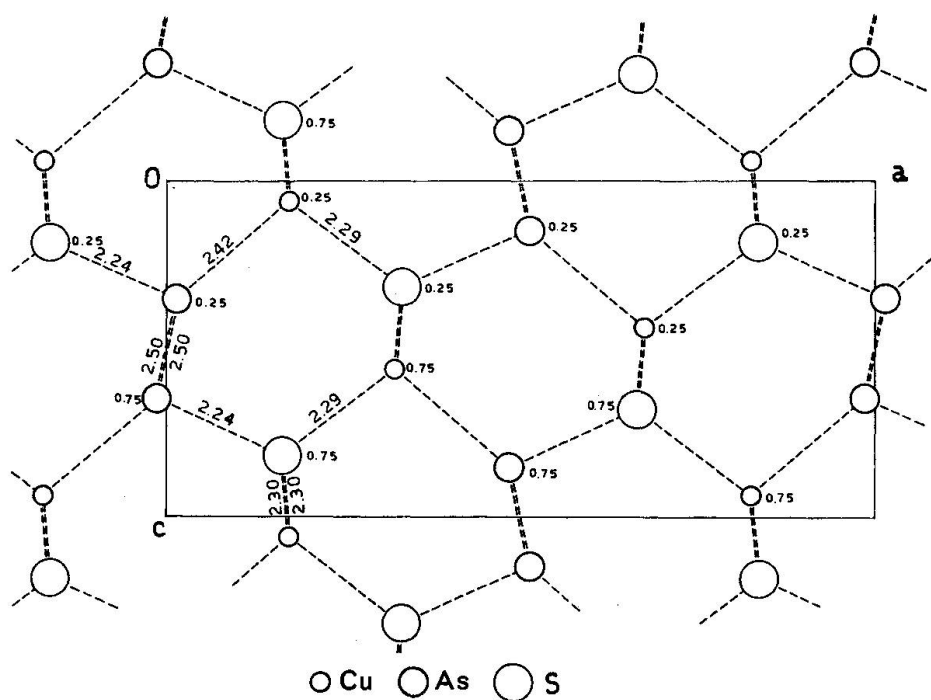
Fig. 5. The structure of lautite viewed along the b-axis. The heights of the atoms are given in fraction of b_0.

Table 3. *Bond distances, bond angles and their standard deviations*

		σ			σ
Cu-S	2.289 Å	0.0035 Å	As-As′	2.498 Å	0.0024 Å
Cu-S′	2.304	0.0030	As-As″	2.498	0.0024
Cu-S″	2.304	0.0030	S-Cu	2.289	0.0035
Cu-As	2.417	0.0026	S-Cu′	2.304	0.0030
As-S‴	2.239	0.0029	S-Cu″	2.304	0.0030
As-Cu	2.417	0.0026	S-As′	2.239	0.0029

		σ			σ
S-Cu-S′	113.1°	0.26°	Cu-As-S‴	114.7°	0.24°
S′-Cu-S″	113.1	0.26	Cu-As-As′	121.6	0.22
S-Cu-S″	109.1	0.26	Cu-As-As″	121.6	0.22
As-Cu-S	110.0	0.21	Cu-S-Cu′	109.1	0.26
As-Cu-S″	110.0	0.21	Cu-S-Cu″	108.2	0.21
As-Cu-S′	101.4	0.19	Cu′-S-Cu″	108.2	0.21
S‴-As-As′	98.3	0.16	As′-S-Cu	106.4	0.18
S‴-As-As″	98.3	0.16	As′-S-Cu″	106.4	0.18
As′-As-As″	97.4	0.19	As′-S-Cu″	118.1	0.26

1S, the S atom is surrounded by 3Cu and 1As atoms. There are fairly large shifts of atoms from the atomic positions in the ideal diamond

structure owing to the difference of the chemical character between the constituent atoms.

The atomic distances are given in Table 3. They are in good agreement with the reported values in the literature. The As-As distance of 2.498 Å is almost identical with the As-As distance of 2.51 Å in the metallic As. The As-S distance is identical with the value of the covalent bond. The direct contact of As and Cu atoms is very rare. In domeykite, Cu_3As, the Cu-As distance of 2.63 Å was observed (B. STEENBERG, 1938); but in this case the As atom has 6 immediate neighbours, while, in lautite, the As atom has 4 nearest neighbours. The bond angles are also given in Table 3. The tetrahedron around the As atom is much more deformed than those around the Cu and S atoms. This is supposed to be caused by the crystallochemical character of As, which forms usually a $As-S_3$ pyramid in arsenosulfides. Among the bond angles around the As atom, the bond angles between the As-S and the As-As bonds are much smaller than the bond angles which contain the As-Cu bond. This fact suggests that the As atom in lautite has the tendency to form a triangular pyramid with the neighbouring 2 As and 1 S atoms.

B. Sinnerite

In the Lengenbach quarry, Binnatal, a small crystal of a steel-gray mineral was found with binnite (W. NOWACKI, F. MARUMO and Y. TAKÉ-UCHI, 1964). The chemical analysis made by X-ray microanalysers showed that this mineral is a copper arsenosulfide, but has a different chemical composition from binnite and lautite (Table 4). It is richer in As than binnite and poorer than lautite.

X-ray photographs taken with Cu K_α showed very complicated super-

Table 4. *Chemical composition of sinnerite. The theoretical values for binnite and lautite are given for comparison*

	sinnerite[1]	sinnerite[2]	mean	binnite	lautite
Cu	41.3 %	39.1 %	40.2 %	51.56 %	37.28 %
As	29.2	29.7	29.5	20.26	43.92
S	29.8	28.7	29.3	28.18	18.80
Total	100.3	97.5	99.0	100.00	100.00

[1]) Applied Research Laboratories, Glendale (Calif.).
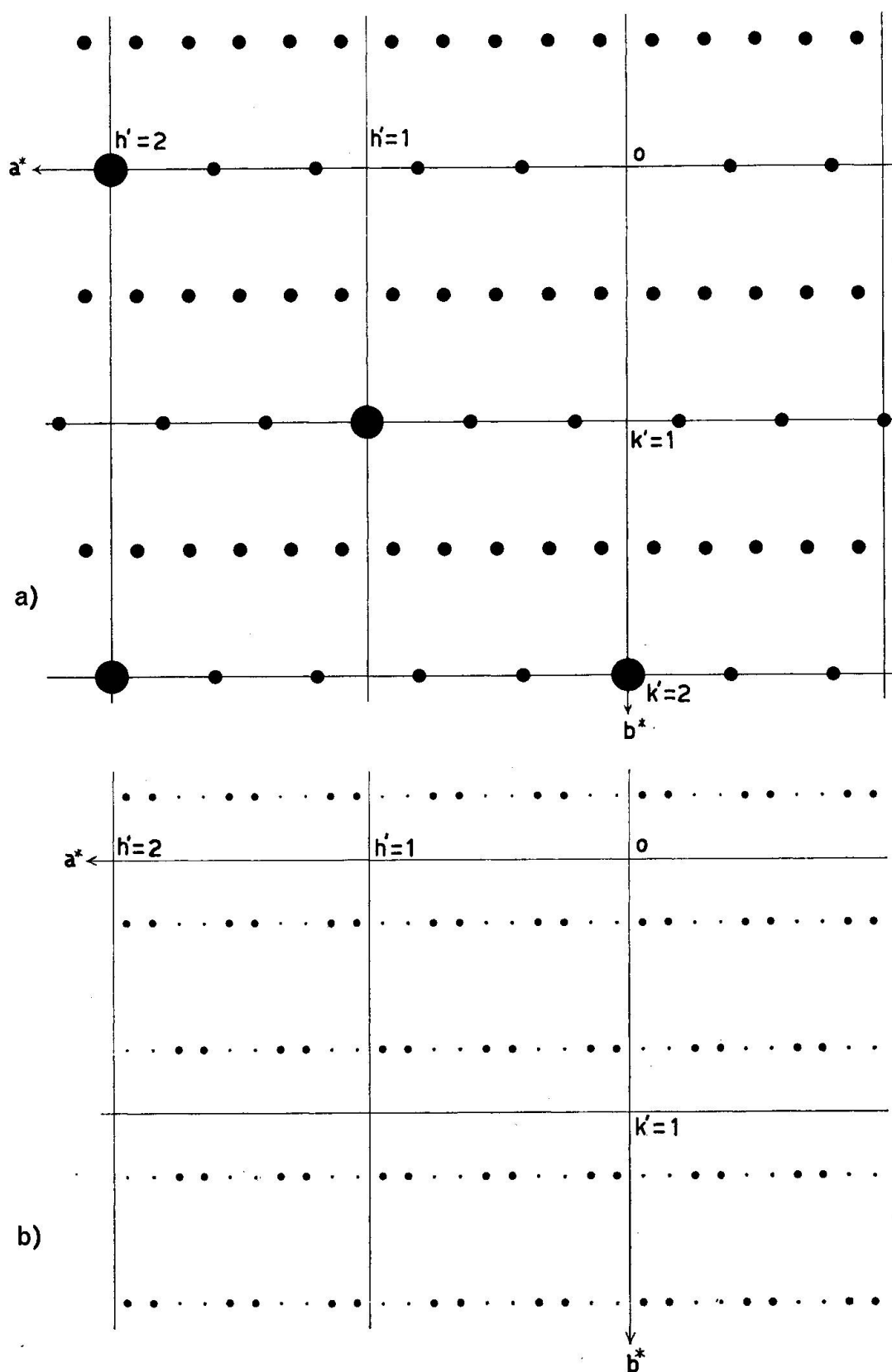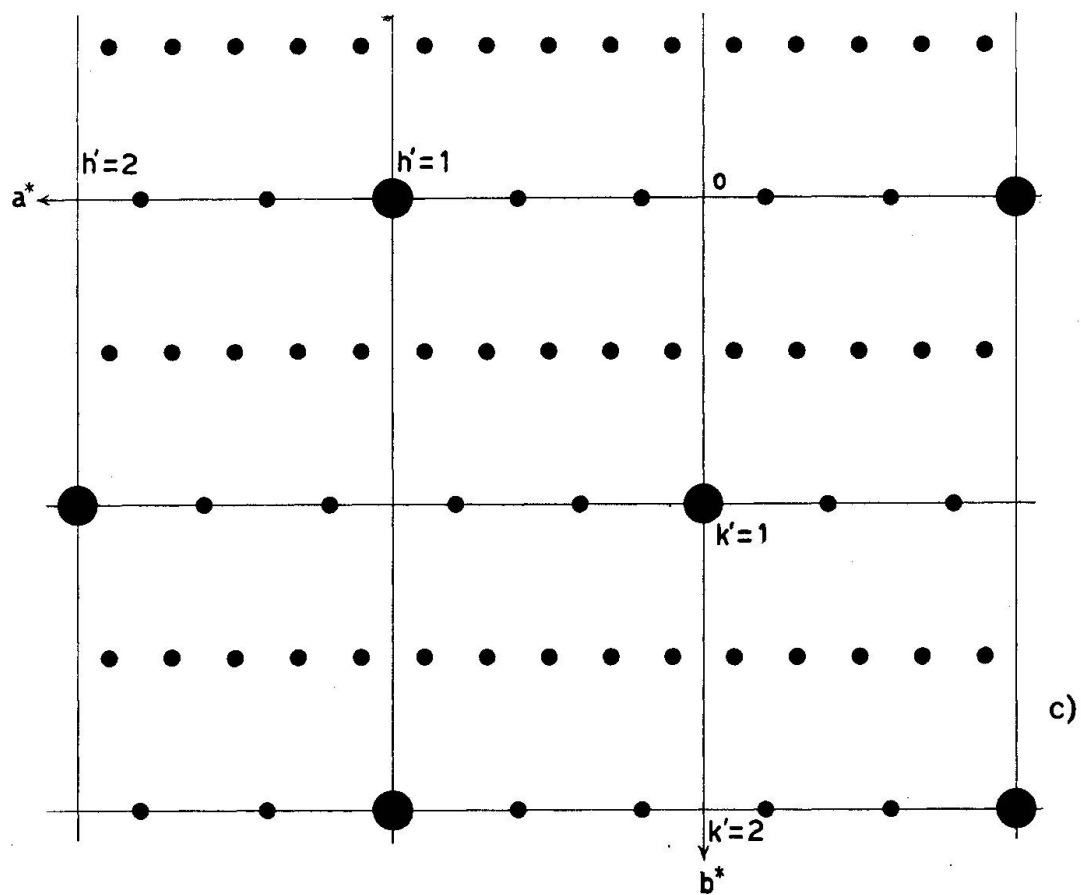[2]) Bureau de Recherches Géologiques et Minières, Paris.

Fig. 6. The reciprocal lattice of sinnerite, **a)** $(h, k, 4n)$, **b)** $(h, k, 4n+1)$, **c)** $(h, k, 4n+2)$ and **d)** $(h, k, 4n+3)$, where $n = $ integer. The reciprocal lattice points are classified

c)

d)

into five groups according to the average intensities of diffraction. Among them, the systematically absent one is omitted in the figure.

lattice patterns with a small subcell. The dimensions of the subcell obtained from the Weissenberg photographs are

$$a' = 3.72 \pm 0.01 \text{ Å}, \quad b' = 3.70 \pm 0.01 \text{ Å}, \quad c' = 5.24 \pm 0.01 \text{ Å}, \quad \alpha' \doteq \beta' \doteq \gamma' \doteq 90°.$$

The symmetry of the strong reflections, which correspond to the subcell, is pseudocubic. By the lattice transformation $a'' = a' + b'$, $b'' = -a' + b'$, $c'' = c'$, we can get the pseudocubic cell with the following cell constants

$$a'' = 5.25 \text{ Å}, \quad b'' = 5.25 \text{ Å}, \quad c'' = 5.24 \text{ Å}, \quad \alpha'' \doteq \beta'' \doteq \gamma'' \doteq 90°.$$

This pseudocubic subcell is almost identical with that of binnite and luzonite, the lattice constants and the space groups of which are $a_0 = 2 \times 5.10$ Å, $I \bar{4}3 m$ for binnite and $a_0 = 5.27$ Å, $c_0 = 2 \times 5.20$ Å, $I \bar{4}2 m$ for luzonite (R. V. GAINES, 1952) respectively.

For the simplest case the positions of the diffraction spots in reciprocal space are shown in Fig. 6 a, b, c and d. Some of the crystals gave more complicated patterns. The apparent unit cell dimensions for the pattern shown in Fig. 6 are, $a_0 = 20 a'$, $b_0 = 4 b'$, $c_0 = 2 c'$, but there are many peculiar systematical absences.

By careful examination of the X-ray photographs, it was revealed that the spots on the reciprocal planes, $k = 4 n$ ($n =$ integer) are composed of at least two spots. This fact, together with the strange extinction rules, suggests that the crystals X-rayed are not single crystals but twinned crystals. Since the smallest crystal, which was X-rayed, is a sphere with the diameter of 0.13 mm, the mineral should be very finely twinned.

The true symmetry of the crystal is probably triclinic. The X-ray patterns shown in Fig. 6 are best explained by assuming the following unit cell and twinning planes,

$$a = 5 a' + 3 b' \ (21{,}7 \text{ Å}), \quad b = -5 a' + b' \ (19{,}0 \text{ Å}),$$
$$c = -5 a' - b' + c' \ (19{,}7 \text{ Å}),$$
$$\alpha = 15° 35', \quad \beta = 155° 20', \quad \gamma = 137° 55'$$

twinning planes: (100), (010), (001) for the subcell. The relation between the triclinic cell and the sub-cell is shown in Fig. 7.

The powder diagram (kindly prepared by Mr. H. HUBER of the Department of Mineralogy and Petrology) yielded the following $[d$ (Å) $- I] -$ data: $3.04_1 - 90$, $2.63_4 - 15$, $1.859 - 70$, $1.584 - 65$, $1.516 - 5$, $1.313 - 20$, $1.206 - 40$, $1.174 - 5$, $1.073 - 90$, $1.010 - 100$. Because of the cubic pseudo-symmetry, we think that some lines are composed of several single lines.

The density of the mineral measured with a pyknometer is 5.2 ± 0.3

gcm^{-3}. With this value, the atomic content of the pseudocubic cell was calculated as $Cu_{1.4}As_{0.9}S_{2.1}$. However, the actual atomic content should be a little bit less than this, since the number of S atoms can not exceed 2 from a structural reason.
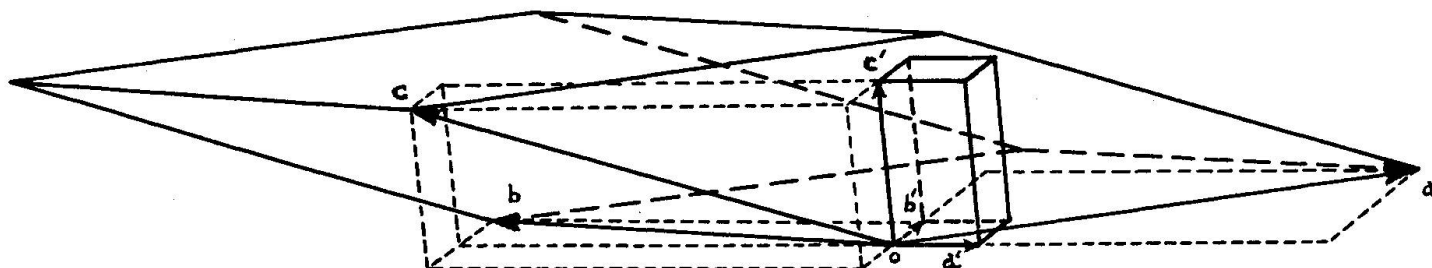

Fig. 7. The relation between the pseudotetragonal subcell and the most probable triclinic cell for sinnerite.

Structurally, sinnerite is not related to lautite but to binnite, since the intensity distribution of the stronger reflections of sinnerite is almost identical with that of binnite. The structure of binnite is very near to the structure of zincblende. The main differences between these two structures are: a quarter of S-atom positions in the zincblende structure is vacant in binnite, there are two extra S-atoms in a unit cell of binnite, which are surrounded by 6 Cu atoms, and Zn atoms are replaced by Cu and As atoms. Since we could not find a single crystal of sinnerite, it was impossible to determine whether the structure of sinnerite has the same difference from the zincblende structure as binnite or not.

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