MINERALOGICAL JOURNAL, VOL. 5, NO. 2, PP. 124–148, FEB., 1967

X-RAY STUDY ON THE α–β TRANSITION OF Ag_2S

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ABSTRACT

The refinement of the structure of α-Ag_2S was undertaken together with an accurate determination of the lattice constants. The final structure gave the R-factor of 16.8% including unobservable reflections.

The crystals found in nature are almost invariably twinned, and a theoretical consideration on the modes of twinning led to the conclusion that twenty-eight twin laws are possible.

Heat treatments of the specimens were carried out in order to know the details of the progress of twin formation premonitory to the α-β transition. The specimens remain substantially unaltered up to 152–156°C, the only change being observed in the β-angle. Above this temperature range, individuals of twins in various orientations appear, and the X-ray reflections take an appearance of trains of spots. At about 165°C these spots along each line fuse into one another, giving an arc-like intensity distribution. Some nodes of strong intensities along these arcs are converted into sharp reflections of the high-temperature form at the transition temperature, 173°C.

As the rise of temperature, therefore, the structure of Ag_2S makes the first approach to the β-form by giving itself more maked cubicity through the change in the β-angle, at the next step simulates the symmetry of the high-temperature form by twinning, and finally at the transition temperature rearranges into parallel orientation the twin individuals which have been deranged owing to their obliquity.

Introduction

It has been recognized that Ag_2S crystallizes into two forms, α and β. The low-temperature α-form named acanthite is monoclinic and stable up to 173°C and above this temperature the cubic β-form appears. On cooling through this temperature, the high-temperature crystal is converted into an aggregate of twinned crystals of low-temperature form but retains its original cubic morphology. This apparently cubic crystal has been named argentite (BRAGG & CLARINGBULL, 1965).

The structure of the α-form was determined by FRUEH (1958) and a reasonable model of the structure of the β-form was proposed by RAHLFS (1936). As the results of these investigations, it has been established that these two structures are based upon the same body-centred cubic arrangement of sulphur atoms, though the distribution of silver is different between them.

Beside this simple relationship between the two structures, the α-β transition is a typical first-order and endothermic one (MALCOLM, 1952; LAWRENCE, 1961) and is moreover easy to study by X-ray means because of its low transition temperature. The present study was therefore undertaken as part of a series of our investigations into the atomic behaviour of crystals during at thermal transitions.

Refinement of the structure of α-Ag_2S (acanthite)

In order to supply with a reliable starting point for the present and future studies of this material, the refinement of α-Ag_2S was carried out at the beginning of this investigation.

The specimen used for this purpose was crystals from the Innai mine, Akita, Japan, and was nearly spherical in shape and about 0.2 mm in diameter. Most of the crystals available, though apparently single, were in fact aggregates of individuals twinned after reflection across ($\bar{1}04$), and only after laborious efforts was found the piece free from the twinning.

Integration Weissenberg photographs were taken with Cu$K\alpha$ radiation (λ=1.5418Å) and a set of intensity data necessary for a three-dimensional work were collected by its *a*- and *b*- axis rotations. The intensities were measured with a microphotometer, and after corrections for the *Lp*-factors and for absorption by assuming the specimen to be ideally spherical, the relative values of structure factors were derived. These were then put on to an absolute scale

Table 1. Lattice constants of α-Ag_2S

	Newly refined values*	Values given in ASTM No. 14–72**
a	4.231Å	4.229Å
b	6.930	6.931
c	9.526	9.527
β	125°29′	125°33′

Powder data

h	k	l	$d^*_{obs.}$ (new)	$d^*_{calc.}$	d^{**}_{obs} (ASTM)
$\bar{1}$	0	2	3.95	3.958	3.96
$\bar{1}$	1	2	3.440	3.435	3.437
0	1	2	3.377	3.383	3.383
1	1	0	3.078	3.072	3.080
$\bar{1}$	1	3	2.832	2.836	2.836
$\bar{1}$	2	1	2.661	2.661	2.664
$\bar{1}$	2	2	2.604	2.603	2.606
0	2	2	2.582	2.582	2.583
1	1	1	2.455	2.458	2.456
1	2	0	2.432	2.444	2.440
0	1	3	2.420	2.422	2.421
$\bar{1}$	0	4	2.382	2.383	2.383
0	3	1	2.211	2.208	2.213
$\bar{2}$	0	2	2.084	2.085	2.093
1	0	2	2.045	2.050	2.047
$\bar{1}$	3	2	1.993	1.991	1.995
$\bar{1}$	2	4	1.961	1.961	1.963
$\bar{2}$	1	4	1.903	1.903	1.903
0	1	4	1.865	1.868	1.866
$\bar{2}$	1	5	1.718	1.718	1.718
$\bar{1}$ $\bar{2}$	4 2	2 5	1.580	1.583 1.578	1.587 1.579
$\bar{2}$	0	6	1.553	1.555	1.554
$\bar{1}$	0	6	1.540	1.540	1.540
0	1	5	1.513	1.514	1.513
0	3	4	1.484	1.485	1.483
$\bar{1}$	3	5	1.459	1.458	1.459

* After the new axial setting described in the text.

** Converted into the axial setting as above.

successively by comparing them with the calculated ones at each stage of refinement.

An accurate determination of the lattice constants was also attempted by pulverizing specimens in liquid nitrogen. The values derived from least squares and the powder data are listed in Table 1 and compared with those given in the ASTM Card No. 14-72.

The refinement was initiated with the use of the atomic coordinates given by FRUEH (1958), but with a change of the c-axis to the [101] direction of his axial setting so as to facilitate the correlation of the structure with that of the β-form in the subsequent study. The space group has thus been converted into $P2_1/c$ from $P2_1/n$. After several cycles of least squares, the final structure was derived with the R-factor of 16.8% including unobservable reflections. The refined atomic coordinates are tabulated in Table 2 together with those given by Frueh but converted after the new axial setting. As recognized in this table these two structures are essentially the same. Tables of observed and calculated structure factors are available

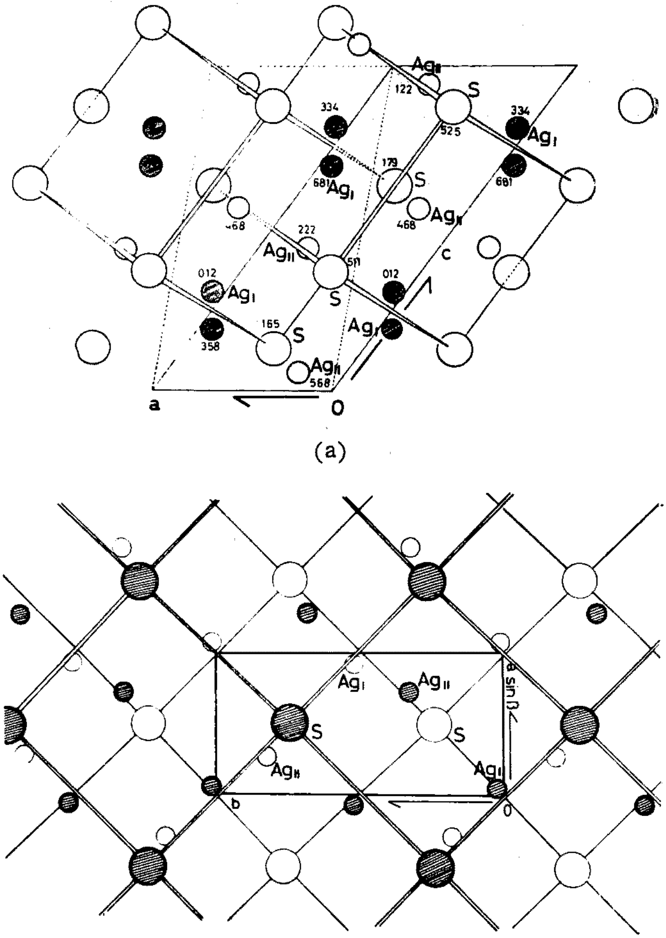
Table 2. Atomic coordinates with standard deviations and isotropic temperature factors.

Newly refined values

	x	y	z	B
Ag_I	0. 0712 (0. 0011)	0. 0169 (0. 0008)	0. 3075 (0. 0005)	4. 27 (0. 09)
Ag_{II}	0. 7259 (0. 0009)	0. 3213 (0. 0008)	0. 4362 (0. 0004)	3. 65 (0. 08)
S	0. 5000 (0. 0025)	0. 2383 (0. 0019)	0. 1306 (0. 0011)	1. 96 (0. 17)

Values determined by Frueh

	x	y	z	B
Ag_I	0. 063	0. 015	0. 305	1. 01
Ag_{II}	0. 721	0. 320	0. 435	1. 16
S	0. 493	0. 239	0. 134	0. 93



(a)

(b)

Fig. 1. Structure of α-Ag_2S. (a) Projection on to (010). (b) Projection along c.

from one of the authors (S. S.) on request.

The structure of α-Ag_2S thus derived is illustrated in Fig. 1, which is compared with three-dimensional Fourier maps in Fig. 2. In this structure the arrangement of sulphur atoms is approximately after a cubic body-centred lattice which is very close to that of the β-form, and shall accordingly be called 'β-lattice' hereafter. Then,

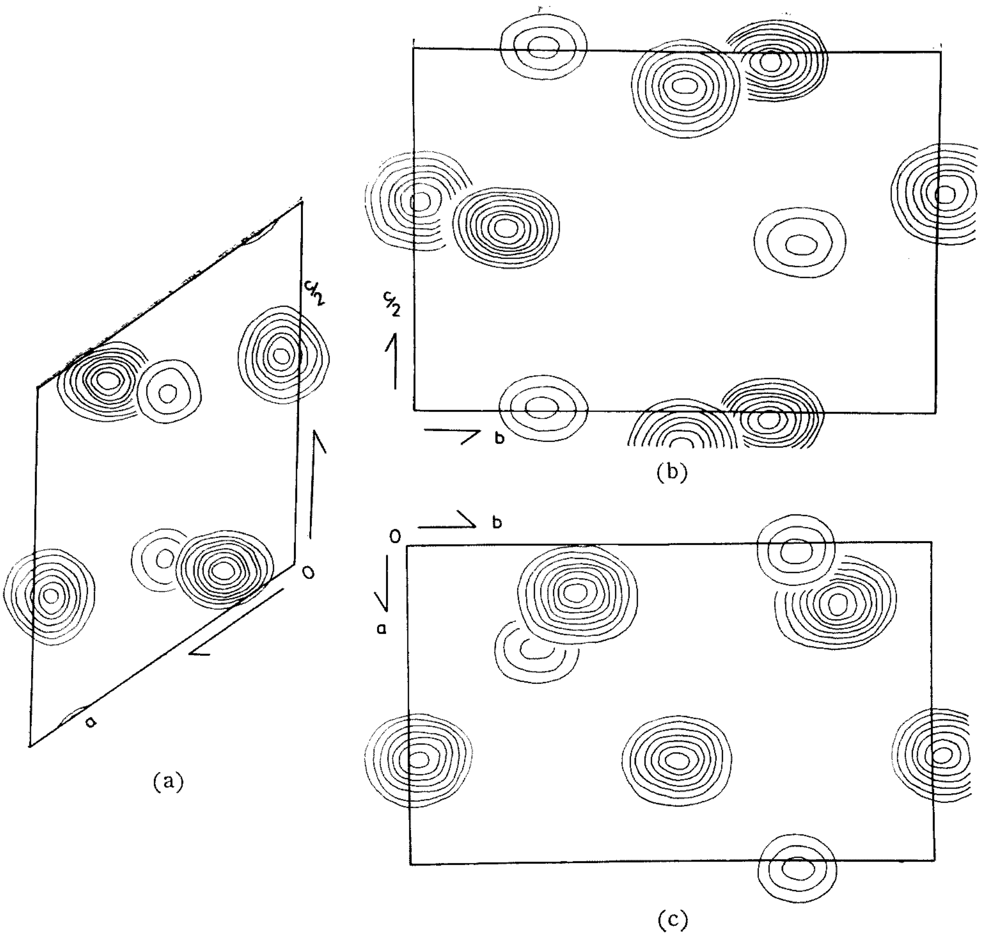


Fig. 2. Three-dimensional electron density maps shown in composite projection of sections, each cutting the centre of an atom. (a) Projection on to (010), corresponding to Fig. 1 (a). (b) Projection parallel to *a*. (c) Projection parallel to c^*.

the mutual orientation between the β-lattice and the monoclinic lattice of the whole edifice of the structure is approximately described as follows:

$$a_\alpha=\frac{1}{2}(a_\beta+b_\beta-c_\beta),$$

$$b_\alpha=a_\beta-b_\beta,$$

and

$$c_\alpha=2c_\beta.$$

If we take into consideration the directional relations only, there hold $[100]_\alpha \| [111]_\beta$ approximately, and $[010]_\alpha \| [1\bar{1}0]_\beta$ and $[001]_\alpha \| [001]_\beta$ strictly. Silver atoms are divided into two groups, Ag_{I} and Ag_{II}. Ag_{I} has two nearest sulphur atoms, showing distorted linear bonds, while Ag_{II} is situated at the apex of a flattened pyramid formed with three sulphurs. The observed bond-lengths are listed in Table 3.

Possible modes of twinning

As mentioned above, twinning is frequently observed with α-Ag_2S and the apparently cubic crystal found in nature has invariably been converted into an aggregate of twinned α-forms. In fact, since the structures of the α- and β-forms are based upon the same cubic arrangement of sulphur atoms, parts of a crystal derived from β on cooling naturally take twin orientations with one another.

In order to derive the possible modes of twinning of the monoclinic α-form, let us suppose after FRIEDEL (1926), that rotation axes and mirror planes, both the elements of pseudosymmetry of the β-

Table 3. Some interatomic distances in α-Ag_2S.

Ag_I —Ag_I	3.35;	3.58;	3.58Å	
〃 —Ag_{II}	3.08;	3.11;	3.11;	3.20
〃 — S	2.47;	2.51;	3.47;	3.83
Ag_{II} —Ag_{II}	3.12;	3.73		
〃 — S	2.56;	2.54;	2.70;	2.99
S — S	4.13;	4.14;	4.15;	4.23

lattice, are qualified to become twin operations. Then, it will be easy to see that there are, for such twin operations, three four-fold rotation axes, four three-fold ones, five two-fold ones, and eight mirror planes in all, and accordingly thirty $(=3\times3+4\times2+5\times1+8\times1)$ twin individuals are formally derived from a crystal in the starting orientation. However, the *c*-axis and the (100) plane of the α-form in this orientation coinside respectively with a four-fold axis and a mirror plane among the twin operations. Therefore, owing to the monoclinic holohedral symmetry of the crystal, a rotation by 180° around [001] is equivalent to a reflection across (100). The same kind of consideration will also be applied to a rotation by 180° around a two-fold axis in the direction of [401] and a reflection across $(\bar{1}04)$. Thus, the total number of independent individuals in twin orientations in respect to the starting crystal will be reduced from thirty to twenty-eight, and we can conclude that there are twenty-eight twin laws altogether as illustrated in Fig. 3 and listed in Table 4. It is to be noted that if the β-lattice in the α-form were strictly cubic, the total number of independent individuals would be reduced

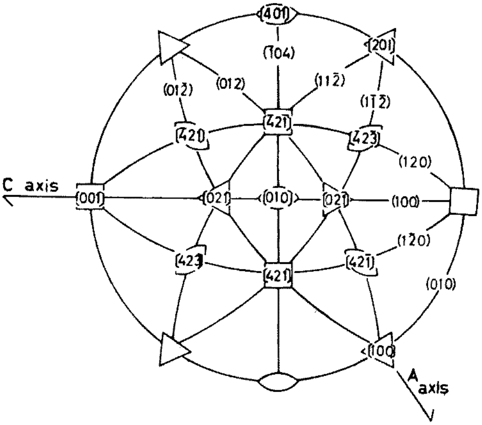


Fig. 3. Stereographic projection of the operations of possible twin laws. The axes of the monoclinic lattice of α-Ag_2S are as indicated, the *b*-axis being perpendicular to the plane of the projection.

to eleven as referred to later.

The twin laws thus derived may be classified into eleven groups according to the similarity of the resulting orientations of individuals as shown in Table 5. If twins in each group are assumed to appear with the same frequency, it will be possible to characterize the group with its twin operation of the highest order. This way of representation has been found to be useful for the description of twin formation during the course of heat treatments, and accordingly three types are set up, mirror, 4-fold, and 3-fold, also shown in Table 5.

Heat treatments and twin formation

The recent study by YOUNG (1962) on the α-β transition of quartz has presented a typical example of twin formation as a premonitory phenomenon to a transition; twins after the Dauphiné law recur the

Table 4. Possible twin laws and obliquities.

No.	Twin law*	Obliquity	No.	Twin law*	Obliquity
1	$(\bar{1}\ 0\ 4)$ $[4\ 0\ 1]_{180}$	1°17′ 1°17′	15	$[\bar{4}\ 2\ \bar{1}]_{270}$	0°50′
2	$(1\ 0\ 0)$ $[0\ 0\ 1]_{180}$	1°17′ 1°17′	16	$[4\ 2\ 1]_{90}$	0°50′
3	$[0\ 0\ 1]_{90}$	1°17′	17	$[4\ 2\ 1]_{180}$	0°50′
4	$[0\ 0\ 1]_{270}$	1°17′	18	$[4\ 2\ 1]_{270}$	0°50′
5	$[1\ 0\ 0]_{120}$	1°59′	19	$[\bar{4}\ 2\ \bar{3}]_{180}$	6°31′
6	$[1\ 0\ 0]_{240}$	1°59′	20	$[4\ 2\ \bar{1}]_{180}$	0°52′
7	$[\bar{2}\ 0\ \bar{1}]_{120}$	2°22′	21	$[4\ 2\ 3]_{180}$	6°31′
8	$[\bar{2}\ 0\ \bar{1}]_{240}$	2°22′	22	$[\bar{4}\ 2\ 1]_{180}$	0°52′
9	$[0\ 2\ 1]_{120}$	1°36′	23	$(1\ 2\ 0)$	0°50′
10	$[0\ 2\ 1]_{240}$	1°36′	24	$(1\ \bar{2}\ 0)$	0°50′
11	$[0\ 2\ \bar{1}]_{120}$	1°36′	25	$(1\ 1\ \bar{2})$	0°52′
12	$[0\ 2\ \bar{1}]_{240}$	1°36′	26	$(1\ \bar{1}\ \bar{2})$	0°52′
13	$[\bar{4}\ 2\ \bar{1}]_{90}$	0°50′	27	$(0\ 1\ 2)$	6°31′
14	$[\bar{4}\ 2\ \bar{1}]_{180}$	0°50′	28	$(0\ 1\ \bar{2})$	6°31′

* Suffixes indicate rotation angles

Table 5. Classification of twin laws.

No. of the group of twin laws	Twin orientation*		Nos. of twin laws in Table 4	Type
	a-axis	*c*-axis		
1	$[2\ 0\ 1]$	$[0\ 0\ 1]$	1, 2	mirror
2	$[0\ \bar{2}\ \bar{1}]$	$[0\ 0\ 1]$	3, 17, 23	4-fold
3	$[0\ 2\ \bar{1}]$	$[0\ 0\ 1]$	4, 14, 24	
4	$[1\ 0\ 0]$	$[\bar{4}\ 2\ \bar{1}]$	6, 19, 28	3-fold
5	$[2\ 0\ 1]$	$[\bar{4}\ 2\ \bar{1}]$	12, 16	
6	$[0\ \bar{2}\ \bar{1}]$	$[\bar{4}\ 2\ \bar{1}]$	8, 22, 26	
7	$[0\ \bar{2}\ 1]$	$[\bar{4}\ 2\ \bar{1}]$	10, 18	
8	$[1\ 0\ 0]$	$[\bar{4}\ \bar{2}\ \bar{1}]$	5, 21, 27	
9	$[2\ 0\ 1]$	$[4\ 2\ 1]$	9, 15	
10	$[0\ 2\ 1]$	$[\bar{4}\ \bar{2}\ \bar{1}]$	11, 13	
11	$[0\ 2\ \bar{1}]$	$[\bar{4}\ \bar{2}\ \bar{1}]$	7, 20, 25	

* Approximate directions of the *a*-and *c*-axes of the twin individuals derived from the starting crystal after the twin laws in the third column.

more frequently, to the higher temperature is a quartz specimen subjected toward the transition temperature, 573°C. A process of the same kind was expected to occur in the present material, and in order to know the details of the progress of twin formation, heat treatments of the crystal were carried out.

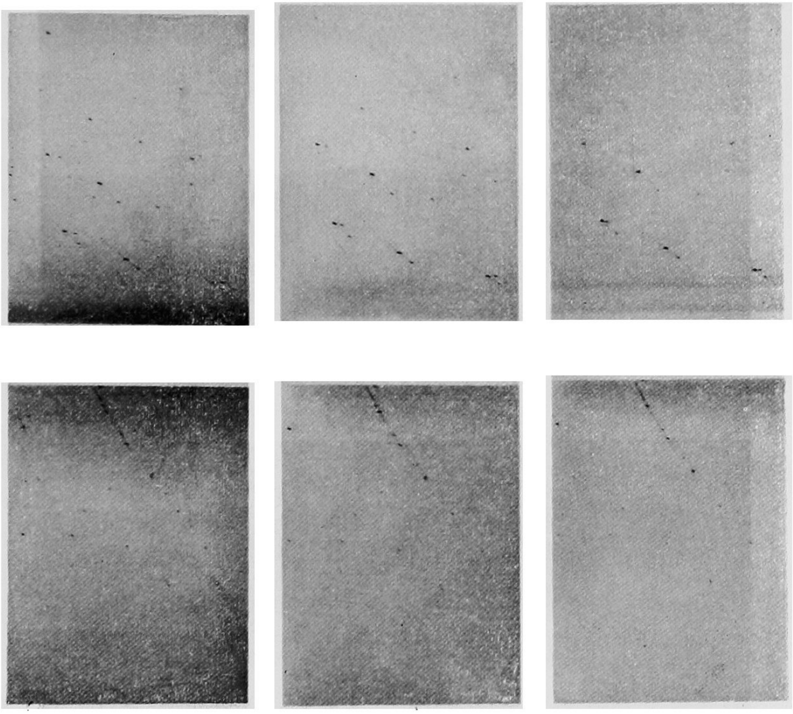
The specimens for this purpose were prepared by crushing the crystals in liquid nitrogen. The fragments thus obtained gave easy identification of their *b*-axes because of the cleavage parallel to (100) and to (001). Oscillation and Weissenberg photographs were taken about the *b*-axis of each specimen at room temperature at the beginning, and an example of the latter is shown in Fig. 5 (a). The twins of mirror type in Table 5 cannot be detected in the oscillation photograph, and therefore Weissenberg photographs must be consulted for identification of this type. The other types can, on the other hand, be easily recognized by the oscillation method; the twins of 4-fold type produce additional reflections along lines parallel to and half-way between a pair of layer lines, and some of 3-fold type give reflections along lines, three of which run between every pair of layer lines. Other members of the latter type give rise to reflections distributed in complicated ways over the oscillation pattern. However, if we take into account the fact that the β-lattice is very nearly cubic and therefore assume that those twins belonging to the 3-fold type occur with the same probability, we may conclude that the three lines of reflections between a pair of layer lines mentioned above serve as the indication of the presence of twins of this type.

The examinations made in this way revealed that all the specimens at room temperature consist of twins of mirror type, about 10% of them show weak reflections indicating the presence of twins of 4-fold type, and some in less proportion give faint and diffuse reflections suggesting the existence of those of 3-fold type.

Each of the specimens was then mounted on the junction of a copper-constantan thermocouple and was placed in a small furnace attached to the goniometer head of a Weissenberg camera. The error in temperature measurements was estimated to lie within ±7°C. Heating was started from 80°C and it was found that the specimens remain substantially unaltered up to 152–156°C, the only change being observed in the β-angle, which become 124°50′ in the above temperature range in comparison with 125°29′ at room temperature. This change in the β-angle is nothing but reducing the deviation of the β-lattice from cubicity and in fact the obliquity of the twins of mirror type was observed to be diminished as temperature was raised. Photographs showing some stages of this change are given in Fig. 4.

At 152–156°C, every reflection becomes to be accompanied, in the b-axis oscillation photograph, by a short diffuse line passing the reflection and along a powder line, and in the Weissenberg photograph with the same rotation axis, also by a short, horizontal and diffuse line passing the reflection. Therefore, each reflection is associated with an intensity distribution over a small region of equal glancing angle. This is immediately followed at the same temperature by sudden appearance of twins of 3-fold type, and the specimen now turns out to be an aggregate of twins of all types. A Weissenberg photograph taken at 155°C is shown in Fig. 5 (b).

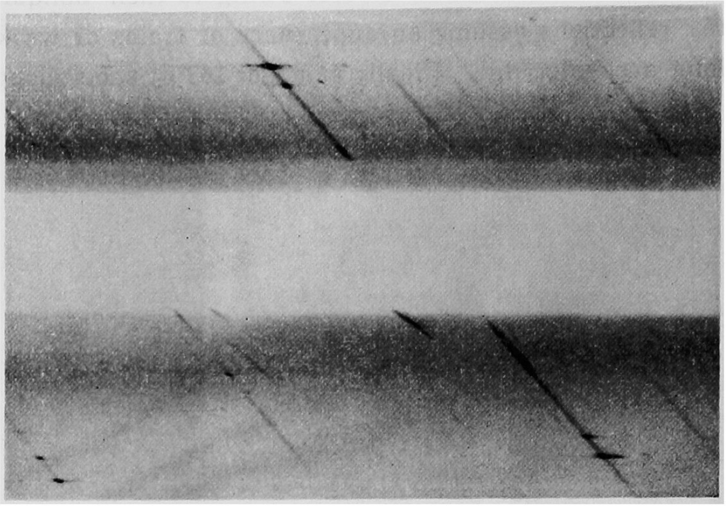
When temperature is still raised, the orientations of newly formed twin individuals become more diverse owing to their obliquity, and the X-ray reflections assume an appearance of trains of weak spots, each along a powder line. Finally at about 165°C, spots along a line



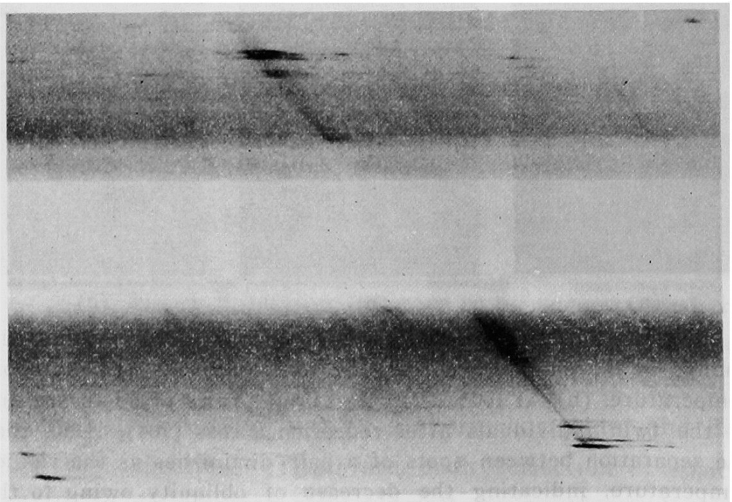
(a) (b) (c)

Fig. 4. Part of Weissenberg photographs, *hll*, showing the change in the β-angle according to temperatures. (a) At room temperature. (b) At 100°C. (c) At 145°C. Pairs of spots are due to the twin individuals after reflection across $(\bar{1}04)$. Note that the separation between spots of a pair diminishes as the rise of temperature, indicating the decrease of obliquity owing to the change in the β-angle.

fuse into one another, thus giving an arc-like intensity distribution as illustrated in Fig. 5 (c) and Fig. 6 (a). Nodes of strong intensity are seen along these arcs, some of them persist at higher temperatures and turn into the reflections of the β-form at the transition point, at which the other nodes as well as arc-like intensity distribu-



(a)



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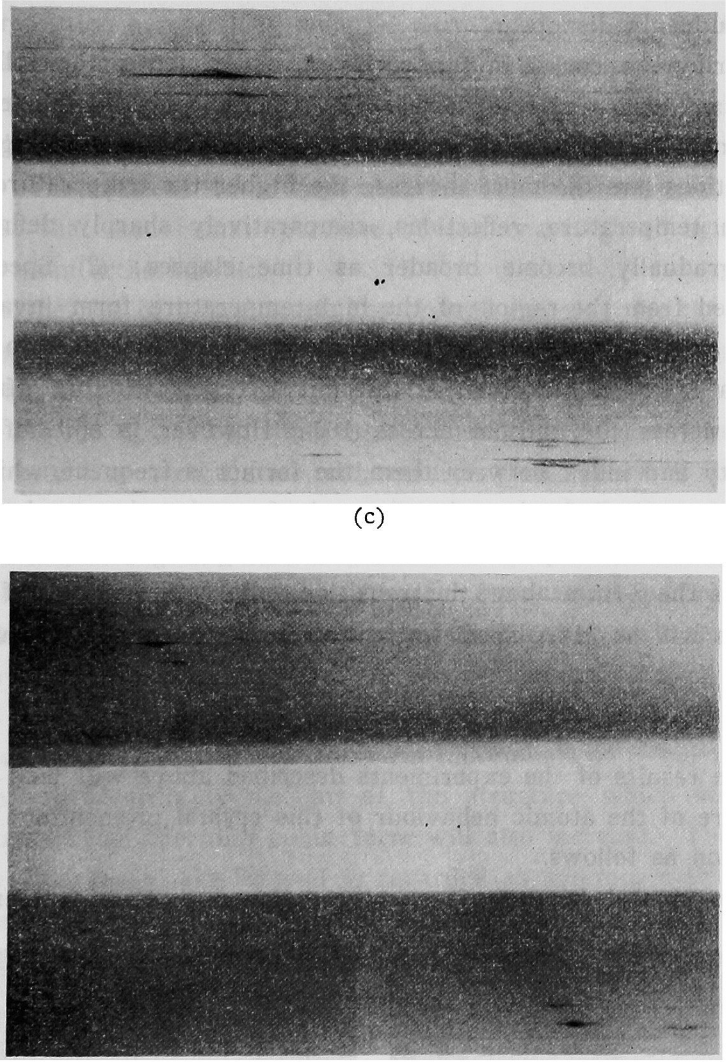

(c)

(d)

Fig. 5. Part of Weissenberg photographs, *h*0*l*, taken at various temperatures. (a) At room temperature. (b) At 155°C; Twins after the laws of 3-fold type begin to occur as indicated by minute spots appearing in the vicinity of each reflection. (c) At 165°C; Twins recur so frequently that reflections due to individuals fuse into streaks. (d) At 190°C; High temperature β-form. Note that the reflections are located at the positions of intensity nodes observed in (c).

tions suddenly disappear.

During the course of this series of experiments, the following facts have also been confirmed: (1) Upon rapid rise of temperature from room temperature to one above 152–156°C, the resulting twin orientations are the more diverse, the higher the temperature, and at each temperature, reflections, comparatively sharply defined at first, gradually become broader as time elapses; (2) Specimens quenched from the region of the high-temperature form invariably exhibit complex twinning as illustrated in Fig. 6(b); (3) Two kinds of twin laws are conceived of the mirror type, twinning after reflection across $(\bar{1}04)$ and one across (100). However, in spite of equal obliquity and index between them, the former is frequent, while the latter rare; (4) Reflections due to newly formed twins tend to converge at the vicinity of each of the reflections that are to become those of the β-form above the transition temperature. Some of these findings will be given special attention in the discussion below.

Discussion

The results of the experiments described above will lead us to a picture of the atomic behaviour of this crystal premonitory to the transition as follows.

The crystal is very frequently twinned at room temperature

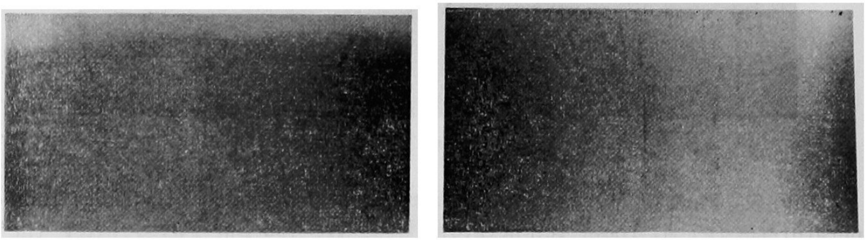
(a) (b)

Fig. 6. Examples of oscillation photographs about *b*. (a) Taken at 169°C, showing streaks along powder lines. (b) Taken with a specimen quenched from the high-temperature form, illustrating the appearance of complex twins.

after reflection across ($\bar{1}04$), and the part of the structure in and near the composition plane has an orthorhombic symmetry. In this respect, the α-form at room temperature is looked upon as having orthorhombic slabs interlacing the monoclinic structure here and there. The twins of 4-fold type observed at room temperature also suggest that some small portions of the crystal bear symmetry higher than orthorhombic.

As the rise of temperature, the crystal prepares for the forthcoming transition first by changing its lattice constants, especially the β-angle so as to bestow its β-lattice more marked cubicity. At about 152–156° C, the twin individuals constituting the crystal seem to get into a perturbed state and some of them are split up into fragments which are more or less deranged from their original orientation, thus giving rise to the diffuse spread of intensity distribution around each diffraction spot. These deranged fragments are immediately rearranged into twins of 3-fold type, and though the process is mostly completed in this temperature range, it tails away perhaps up to the vicinity of the transition temperature. In fact, as the rise of temperature, twin individuals of 3-fold type increase, and accordingly the part of the structure which simulates the structure of the high cubic form will also increase. Therefore, up to this stage, the crystal is regarded as making, within short ranges, for the structure of the β-form.

However, this effort of the crystal to approach the high-temperature form seems to defeat its own purpose owing to the obliquity inherent to this mode of twinning and still persisting at these high temperatures, the orientations of the minute individuals eventually become so diversified that a large part of the crystal takes an appearance of an aggregate of crystalline powder, and accordingly the long-range order the crystal originally possessed has now been seriously impaired. Judging from the fact that nodes of strong intensity are observed at the positions of reflections which are to turn into those of the β-form after the transition, we may conclude that twin individuals prefer such orientations as to facilitate the β-lattice to conserve itself throughout the course of these changes. However, it is also true that to complete the transition, some large number of individuals should be brought back parallel to the original orientation of the β-lattice.

This process of lining up deranged individuals will be executed at the transition point by rotating them; by the time the crystal arrives at the transition temperature, the twin individuals will have become so minute that they can easily be given rotational movements perhaps by the function of active grain-boundaries. Certain amount of energy is naturally required for this process and accordingly the transition is of the first order.

Now, if we compare the structure of the α-form with that of the β-form, we shall find an interesting feature of this transition. In Fig. 7, the structure of the α-form according to a unit cell of the β-lattice is shown together with the structure of the β-form studied by RAHLFS (1936), in which four silver atoms per unit cell statistically occupy forty-two positions as indicated in the figure.

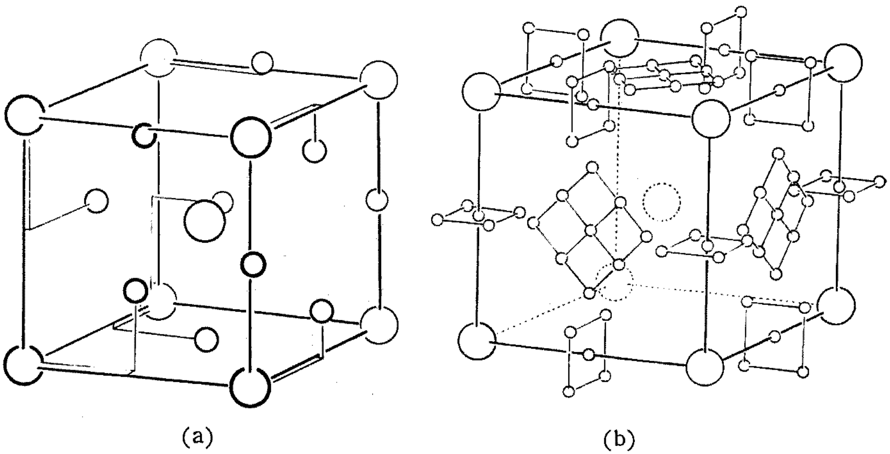
(a) (b)

Fig. 7. Comparison of structures of the α- and β-forms. (a) Structure of the α-form according to a unit cell of the β-lattice. (b) Structure of the β-form determined by RAHLFS (1936).

If the β-lattice were ideally cubic, no obliquity would be met with upon twinning of the monoclinic α-form, and the twin operations would constitute part of the symmetry of $m3m$. Then, eleven independent twin individuals would be derived from the starting crystal, and the result, though twins as far as silver positions are concerned, would have one and the same continuous β-lattice. If so, and if the crystal is composed of twelve individuals, all in an equal amount, it will be easy to see in Fig. 7 that when all the individuals are supposed to be brought by translations into superposition so as for their β-lattices to coincide with one another, the resulting structure will be that of the β-form*. Thus, the β-crystal can be looked upon as the disordered form of the α-crystal, where twinning produces positional disorder of silver atoms, and the α-β transition of Ag_2S may in this respect be regarded as of the order-disorder type. It would be strictly so, were the β-lattice always to retain cubic symmetry. However, the fact is that the β-lattice suffers some distortion below the transition temperature and as the result rotational adjustments of the twin individuals are necessary for the transition, thus requiring a certain amount of latent heat for it.

Finally, the fact that among the twin laws of mirror type, one after reflection across $(\bar{1}04)$ is frequently realized, while the other after reflection across (100) rarely, must briefly be considered. The most probable structures of these twins in and near the composition planes are shown in Fig. 8. From this figure, it will be recognized that while the former shows a reasonable way of atomic linkage across $(\bar{1}04)$, the latter reveals extraordinarily short Ag-Ag

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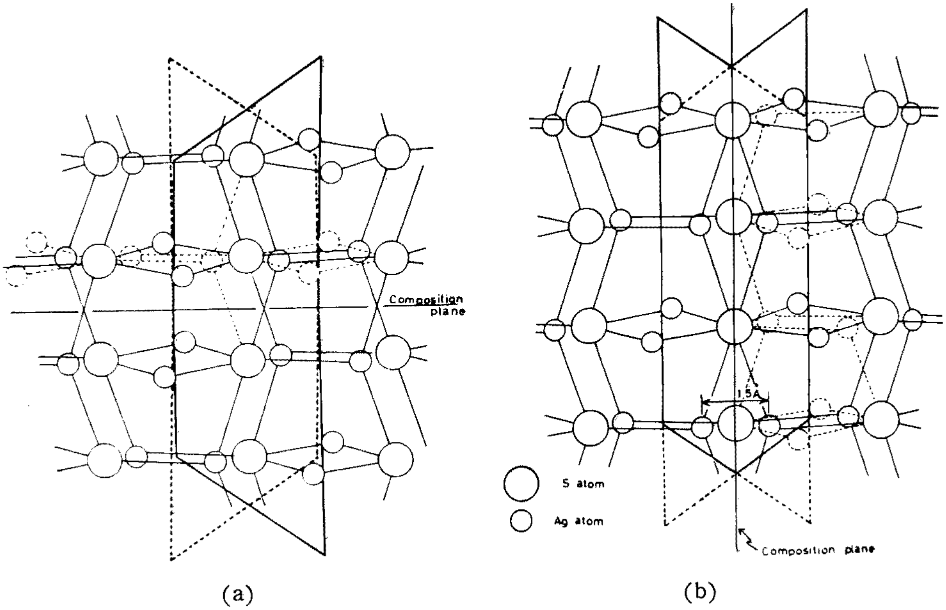
* Mathematically, this procedure can be expressed by convolutions as

$$d^{\beta}(\boldsymbol{r}) = \sum_{j=1}^{12} \int d_j^{\alpha}(\boldsymbol{r}) \cdot \delta(\boldsymbol{r}+\boldsymbol{r}_j) dV,$$

where $d^{\alpha}(\boldsymbol{r})$ is the electron-density distribution function of the α-form, $d^{\beta}(\boldsymbol{r})$ that of the β-form (at least when $\boldsymbol{r}$ is small), the suffix j for the j-th individual, $\delta(\boldsymbol{r}+\boldsymbol{r}_j)$ a delta function normalized to 1/12, $\boldsymbol{r}_j$ the vector to the origin of the j-th individual, δV a volume element, and the integration extends over the entire volume of the j-th individual.



(a) (b)

Fig. 8. Probable structures of the twins of mirror type in and near the composition planes. (a) Reflection across ($\bar{1}04$). (b) Reflection across (100). Note the extraordinarily short Ag-Ag approaches in the latter.

approaches, about 1.5 Å. Therefore, it is certainly unstable and difficult to appear.

Conclusion

The mechanism of the transition will thus be summarized as follows. The crystal, when heated, prepares for the forthcoming transition by repeating twinning and realizes the structure characteristic of the high-temperature form here and there in short ranges in the crystal. However, this premonitory behaviour does not straightforwardly lead to the high-temperature structure owing to the loss of the long-range order. At the transition point, the latter is recovered through rotations of deranged twin individuals perhaps by the function of active grain-boundaries.

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Received 11 November 1966.