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THE CRYSTALLOGRAPHY OF ACANTHITE, Ag_2S

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ABSTRACT

An x-ray investigation of acanthite indicates a monoclinic unit cell, with $a=9.47$Å, $b=6.92$Å, $c=8.28$Å, and $\beta=124°$. The probable space group is $B2_1/c$. The unit cell contains 8 Ag_2S. Polysynthetic twinning parallel to (001) and contact twinning parallel to (100) were both found. The observed cell dimensions and the twinning are such that the monoclinic symmetry is readily reconciled with the previous assignment of acanthite to the orthorhombic and to the cubic systems.

INTRODUCTION

Silver sulfide, Ag_2S, is dimorphous, occurring in a high-temperature cubic modification known as argentite, and in a low-temperature form, acanthite. Acanthite has usually been considered to be orthorhombic and the axial ratio in common use is that of Dauber (1857), with $a:b:c=0.6886:1:0.9944$. The close approach of its interfacial angles to those characteristic of the cubic system has led some, including Krenner (1888), to regard acanthite as merely a distorted form of argentite. On the other hand, Groth (1878) described crystals from Annaberg, Saxony, which showed marked monoclinic symmetry. Several of the drawings of acanthite in Goldschmidt's *Atlas der Kristallformen* likewise are distinctly monoclinic in appearance.

It was pointed out by the author (1925, 1927) that powder photographs of Ag_2S indicate that at ordinary temperatures only the non-cubic modification exists, and that all cubic "crystals" of argentite are in reality acanthite paramorphs after argentite. Powder photographs of synthetic Ag_2S gave a pattern identical with that obtained from the natural minerals. No attempt was made to interpret this pattern. Emmons, Stockwell and Jones (1926) made powder photographs above 180°C. and obtained a pattern for the cubic form.

Palacios and Salvia (1931) made both powder photographs and spectrographic measurements from the cube face of an argentite "crystal." From the latter they obtained a "split" reflection, the two parts corresponding to interplanar spacings of 2.45 and 2.39Å, respectively. They correlated the first value with a cubic lattice, and assumed that the second pertained to the orthorhombic modification. Their powder photograph pattern consisted of 32 lines. Considering the above value of 2.45Å to be d_{200}, thirteen of their powder photograph lines were interpreted as cubic. These were believed to be characteristic of a Cu_2O-type of structure. The remaining lines of the powder photograph were assumed to belong to an orthorhombic unit cell, whose dimensions were obtained by combining the above value of 2.39Å, considered to be d_{200}, with the orthorhombic axial ratio. However, these remaining lines were not indexed. Identical patterns were obtained from argentite, acanthite and artificial material. Thus according to their interpretation both the high and the low temperature modifications are present in all samples at room temperature.

DESCRIPTION OF SPECIMENS USED

Two types of acanthite crystals were used for the x-ray investigation. Type 1 consists of very slender crystals from Porco, Bolivia; U. S. National Museum No. C-402. The writer wishes to take this opportunity to acknowledge the kindness of Dr. W. F. Foshag of the National Museum in making available this specimen. The crystals used are several millimeters in length, and from 0.2 to 0.3 mm. across. They consist of a nearly square prism, truncated by one main terminal face (Fig. 1*a*). This face has a value for ρ of about 36°, and is located over the intersection of two prism faces. There appears to be a plane of symmetry bisecting this terminal face, and the combination suggests a monoclinic prism with either a basal pinacoid or a hemi-orthodome.[1] A few minute and imperfect faces are present in addition to these larger faces. In general the reflections obtained on the optical goniometer were of fair quality.

Type 2 is represented by a specimen from Himmelsfürst, near Freiberg, Saxony. Dauber made his axial ratio measurements on crystals from this locality, and the majority of the crystals pictured in Goldschmidt's *Atlas der Kristallformen* are likewise from there. From this Himmelsfürst specimen there was obtained a crystal much larger than those of type 1, being nearly 2 cm. in length, and about 1.5 mm. in greatest width. This crystal has been bent nearly at right angles, but fortunately near the tip there is a straight undistorted portion. The cross section is rectangular, and on the two opposite narrow faces there is a herring-bone pattern of striations, suggesting contact twinning (Fig. 1*c*). The crystal is tapered at the end, but the terminal faces are indistinct. In general appearance it is somewhat like Nos. 37 and 43 in Goldschmidt's *Atlas*. Out of the 46 drawings of acanthite crystals in the *Atlas*, there is nothing corresponding to the type 1 crystals.

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[1] The interfacial angles are such that they are very close to those of a cubic combination consisting of four vertical cube faces, truncated by a 112 face.

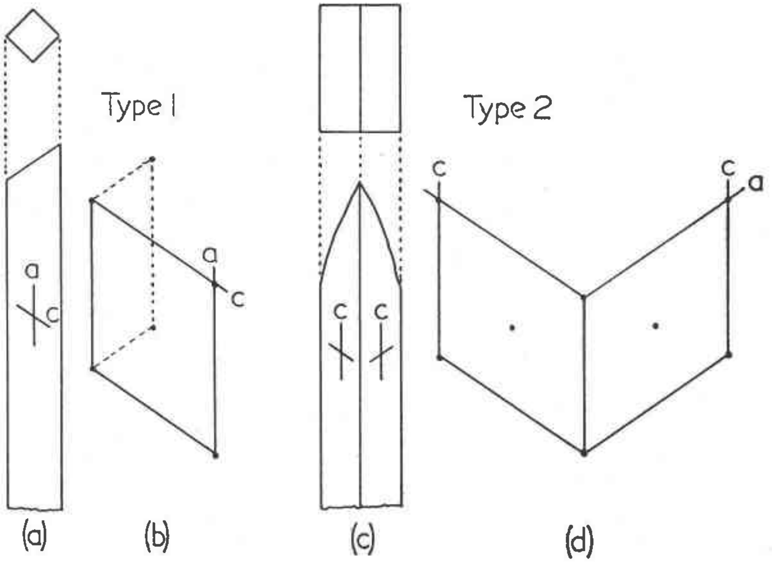

FIG. 1. Relationship of type 1 and type 2 crystals to the unit cell.
(a) Type 1 crystal.
(b) Unit cells: 010-centered (*B*) cell, solid lines; simple (*P*) cell, dashed lines.
(c) Type 2 crystal, showing contact twinning.
(d) Two B cells in twinned position as found in type 2.

X-RAY INVESTIGATION. TYPE 1 CRYSTALS

The crystals were assumed to be monoclinic, and the direction perpendicular to the symmetry plane was therefore chosen as the *b* axis. If the convention $c<a$ is observed, the direction of elongation is the *a* axis. This is in contrast to the type 2 crystal, which is elongated parallel to *c*. Rotation photographs, and zero, first, second and third level equi-inclination Weissenberg photographs were obtained about the *a* axis. From the rotation photographs the value of the identity period along the *a* axis was determined to be about 9.50Å.

The quality of the Weissenberg photographs varies greatly, some being excellent and others poor. This is chiefly due to the high absorption by Ag_2S of the CuK_α radiation used. Some areas of the films have large numbers of reflections clearly recorded, while adjacent areas may be practically blank. In general the reflections are sharp, showing that in spite of the ease with which the crystals may be distorted, no such distortion has occurred.

Zero level films about the *a* axis were obtained from three different crystals of type 1. These all show two central lattice lines 90° apart, corresponding to b^* and c^*. (Throughout this paper, an asterisk * will be used to denote a direction in the reciprocal lattice, as contrasted with the unit cell directions.) The reflections on these films are symmetrical to both the b^* and c^* lattice lines, and hence show the plane symmetry C_{2l}. In the successive levels 1, 2 and 3, the reciprocal lattice rows parallel to c^* remain in the same relative positions, while those rows parallel to b^* are shifted a definite distance in each level, the shift being in the c^* direction. These upper levels accordingly are symmetrical only with respect to the c^* direction, and show plane symmetry C_l. This combination of symmetry and the shift in the upper levels are characteristic of the monoclinic system.

A simple monoclinic cell (*P*) could be chosen, in which case the *c* axis would be parallel to the main terminal face of the crystals. However, because of the development of the type 2 crystals, as described later, it was considered preferable to use a 010-centered (*B*) unit cell. The relationships between the *P* and the *B* cells and the crystal are shown in Figs. 1*a* and 1*b*.

Using the values of b^* and c^* from the zero level *a* axis film, the value of *a* from the rotation photograph, and the value of a^* as subsequently determined from the *b* axis films, the following dimensions are obtained for this *B* unit cell:

$$a = 9.47\text{Å}$$
$$b = 6.92$$
$$c = 8.28$$
$$\beta = 124°$$

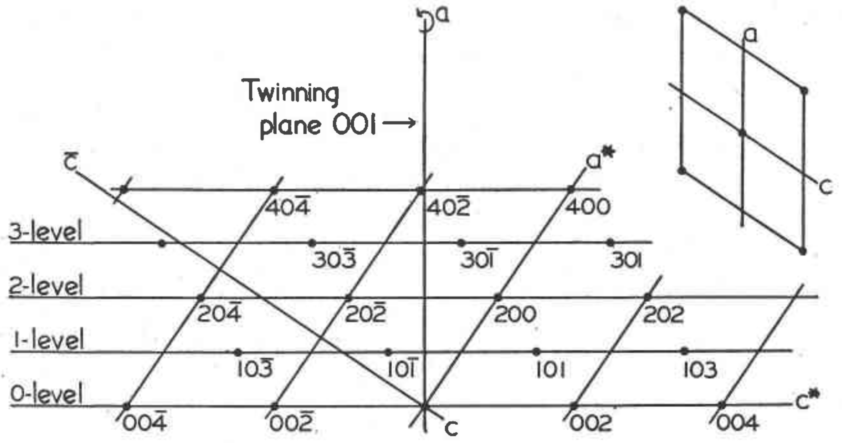

FIG. 2. Cross section through reciprocal lattice, showing sequence of levels in the a^*–c^* plane. Rotation axis is *a*.

The sequence of lattice rows parallel to c^* in the successive levels is shown in Fig. 2. This figure represents a cross section through the reciprocal lattice including the a^* and the c^* directions. Because of the 010-centering, there should be no reflections from hkl planes when $h+l\neq 2n$, or in other words, no reflections unless h and l are both even, or both odd. Such points are the only ones marked in the reciprocal lattice in Fig. 2. This applies also to all of the lattice levels parallel to the plane of the figure, for all successive levels in the b^* direction have identical patterns, and differ only in the value of k. Hence the only lattice rows perpendicular to the plane of Fig. 2 are those which pass through the points marked in the figure.

Actually, on the first and third level films, some extra reflections are present which appear to be on rows passing through points for which $h+l\neq 2n$, having indices such as $1k2$ and $3k2$. No such extra reflections are to be observed in the zero and second level films. This is not a normal set of absences, with $h+l\neq 2n$ reflections missing in the even numbered levels, but present in the odd. Inspection of the films shows two facts which furnish a clue to this apparent anomaly. First, the extra reflections on the odd level films are not precisely half-way between the rows for which $h+l=2n$. Second, these extra reflections are fairly weak, and in every case are located symmetrically across the central lattice line parallel to b^*, with respect to intense reflections of the $h+l=2n$ type. In the monoclinic system such symmetry should not be present.

This pseudo-symmetry, with strong reflections appearing mirrored across the (001) plane, must be due to twinning parallel to (001). This twinning is probably microscopic, for there is no visible external evidence of twinning. The fact that only strong reflections are thus repeated suggests that the greater part of the crystal consists of one orientation, with the reversed twinned position making up only a small portion and therefore contributing little to the reflections.

The fact that these extra spots resulting from twinning apparently fit into the regular sequence of reflections in the odd levels and are missing in the second level is due entirely to a fortuitous situation, arising from the particular values of a, c and β existing in the structure. This can be seen from Fig. 2, in which the rotation axis a represents the trace of the twinning plane. The effect of the twinning is to reflect all lattice points on one side of the plane to symmetrical positions on the other. Thus in the zero level all points $0k\bar{l}$ are mirrored across the twin plane and coincide with identical $0kl$ points, so that there is no effect observable. In the first level, the point $10\bar{1}$ is reflected across the twin plane and appears almost exactly at the position where 100 would be, if present. Likewise $10\bar{3}$ in the twinned position appears where 102 would be. In general, the lattice rows $1k\bar{1}$ and $1k\bar{3}$ from one portion of the twin appear in the positions $1k0$ and $1k2$, respectively, of the other. Thus legitimate reflections ($h+l=2n$) from one twin orientation appear approximately in forbidden positions ($h+l\neq 2n$) of the other.

A different situation exists in the second level. Here $20\bar{2}$ is reflected across the twin plane and practically coincides with 200, and $20\bar{4}$ with 202, etc. Or in general, lattice rows $2k\bar{2}$ and $2k\bar{4}$ when reflected practically coincide with the rows $2k0$ and $2k2$, respectively. A careful inspection of the second level films reveals that some of the spots are doublets. This doubling is due to the lack of exact coincidence between the position of a given reflection from one part of the twin and that of the extra one from the other. Not all spots show this doubling, because one or the other of the two possibilities may be absent. If only a single spot occurs, there may be doubt as to its identity, but since both possible reflections belong to the category of $h+l=2n$, there is no ambiguity about the type of missing reflections. The degree of coincidence of pairs of reflections from the two parts of the twin decreases with decreasing interplanar spacing, or, in terms of the reciprocal lattice, decreases with increasing distance from the origin. Consequently the doublets of reflections with high values of θ are clearly separated, and can always be distinguished.

In the third level the situation is similar to that in the first level. Rows in the reciprocal lattice of the type $3k\bar{3}$ and $3k\bar{5}$ (Fig. 2) are mirrored across the twin plane and fall approximately in the positions of $3k0$ and $3k2$, respectively, which are forbidden reflections. However, the degree of approximation is much less, because of the increasing divergence with increasing distance from the origin. On the third level films it is plainly evident that the lattice rows $3k\bar{3}$ and $3k\bar{5}$ in their mirrored positions are not exactly half-way between the adjacent regular rows $3k\bar{1}$, $3k1$ and $3k3$.

The particular values of a, c and β which bring about this situation are such that the lattice is very strongly pseudo-orthorhombic. Thus in Fig. 2 the nearly rectangular block with $40\bar{2}$, 400 and 002 at the corners, and 200 at the center, is clearly apparent.[2] The lattice points outlining all such blocks have both h and l even. The pseudo-symmetry means that for any point of this type there is a corresponding point across the trace of the (001) plane. This corresponding point has different values of h and l, but both are still even. Thus both points of such symmetrical pairs correspond to legitimate reflections. This pseudo-symmetry is so pronounced that two second level films about a, taken 180° apart, appear almost identical. Ordinarily in the monoclinic system two such films

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[2] As will be shown later, this block of the reciprocal lattice is derived from a pseudo-orthorhombic cell, with dimensions in agreement with the usual orthorhombic axial ratio.

would be symmetrical, but not superposable. In this case the shift in successive levels is such that pairs like 200 and 202 are practically equidistant from the rotation axis. In general there is a direct correspondence in position and to a considerable extent a correspondence in intensities on the two films taken 180° apart. This must mean that there is a strong pseudo-symmetry in the atomic positions, at least with respect to the heavier Ag atoms.

In the odd levels, the lattice points have both *h* and *l* odd, and the positions symmetrical to these are unoccupied because they are points with $h+l\neq 2n$. This relationship, and those previously mentioned, are shown in Fig. 3 in terms of the unit cell rather than the reciprocal lattice.

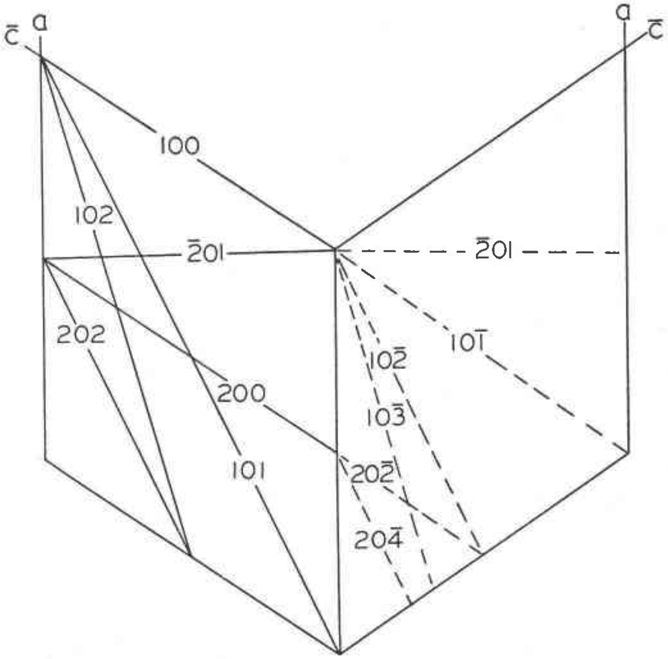

FIG. 3. 010 cross section through twinned *B* cells, showing near parallelism of pairs of planes from the two cells. In pairs such as $10\bar{1}$–100, 101–$10\bar{2}$ and $10\bar{3}$–102 the first member has indices with $h+l=2n$ and the second with $h+l\neq 2n$. The legitimate reflections ($h+l=2n$) from one cell appear in forbidden positions ($h+l\neq 2n$) of the other. Other pairs as 200–$20\bar{2}$ and 202–$20\bar{4}$ have both indices with $h+l=2n$. Note that $\bar{2}01$ is nearly continuous in the two cells.

Planes *hkl*, with both *h* and *l* even, in one twin orientation are practically parallel to planes *hkl* with *h* and *l* even in the other orientation, and have almost the same interplanar spacings. Such pairs are 200-$20\bar{2}$ and 202-$20\bar{4}$. Reflections from such pairs would practically coincide, and hence occur as doublets. But planes *hkl*, with both *h* and *l* odd, in one orientation are practically parallel to planes in the other orientation whose values for *h* and *l* are one odd and one even. Thus 101 is parallel to $10\bar{2}$, $10\bar{3}$ to 102 and $10\bar{1}$ to 100. The second plane of each of these pairs does not reflect in a *B* lattice, but its reflection may be simulated by a reflection from the other twin orientation.

It is thus evident that the assumption of a (001) twinning plane accounts for the presence of doubled reflections, and for the appearance of reflections apparently of the forbidden type, and leaves valid the original choice of a monoclinic *B* cell, with the dimensions stated.

Weissenberg photographs were also taken about the *b* axis of a type 1 crystal. The slender crystals are so easily deformed that no attempt was made to cut an equi-dimensional specimen for these *b* axis films. By inserting just the tip of one of the crystals in the *x*-ray beam, zero and first level films were secured. Because of the unequal absorption due to the great variation in dimensions, these photographs are of poor quality. About twenty reflections are recorded on the zero level film, which shows the a^* and c^* central lattice lines 56° apart. This corresponds to a β angle of 124°, which agrees closely with the value obtained from the measured values of *a*, a^* and c^*, as previously given. Both the a^* and the c^* spacings are doubled throughout, there being no *h*0*l* reflections with either *h* or *l* odd. These same absences are to be noted also on the first and third level films about the *a* axis. On those films no reflections are present on the central lattice lines parallel to c^*, although those of the type *h*0*l*, with *h* and *l* both odd, are permissible in a *B* lattice. These absences are characteristic of a *B* lattice in which the (010) symmetry plane is a glide plane, with the glide parallel to *c*. Moreover, the only 0*k*0 reflections to be observed are those with *k* even, although reflections with $k=1$, 3, 5 and 7 could have registered. Unless this is due to some special positions of the heavy Ag atoms. it indicates a screw axis parallel to *b*, so the probable space group is $B2_1/c$.

In the zero level photographs about *b* the only evidence of twinning is the doubling of some of the reflections, just as was observed in the zero level of the *a* axis films. The absence of all *h*0*l* reflections with either *h* or *l* odd gives no opportunity for the twinning to introduce extra reflections apparently of the forbidden type. In Fig. 2 it will be noticed that the lattice line from the origin through $40\bar{2}$ is very near perpendicular to c^*. On the zero level film this lattice line is doubled, with one strong and one weak reflection, corresponding to the two twin orientations. These reflections are separated by about 1 mm., which represents a divergence of about 2° between the $[40\bar{2}]$ lattice directions in the two parts. This means that the $(20\bar{1})$ planes in the two parts of the twin are within 2° of being parallel. The actual geometrical construction, using the measured values of a, c and β checks this result closely (Fig 3).

The first level films about b are very poor. As would be expected with rotation about the b axis, there is no shift in the relative positions of the lattice rows, and the reflections correspond to the regular (i.e., not doubled) reciprocal lattice spacings. This is because the effect of the glide plane is limited to $h0l$ reflections. Twinning is evidence by the doubling of some spots, and the appearance of some reflections apparently of the $h+l\neq 2n$ type, symmetrically located with respect to reflections in the normal positions.

TYPE 2 CRYSTAL

As previously stated, this crystal is striated in such a manner as to indicate contact twinning. It is much less slender than the type 1 crystals, having a cross section of about 1×1.5 mm. Because of this greater thickness, it would seem probable that most of the reflections obtained would be from the surface. Consequently the reflections on a given area of the film should be chiefly from one or the other half of the contact twin, and the patterns from the two halves should not be blended as they are in the case of the microscopic twinning such as found in type 1. Such blending as does occur would be expected to be limited to film areas close to the b^* direction, which lies in the twinning plane.

The direction of elongation of this crystal proved to be that corresponding to the c direction of the type 1 crystals, and the contact twinning plane is (100). More properly, it might be stated that the B lattice was chosen so as to bring about this situation (Fig. 1*d*). If the simple P lattice were used, the direction of elongation of type 2 would be [102] and the twinning plane $(20\bar{1})$.

The faces gave such poor signals on the goniometer that difficulty was encountered in adjusting the crystal. The rotation photograph is poor, but gives an approximate value of $c=8.24$Å. The zero level Weissenberg film is of better quality, and shows two central lattice lines 90° apart, with the reflections symmetrical about both $-(C_{2l})$. The spacings along these lines agree with those of a^* and b^* as found for type 1. However, this film shows rows of reflections corresponding to $1k0$, $3k0$ and $5k0$, all with $h+l\neq 2n$, in addition to those with $h+l=2n$. The presence of such supposedly forbidden reflections is completely explained by assuming that the same polysynthetic twinning on (001) as found for type 1 is present here, as well as the visible contact twinning on (100).

The relationships involved in this situation are shown in Fig. 4. Like Fig. 2, this is a section through the a^*-c^* plane of the reciprocal lattice, but with the rotation about the c instead of the a axis. The twinning across the (001) plane has the effect of repeating certain lattice rows from one twin orientation in such a way that they appear as rows in the other. The zero level corresponds to the a^*-b^* plane of the reciprocal lattice, being perpendicular to the plane of Fig. 4. Rows of lattice points, likewise perpendicular to the plane of Fig. 4, and represented by the points $\bar{1}01$, $\bar{2}02$, $\bar{3}03$, etc., are repeated across the (001) twin plane and fall almost exactly on the zero level. These appear to be lattice rows passing through the points $\bar{1}00$, $\bar{2}00$, $\bar{3}00$, etc. Half of these, with h even,

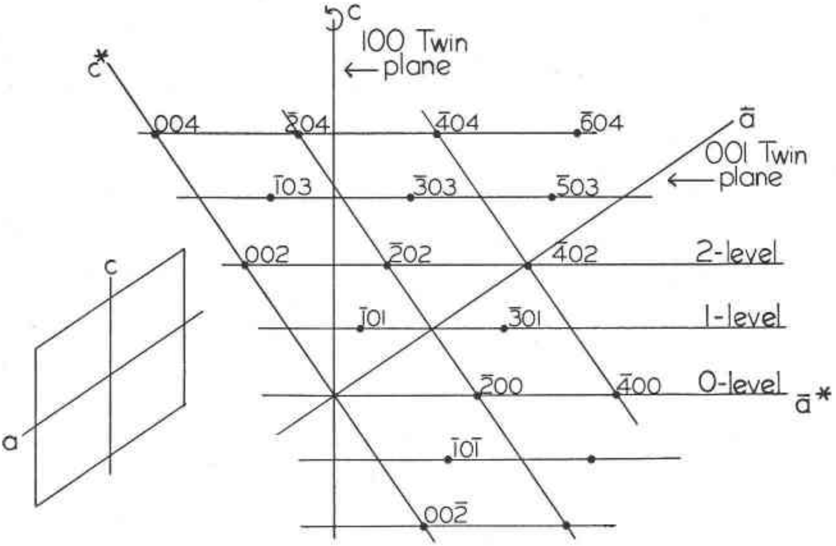

FIG. 4. Cross section through the a^*–c^* plane of the reciprocal lattice. Rotation axis c. Both (001) and (100) twin planes are indicated.

are legitimate reflections for a B lattice, and cause doubling of spots, since the coincidence is only approximate. The other half, with h odd, will appear as forbidden reflections. Actually, of course, they are legitimate reflections from the other twin orientation.

In the first level the only lattice rows in such a position that they could be repeated across the twin plane from the other orientation are all unoccupied. Rows through $\bar{3}02$ and $\bar{4}03$ are examples of this. Accordingly the films for the first level show no extra reflections, either in forbidden positions, or as doublets.

The second level resembles the zero level. Here rows represented by the lattice points $\bar{3}01$, $\bar{2}00$, $\bar{1}0\bar{1}$, $00\bar{2}$, etc., are repeated across the (001) twin plane and fall into positions approximately on the second level. They are able to reflect, and the reflections appear with the normal reflections on the film. Those with h even fall on legitimate positions and cause doubling. Those with h odd appear as single spots in the forbidden positions $h+l\neq 2n$. These single spots alternate with the doublets. This effect is very noticeable in the second level films, because the divergence is sufficient to make the separation of the doublets appreciable.

This effect is so definitely present that it seems to offer complete verification of the assumption of the polysynthetic twinning across (001), in addition to the contact twinning, (100). Moreover, the effect is continuous over the entire film, for any portion of the crystal giving rise to reflections is made up of both orientations. The contact twinning results in an entirely different appearance. As stated previously, the crystal is of such thickness that the reflections must be chiefly from the surface, and hence the spots registered on any given area of the film in general should be from one half or the other of the twin, without much blending.

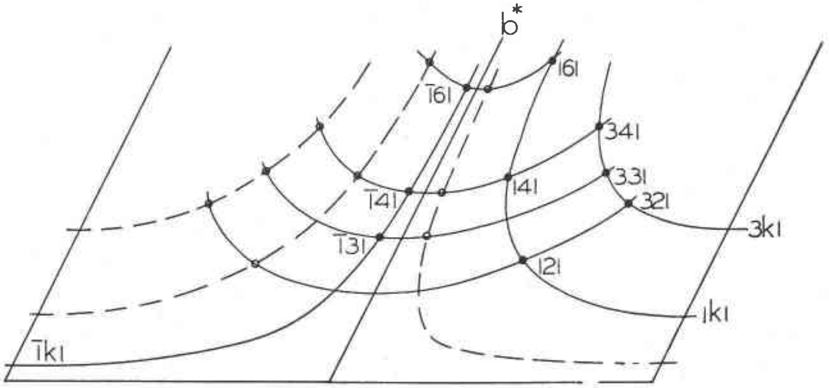

FIG. 5. Diagrammatic representation of 1-level Weissenberg photograph about the c axis of type 2 crystal. Solid points represent reflections from one twin (100) orientation; circles represent reflections from the other orientation.

In the zero level, no effect of the contact twinning should be present, and none is apparent on the films. In the first level, however, the shift due to monoclinic symmetry is in opposite directions in the two halves of the twin. The central lattice line parallel to b^* is common to both parts, and on either side of this direction the opposite shifts are symmetrically located. There is little blending of the patterns, for only a few reflections from one half persist across the central lattice line into the domain of the other. The appearance of the film is shown diagrammatically in Fig. 5. As stated previously, no effect of the (001) twinning is evident in the first level, so there are no doublets nor reflections apparently in forbidden positions. However, both of these effects again appear in the second level films, together with the effect of the contact twinning. This latter consists of the symmetrical shifting of the lattice rows in opposite directions on either side of the central lattice line parallel to b^*, with a few reflections from one orientation appearing on the opposite side.

LAUE PHOTOGRAPHS

Laue photographs of type 1 crystals were taken perpendicular to (001) and (010). The former shows the (010) symmetry plane, and a suggestion of symmetry across the trace of the (100) plane. If both orientations of the polysynthetic twinning were present in equal proportions, the reflections should appear entirely symmetrical across the (100) plane. Preponderance of one orientation, such as was indicated by the Weissenberg photographs, is revealed in the Laue photographs by the lack of this apparent symmetry. Likewise, the photograph perpendicular to (010), although showing many reflections symmetrical to both (100) and (001), actually possesses only a two-fold axis of symmetry.

POWDER PHOTOGRAPHS

Different specimens of Ag_2S gave widely varying qualities of powder photographs. The best film obtained was made with MoK_α radiation in a camera with an eight inch radius. The shorter wave-length resulted in more reflections, and the large radius was sufficient to resolve pairs of lines that appeared as single lines with a smaller camera, even when using CuK_α radiation. A composite list of reflections with their estimated intensities, together with the assigned indices are given in Table 1. The values was obtained are in good agreement with those given by Harcourt (1942). Some of the powder photograph data of Palacios and Salvia are included in the table.

TABLE 1

This table gives the spacings as determined from the powder photographs; the observed intensities, with the strongest lines rated as 10; the monoclinic indices *hkl*; the spacings as calculated for the monoclinic unit; and the intensities of the corresponding reflections as observed on the Weissenberg photographs.

d Å	*I* obs.	Mono. *hkl*	*d* calcd.	*I* Weiss.
3.91	1	200	3.92	m
		$20\bar{2}$	3.87	s
3.40	7	002	3.43	m
		210	3.41	ms
		$21\bar{2}$	3.37	m
3.07	8	012	3.075	m
2.81	8	$31\bar{1}$	2.81	s
2.66[3]	6	121	2.655	s
2.58[3]	10	220	2.595	ms
		$22\bar{2}$	2.578	m
2.44	10	$11\bar{3}$	2.453	m
		022	2.435	vs
		$31\bar{3}$	2.415	ms
2.37	9	$40\bar{2}$	2.36	s
2.315[2]	a			
2.205	7	$13\bar{1}$	2.21	ms
2.08	8	$12\bar{3}$	2.09	ms
		202	2.07	m
2.05	4	$32\bar{3}$	2.065	ms
		$20\bar{4}$	2.045	m
1.99	4	230	1.988	w
		212	1.984	m
		$23\bar{2}$	1.981	w
1.96	5	$21\bar{4}$	1.962	m
		400	1.96	w
1.51	4	$34\bar{1}$	1.507	w
1.475	3	133	1.477	s
1.46	5	$11\bar{5}$	1.467	m
1.44	4	$14\bar{3}$	1.444	m
		$34\bar{3}$	1.435	w
1.41	<1	$62\bar{2}$	1.407	m
1.38	<1	034	1.376	vw
1.335	2	$33\bar{5}$	1.343	ms
(broad)		341	1.331	w
		341	1.331	w
		242	1.328	m
		204	1.32	w
1.30	1	600	1.31	w
		250	1.305	w
		214	1.30	w
		422	1.296	m
		440	1.296	w
		$60\bar{6}$	1.29	m
		052	1.285	m
1.265	1	323	1.27	w
		$35\bar{1}$	1.26	m
1.23	3	224	1.236	w
(broad)		$22\bar{6}$	1.228	w
		$15\bar{3}$	1.223	m
		115	1.22	w
		044	1.218	m
1.18	<1	333	1.185	m
		804	1.18	w
1.155	<1	060	1.15	m
		252	1.15	w

TABLE 1—*continued*

d Å	*I* obs.	Mono. *hkl*	*d* calcd.	*I* Weiss.	*d* Å	*I* obs.	Mono. *hkl*	*d* calcd.	*I* Weiss.
1.905	4	032	1.914	m			234	1.15	m
		410	1.885	w			25$\bar{4}$	1.145	w
1.865	4	41$\bar{4}$	1.86	m	1.13	<1	016	1.13	w
1.72	7	13$\bar{3}$	1.732	vw	1.09	<1	062	1.092	m
		040	1.73	m			135	1.091	mw
		33$\bar{3}$	1.717	w					
					1.08[2]	a			
1.68[1]	a								
1.60[2]	a				1.04	<1	337	1.03	w
1.58	5	240	1.595	mw	1.01	<1	262	1.01	m
		24$\bar{2}$	1.579	mw			361	1.01	w
1.54	4	331	1.546	m	.965	<1	800	.98	m
		042	1.545	m			254	.965	w
		232	1.541	w					
		024	1.537	m					
					.94	<1	216	.95	w
							226	.93	w

[1] This line was the only one listed by Palacios and Salvia as strong, but does not appear on any of the author's films.

[2] These lines were reported as weak by Palacios and Salvia, but were not observed by the author.

[3] Both Harcourt and Palacios and Salvia report these two lines as one strong line, but on the author's films they are clearly separated.

Correlation of the Monoclinic Symmetry with Previous Assignments to the Orthorhombic and Cubic Systems

If the low temperature form of Ag$_2$S is monoclinic, there arises the problem of reconciling this fact with the x-ray data of Palacios and Salvia, and with the morphological data in the literature, which refer acanthite both to the orthorhombic and the cubic systems.

With one exception there is good agreement between the positions of the powder photograph lines of the author and those of Palacios and Salvia. They list 32 lines, three of which, of low intensity, were not observed on the author's films. On the other hand, their list of 32 did not include eight which were found by the author. Moreover, they rated only one line (1.68Å) as having a strong intensity, and this line was not found on any of the author's films, nor does it appear in the list given by Harcourt. In addition to this discrepancy, there are some differences in the estimated intensities of certain of the lines. All of the powder photograph lines are listed in Table 1.

The erroneous interpretation of acanthite as orthorhombic is due to the fact that the monoclinic cell is pseudo-orthorhombic. Figure 6 shows this relationship. The commonly accepted axial ratio for acanthite applies to this pseudo-cell. Palacios and Salvia obtained their unit cell dimensions by combining an accidentally correct value for d_{200} with the axial ratio, and hence their figures are in agreement. They give 4.77Å as the length of *a*, which value is almost exactly one-half of *a* in the monoclinic cell, 9.47Å. Their value for *c*, 6.88Å, checks closely with that of 6.86Å for d_{001} in the monoclinic unit, while the two values for *b* are the same, 6.92Å.

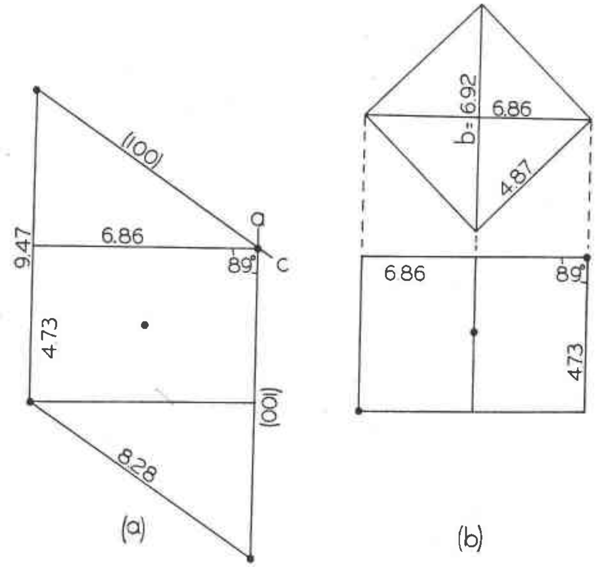

FIG. 6. (a) Cross section through *B* cell, showing relation to pseudo-orthorhombic unit. (b) Diagram showing relation of pseudo-orthorhombic unit to the pseudo-cubic unit.

It must be noted, however, that this orthorhombic unit is not a true unit cell, for only half of the lattice corners are occupied, and only every other unit has the *B*-centered lattice position. Moreover, as shown in Fig. 6, the orthorhombic unit is not truly orthogonal, the angle between (100) and (001) being approximately 89°. The correspondence between the two cells is so close, however, that any $h'k'l'$ plane in the orthorhombic cell can be given monoclinic indices *hkl*, and the spacings calculated for such a unit on the basis of an orthogonal cell will agree with the actual spacings practically within the limits of error in measurement.

However, the monoclinic lattice has certain spacings which have no direct counterpart when referred to the orthorhombic lattice. They are just twice as great as the orthorhombic spacings should be. This is because the orthorhombic cell is a fictitious one, with some of the lattice points missing. Every real plane, of course, must pass through lattice points. In the case of the orthorhombic lattice, there are certain families of planes such that every other plane passes through occupied lattice points, while the planes in between pass only through the unoccupied points, and hence are fictitious planes. In these cases the actual interplanar spacing is just twice what it would be in a normal lattice. This is illustrated by the monoclinic plane $31\bar{1}$, which is parallel to 321 in the orthorhombic, but whose spacing is $2\times d_{321}$. A direct, but possibly unorthodox way in which such a sequence of spacings can be given Miller indices is by using fractions.[3] Likewise the transformation formula must use fractions to express this relationship properly. The transformation formula for monoclinic to orthorhombic is $\frac{1}{2}00/010/\frac{1}{2}01$. Using this formula, the above mentioned monoclinic plane $31\bar{1}$ transforms to $\frac{3}{2}\ 1\ \frac{1}{2}$, which represents the actual plane in the orthorhombic cell. To eliminate the fractions these indices must be multiplied by two, giving 321. But this multiplication of the indices by two is equivalent to halving the spacing, and thus d_{321} is only half as great as the actual spacing in the lattice.

In consequence of the above relationships, every line of the powder photograph can be given monoclinic indices *hkl*; most of the lines can be given directly orthorhombic indices $h'k'l'$; the remainder, when referred to the orthorhombic unit, have spacings equal to $2\times d_{h'k'l'}$. Table 2 shows this relationship for the first twelve lines of the powder photograph.

Palacios and Salvia did not attempt to assign indices to the nineteen powder photograph lines which they assumed to be orthorhombic, so no comparison can be made. The assignment of monoclinic indices would be even more difficult, were it not for the fact that completely indexed Weissenberg photographs were available. Interplanar spacings were calculated for all planes whose reflections were at least moderately strong on the Weissenberg films, and these were checked against the spacings determined from the powder photographs. In many cases there is more than one choice, and it is quite probable that the powder photograph

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[3] This is the reverse of the convention whereby multiple indices such as 200, 300, etc., are used to indicate fractional spacings of 100; in this case fractional indices are used to indicate multiple spacings.

TABLE 2. OBSERVED SPACINGS FOR SOME OF THE LINES OF THE MONOCLINIC POWDER PHOTOGRAPH, WITH CALCULATED SPACINGS FOR THE PSEUDO-CELLS

Monoclinic		Pseudo-orthorhombic		Pseudo-cubic		
d (obs.)	*hkl*	*h'k'l'*	*d* (calcd.)	*h''k''l''*	*d* (calcd.)	$\frac{a_0}{d}$
3.91	200	101	3.90	211×2	3.96	
	$20\bar{2}$	$10\bar{1}$				
3.40	002	002	3.42	011	3.40	$\sqrt{2}$
	210	111	3.393	110		
	$21\bar{2}$	$11\bar{1}$		$10\bar{1}$		
3.07	012	012	3.073	031×2	3.06	
2.81	$31\bar{1}$	321×2	2.809	$63\bar{1}$×4	2.85	
2.66	121	143×2	2.65	$27\bar{1}$×4	2.63	
2.58	220	121	2.586	231×2	2.58	
	$22\bar{2}$	$12\bar{1}$				
2.44	$11\bar{3}$	$12\bar{5}$×2	2.46	$2\bar{3}\bar{7}$×4	2.46	
	$31\bar{3}$	$32\bar{3}$×2	2.43	651×4	2.46	
	022	022	2.436	020	2.42	$\sqrt{4}$
2.37	$40\bar{2}$	200	2.367	200		
2.205	$13\bar{1}$	$16\bar{1}$×2	2.21	275×4	2.19	
2.08	$12\bar{3}$	$14\bar{5}$×2	2.095	291×4	2.09	
	202	103	2.055	233×2	2.06	
2.05	$20\bar{4}$	$10\bar{3}$				
1.99	230	131	1.985	$12\bar{1}$	1.98	$\sqrt{6}$
	$23\bar{2}$	$13\bar{1}$		$11\bar{2}$		
	212	113	1.97	121		
1.96	$21\bar{4}$			$1\bar{1}\bar{2}$		
	400			211		
1.72	040			$02\bar{2}$	1.71	$\sqrt{8}$
1.54	042			$03\bar{1}$	1.53	$\sqrt{10}$
	232			130		
	024			031		
1.30	250			$13\bar{2}$	1.29	$\sqrt{14}$
	214			132		
	422			231		
	440			$23\bar{1}$		
1.23	044			040	1.21	$\sqrt{16}$
1.155	060			$03\bar{3}$	1.14	$\sqrt{18}$
	252			$14\bar{1}$		
	234			141		
	$25\bar{4}$			$11\bar{4}$		
1.09	062			$04\bar{2}$	1.08	$\sqrt{20}$
.965	800			422	.99	$\sqrt{24}$
	254			150	.95	$\sqrt{26}$
.94	216			143		

line is a composite one. A few lines had to be indexed in terms of planes whose Weissenberg reflections were rated as weak, and in a few cases alternative indices are given, corresponding to planes which could not have reflected on any of the particular photographs taken.

Palacios and Salvia conclude that both the high and the low temperature modifications are present simultaneously at room temperature, the former being in a metastable condition. They assume that the two forms occur in a mosaic, in which orthorhombic (100) is parallel to the three cube planes (100), (010) and (001). When using the Bragg spectrographic method, this should result in a split reflection from a cube face of argentite, one reflection being from cubic d_{200} and the other from orthorhombic d_{200}. They obtained a split reflection, and in further support of this hypothesis, they cite their powder photographs, supposedly consisting of both cubic and orthorhombic lines.

The writer believes that this hypothesis is entirely without foundation. If for some unexplained reason, a cubic crystal of argentite, formed above 180°C., remains partly cubic upon cooling, while a portion inverts, how could a monoclinic (pseudo-orthorhombic) crystal of acanthite, formed below 180°C., have both the high and low temperature modifications present? This would have to be the case, for argentite and acanthite give identical powder photographs.

It has already been pointed out that all of the lines of the powder photograph can be indexed as monoclinic. The indexing of some of the lines as cubic, and the occurrence of the split reflections remain to be explained. The monoclinic unit cell is not only pseudo-orthorhombic, but also pseudo-cubic. The pseudo-orthorhombic cell has values of a, b and c such that a, $b/\sqrt{2}$ and $c/\sqrt{2}$ are almost equal. This makes possible the pseudo-cube shown in Fig. 6*b*, with a_0 having an average value of about 4.82Å. Like the orthorhombic cell, this cube is only a ficticious unit, for not all of its corners are marked by lattice points, and adjacent cubes are not identical. Also, the three cubic axes are not quite at right angles to each other. But any $h''k''l''$ plane in this pseudo-cube will be an hkl plane in the monoclinic cell. Because of the vacant lattice positions in the cube, the reverse is not always true. Certain monoclinic spacings have no direct counterpart in the cubic lattice, being either two or four times as large as the cubic spacings should be. Thus not all of the powder photograph lines can be indexed directly as cubic. The transformation from monoclinic to cubic is

$$\tfrac{1}{2}00/\tfrac{1}{4}\tfrac{1}{2}\tfrac{1}{2}/\tfrac{1}{4}-\tfrac{1}{2}\tfrac{1}{2}.$$

With this formula it is possible to determine which of the monoclinic planes can be referred directly to the cubic lattice. There are twelve of these planes, as shown in Table 2. Nine of these twelve are among the lines listed by Palacios and Salvia as cubic. They missed the other three, but had four additional ones, which are incorrect. In any pattern with a large number of lines, it usually happens that certain ones will have spacings which by chance agree approximately with any choice of unit cell. The four extra lines are of this type. They were indexed as 111, 311, 331 and 333, respectively, by Palacios and Salvia. These particular cubic planes, when transformed to the true monoclinic cell, become 201, $60\bar{1}$, 621 and 603. All of these have $h+l\neq 2n$, and hence none may reflect in a B-centered lattice, and should not occur. The interplanar spacings in the cubic system are calculated by the formula $d_{hkl}=\frac{a_0}{\sqrt{h^2+k^2+l^2}}$. Thus the spacings for cubic 111, 311, 331 and 333 are respectively as follows: $\frac{a_0}{\sqrt{3}}, \frac{a_0}{\sqrt{11}}, \frac{a_0}{\sqrt{19}}$ and $\frac{a_0}{\sqrt{27}}$. These four lines, mistaken by Palacios and Salvia for cubic, are actually reflections from monoclinic $31\bar{1}$, 133, 016 and 226. When converted to the cubic lattice, their spacings are 631×4, 2·13·1×4, 075×2 and 295×2, which are equivalent to $\frac{4a_0}{\sqrt{46}}, \frac{4a_0}{\sqrt{174}}, \frac{2a_0}{\sqrt{74}}$ and $\frac{2a_0}{\sqrt{110}}$, respectively. The comparable spacings for the four planes listed by Palacios and Salvia may be written as $\frac{4a_0}{\sqrt{48}}, \frac{4a_0}{\sqrt{176}}, \frac{2a_0}{\sqrt{76}}$ and $\frac{2a_0}{\sqrt{108}}$. These are so close to the actual spacings that it is easy to see how the error was made.

From the foregoing, two conclusions may be drawn. (1) The fact that twelve lines of the powder photograph can be given cubic indices $h''k''l''$ does not imply the presence of a cubic modification, but results solely from the pseudo-cubic character of the monoclinic cell. (2) The pseudo-cubic cell cannot be based on a Cu_2O-type of structure, for the twelve reflections do not correspond to those to be expected from such a type. The four reflections, 111, 113, 133 and 333, all supposed to be present by Palacios and Salvia, are actually missing. These reflections would all be required by a Cu_2O-type structure, and would be comparatively strong.

In order to determine the significance of the split reflections reported by Palacios and Salvia, zero level Weissenberg photographs were taken about each of the three a axes of an argentite cube. The specimen was from Freiberg, Saxony, and showed well developed {211} faces truncating the cube corners. The photographs indicate that the argentite cube consists of a mosaic, not of the high and low temperature modifications as proposed by Palacios and Salvia, but rather of monoclinic pseudo-cubes in various orientations.

The pseudo-cube in a crystal of acanthite is bounded by monoclinic $(\bar{2}01)$, (011) and $(01\bar{1})$. When an argentite crystal inverts, it would seem reasonable to assume that any one of the three cube planes might become monoclinic $(\bar{2}01)$. Since the three cube planes are identical, there should be an equal probability for each, and hence all three orientations might be expected. That is, in different portions of the inverted crystal, monoclinic $(\bar{2}01)$ may be parallel to the original cubic (100), (010) and (001). Furthermore, each of these orientations could have either of two positions, 90° apart. The identical cubic directions [011] and $[01\bar{1}]$ are parallel to the b^* and c^* directions in the monoclinic. After inversion, either of the two cubic directions may be b^* or c^*. The two possibilities represent two positions about the monoclinic a axis, 90° apart. Hence an argentite crystal at ordinary temperatures should consist of a mosaic of monoclinic pseudo-cubes in six different orientations, but with these orientations all having marked parallelism of nearly equivalent directions.

Under these conditions, any single cube face of an argentite crystal after inversion would have parallel to it both $(\bar{2}01)$ and (011) or $(01\bar{1})$ of the monoclinic. The first has a spacing of 4.76Å, the two latter 4.88Å. First order reflections are missing from both. The second order reflections correspond to spacings of 2.38Å and 2.44Å, respectively. These must be the split reflections obtained by the Bragg method from cube faces of argentite by Palacios and Salvia, and attributed by them to d_{200} from both the high and low temperature modifications. Since monoclinic $(\bar{2}01)$ is equivalent to orthorhombic (100), this assumption gave them a correct value for their orthorhombic cell dimensions.

Although not identical, the Weissenberg zero level photographs about the three a axes of an argentite cube show no distinctive differences, thus indicating that the various orientations are randomly distributed. For a given axis rotation, the Weissenberg pattern is essentially equivalent to two superimposed monoclinic Weissenberg zero level, a axis photographs, 90° apart. The monoclinic a axis is almost exactly perpendicular to $(\bar{2}01)$, and the two possible orientations with $(\bar{2}01)$ parallel to a cube face produce this effect. Monoclinic b^* and c^* are at right angles to each other, while the directions [011] and $[01\bar{1}]$ are not quite at 90°. This causes the central lattice lines parallel to [011] and $[01\bar{1}]$ to be doubled, while those parallel to b^* and c^* are single.

In addition to the Weissenberg pattern just described, due to the two orientations of the pseudo-cube parallel to the argentite cube face, there is also the effect of the remaining possible orientations of the pseudo-cube, with monoclinic (011) or (01$\bar{1}$) parallel to the argentite cube face. For these orientations the main central lattice lines are [$\bar{2}$01] and [011] or [01$\bar{1}$]. The latter two are identical with, and fall right upon similar lattice lines of the previous orientation. The [$\bar{2}$01] central lattice line falls upon [011] or [01$\bar{1}$] of the previous orientation, and the slight difference in spacing causes doubled reflections. Other reflections between the main central lattice lines are so much alike that they are indistinguishable. Certain pairs of entirely different planes have almost equal spacings and nearly symmetrical positions. The reflections arising from such planes in the various orientations cannot be distinguished with certainty, especially since the films are of mediocre quality.

The implications of this parallelism between the monoclinic pseudo-cube and the actual high temperature cubic lattice are uncertain. It would seem reasonable to conclude that there is a close relationship between the two structures. Powder photographs of Ag_2S above 180°C. taken by Emmons, Stockwell and Jones (1926) and also verified by the author, show a cubic pattern consisting of only four lines. They are 3.40Å (*ms*), 2.42 (*s*), 1.98 (*w*) and 1.71 (*m*). They correspond closely in position, but not in intensity, to the first four lines of the monoclinic pattern to which cubic indices can be directly assigned (Table 2). The four spacings are in the simple ratio of $\frac{1}{\sqrt{1}}:\frac{1}{\sqrt{2}}:\frac{1}{\sqrt{3}}:\frac{1}{\sqrt{4}}$, and by themselves may be indexed in several ways. But the indices 110, 200, 211 and 220 are the only simple ones which correspond to a unit cube containing an integral number of formula weights, providing that the density of Ag_2S at room temperature, 7.2, is assumed also to be the density of the cubic form. This unit cube has $a_0=4.84$Å, contains $2Ag_2S$, and corresponds directly with the monoclinic pseudo-cube. The four lines of the cubic pattern, and the twelve of the pseudo-cubic, are those characteristic of a body-centered lattice. But there are objections to such a simple solution. No cubic space groups based on a body-centered (*I*) lattice have special positions for four atoms. Among all of the cubic space groups there are only five which provide special positions accommodating both 2 and 4 atoms, and because of duplication, these five actually represent only two different structure types. In both, the two S atoms would be at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, while the four Ag atoms would have either positive or negative tetrahedral arrangements at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, etc., or *xxx*, etc. The former represents the Cu_2O-type; the latter would not be expected unless the two atoms at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ were different in size. The light S atoms at the positions 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ would not be able to influence sufficiently the diffraction effects to give a body-centered pattern. There is no way in which a tetrahedral arrangement of four Ag atoms could even remotely simulate a body-centered structure.

Because of the wrong assignment of indices to their pseudo-cubic pattern, Palacios and Salvia thought they had proof of a Cu_2O-type of structure. This would require a Ag-S distance of about 2.10Å. The exact type of bonding in Ag_2S is not known; it might be expected to be intermediate between the metallic and electron-pair bond types. The interatomic distance of 2.10Å is very small for either type, and would require such a high degree of polarization that it seems improbable. Moreover, as already stated, a Cu_2O-type of structure would require strong reflections from planes such as 111, 113, etc., which are not found on photographs taken above 180°C.

Two possible solutions of this dilemma might be mentioned. The fact that the pseudo-cube is a ficticious unit, with only part of the lattice corners occupied, and with adjacent cubes different, suggests that the true cubic unit might be a multiple of this pseudo-cube, with $a_0 = n \times 4.84$Å. This larger unit could then legitimately have missing atoms at the corners of some of the sub-cubes, and the possible positions for the $n^3 \times 4$ Ag atoms would be greatly increased. However, when a complex structure gives diffraction effects simulating those of a simple structure, it usually means that it actually deviates only slightly from such a simple structure. On the average, there would still have to be four Ag atoms in each sub-cube, and although no longer restricted to a tetrahedral arrangement, the possibility of simulating a body-centered structure seems remote. The second possible solution would be a defect lattice, in which the Ag atoms were distributed at random over only a portion of the positions normally required by cubic symmetry. Conjectures concerning these and other possibilities might better be left until Weissenberg data from argentite crystals above 180°C. are available.

No light is thrown on the cubic structure of Ag_2S by the chemically similar compound Cu_2Se. This compound is cubic, and was reported by Davey (1923) to have a CaF_2-type of structure. The author has checked this by means of both powder and Weissenberg photographs of octahedral crystals of Cu_2Se, obtained by passing Se vapor over hot Cu. Cubic Ag_2S and cubic Cu_2Se are not isomorphous.

MORPHOLOGY OF ACANTHITE

The very close approximation of the true monoclinic unit cell to an orthorhombic unit is sufficient to account for the previous classification of acanthite as orthorhombic. Pairs of planes, such as (100) and $(10\bar{1})$, (101) and $(10\bar{2})$, etc., are so nearly symmetrical in position that their measured angles would be practically indistinguishable, especially when the poor quality of the usual goniometric measurement on acanthite is considered. This pseudo-symmetry is very apparent in a gnomonic projection constructed normal to the *a* axis (Fig. 7). In such a projection the center is almost exactly halfway between the face poles for (100) and $(10\bar{1})$.

Added to this pseudo-symmetry is the mimetic effect of the polysynthetic (001) twinning. Thus on type 1 crystals, the main terminal face is not $(10\bar{1})$ but a combination of (100) from one twin orientation and $(10\bar{1})$ of the other. A similar situation prevails for all other terminal faces. It might be expected that when there is a distinct monoclinic character, as in the type 1 crystals, or in that described by Groth from Annaberg, the crystal would consist chiefly of one of the two twin orientations. If the two orientations are present in nearly equal proportions, orthorhombic symmetry would be simulated. Even in the former case, however, the measured angles could be interpreted as orthorhombic.

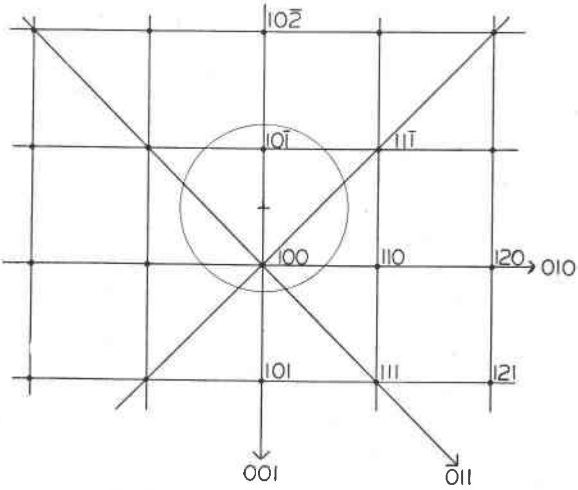

FIG. 7. Gnomonic projection perpendicular to the *a* axis. The points do not represent observed faces, but merely internal planes. Poles 100 and 101 are nearly equi-distant from the projection center, resulting in a pronounced pseudo-symmetry. Because of the near equivalence of *b* (6.92Å) and *c* sin *β* (6.86Å) the projection appears tetragonal.

The possible interpretation of acanthite as cubic was pointed out by Krenner (1888), who concluded that acanthite actually is cubic. In a personal communication, Professor Charles Palache told the author that he had never measured a crystal of acanthite that could not be interpreted as cubic. The explanation of this of course lies in the fact that the monoclinic lattice is not only pseudo-orthorhombic, but also pseudocubic. In this connection it should be pointed out that although in some cases the monoclinic *spacings* d_{hkl} have no direct counterpart in the two pseudo-cells (Table 2), every monoclinic *plane hkl* is parallel to a corresponding plane $h'k'l'$ and $h''k''l''$ in the pseudo-cells. As a result, every monoclinic face can also be given both orthorhombic and cubic indices. Krenner gives a table of corresponding angles and indices for the cubic and orthorhombic interpretations, and this is exactly what would be expected from the two pseudo-cells. The measured range of angles between any pair of faces almost invariably extends on both sides of the value to be expected from a cubic crystal.

As can be seen readily from the gnomonic projection in Fig. 7, as well as from the orthorhombic axial ratio $a:b:c = 0.6886:1:0.9944$, the structure also possesses a pronounced pseudo-tetragonal character. But so far as the author is aware, no one has considered the true symmetry of acanthite to be tetragonal.

SUMMARY

The data obtained from the Weissenberg and powder photographs of Ag_2S at room temperature may be summarized as follows:

Acanthite, Ag_2S
$a = 9.47$Å
$b = 6.92$
$c = 8.28$
$c \sin\beta = 6.86$
$\beta = 124°$
Cell volume $= 449.8$Å^3
Cell contents $= 8\ Ag_2S$
$d_{(\text{lit.})} = 7.22$
$d_{(\text{calc.})} = 7.27$

Monoclinic; $a:b:c = 1.368:1:1.96$ (x-ray).
Probable space group $B2_1/c$ (C_{2h}^5).

hkl absent when $h+l$ is odd.
$h0l$ absent when either h or l is odd.
$0k0$ absent when k is odd.
Polysynthetic twinning (001) observed on all crystals.
Contact twinning (100) on type 2 crystals only.

The previous assignment of acanthite to the orthorhombic and cubic systems on the basis of morphology, and the interpretation of the x-ray data as indicating orthorhombic and cubic lattices, are both explained by the pseudo-orthorhombic and pseudo-cubic character of the actual monoclinic cell. The close correspondence of the interfacial angles with those of systems with higher symmetry is due to the cell dimensions. The occurrence of crystals with apparent orthorhombic symmetry is due both to cell dimensions and to the mimetic effect of the polysynthetic twinning.

It seems probable that the high-temperature cubic lattice is closely related to the pseudo-cubic cell, and that neither is based on a Cu_2O-type of structure. It is not isomorphous with cubic Cu_2Se. No other conclusions are drawn as to the structure of the cubic form, either with respect to dimensions or atomic positions.

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