References

BUERGER, M. J. & PREWITT, C. T. (1961). *Proc. Natl Acad. Sci. USA*, **47**, 1884–1888.

CHOISNET, J., DESCHANVRES, A. & RAVEAU, B. (1972). *J. Solid State Chem.* **4**, 209–218.

DORNBERGER-SCHIFF, K. (1962). *Sov. Phys. Crystallogr.* **6**, 694–700.

FISHER, K. (1969). *Z. Kristallogr.* **129**, 222–243.

GLASSER, F. P. & DENT GLASSER, L. S. (1961). *Z. Kristallogr.* **116**, 263–265.

GRABMAIER, B. C., HAUSSÜHL, S. & KLÜFERS, P. (1979). *Z. Kristallogr.* **149**, 261–267.

HENSHAW, W. (1955). *Mineral. Mag.* **30**, 585–595.

HILMER, W. (1963). *Sov. Phys. Crystallogr.* **7**, 537–576.

ITO, T. (1950). *X-ray Study on Polymorphism.* Tokyo, Japan: Maruzen.

JEFFERY, J. W. & HELLER, L. (1953). *Acta Cryst.* **6**, 807–808.

NIGGLI, A. (1959). *Z. Kristallogr.* **111**, 288–300.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

TROJER, F. J. (1968). *Z. Kristallogr.* **127**, 291–308.

TROJER, F. J. (1969). *Z. Kristallogr.* **130**, 185–206.

YAMANAKA, T., TAKÉUCHI, Y. & SADANAGA, R. (1980). *Z. Kristallogr.* In the press.

Structures and Phase Transition of β- and γ-Ag₃IS

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Abstract

Single-crystal X-ray data for the fast ionic conductor Ag₃IS were measured in the temperature range 135–295 K. Structure refinement was carried out for the cubic room-temperature (β) phase in space group $Pm3m$ with three Ag⁺ ions distributed among twelve (I,S) tetrahedra. The final refinement [$R(w) = 0.041$ for 49 reflections] resulted in very anisotropic temperature factors for Ag (r.m.s. displacement 0.19–0.39 Å). An alternative structure model with Ag on octahedral sites and anharmonic temperature factors up to the sixth order resulted in $R(w) = 0.042$. At the transition to the γ phase (155 K) the reflection symmetry did not change; the intensities of only a few reflections increased considerably (a maximum of more than 100 times). The single-crystal features were not destroyed by cycling between the β and γ phases. It could be shown definitely by Patterson synthesis that in the γ phase the crystal was composed of 16 differently oriented domains with completely occupied Ag sites. The domains scattered incoherently. The space group of each domain is $R3$. A special program was written to calculate a least-squares refinement for the superimposed intensities of this 16-domain crystal. The weighted R value for the intensities was $R_w(I) = 0.16$

for 55 independent reflections. Additional weak reflections were found in the β and the γ phases, indicating that small domains of monoclinic α-Ag₂S were included in the crystal.

1. Introduction

Silver iodide sulfide is a fast ionic conductor with a close structural relationship to the archetype superionic conductor α-AgI. The major difference is the much higher density of mobile ions: the cubic unit cell with $a = 4.987$ Å contains 3Ag⁺ in Ag₃IS compared to $a = 5.05$ Å and 2Ag⁺ in α-AgI. As a consequence, both the structural and the dynamic properties of Ag₃IS are expected to be much more affected by the repulsive interaction between the Ag⁺ ions than is the case for α-AgI.

All presently known structural data on Ag₃IS have been derived from powder investigations, but they already evidence the considerable structural richness of this compound.

Reuter & Hardel (1961) reported the existence of a room-temperature (β) phase and a high-temperature (α) phase with the β→α transition at 508 K. They measured an ionic conductivity of 0.001 Ω⁻¹ mm⁻¹ at

room temperature and $0 \cdot 1$ Ω^{-1} mm^{-1} at 523 K in the α phase (Reuter & Hardel, 1966).

According to Reuter & Hardel (1965), the α phase is body-centered cubic, very similar to that of α-AgI with I and S statistically distributed over the corners and the centers of the cubes; the three Ag$^+$ ions per unit cell randomly occupy 42 sites. In the β phase the I$^-$ and the S^{2-} ions are ordered, whereby the former are on the 0,0,0, and the latter on the $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ sites. The Ag$^+$ ions are statistically distributed over 12 equivalent sites on the faces of the cube, each only $0 \cdot 5$ Å apart from the face center. The β phase is thus simple cubic (space group $Pm3m$) and may be regarded as a modified anti-perovskite structure.

Recently, the existence of a low-temperature (γ) phase, stable below 155 K, was reported by Hoshino, Sakuma & Fujii (1978) and by Magistris, Chiodelli & Schiraldi (1978). From powder data Hoshino, Sakuma & Fujii (1979) deduced that the γ phase exhibits the symmetry of space group $R3$ with I at 0,0,0, S at x,x,x, $x = 0 \cdot 53$, and with three fully occupied Ag sites [atomic position 3(b)] with coordinates $0 \cdot 528$, $0 \cdot 386$, $0 \cdot 02$. Regardless of the rhombohedral symmetry $R3$ the rhombohedron is a cube with $a = 4 \cdot 890$ Å.

In an extended X-ray investigation on single-crystal Ag$_3$IS we were able to refine the structural parameters of both the β and the γ phases, to obtain accurate anisotropic temperature factors for the β phase (which may be of importance for the elucidation of the ionic conduction paths), and to study the nature of the β–γ transition. For the β phase an ordered structure model with Ag on the face-center positions but with a strongly anharmonic potential seems to be possible too, but this could not be definitely verified.

Beyeler & Brüesch (1977) have reported the observation of tetragonal superstructure reflections within the β phase. In this paper we show that these reflections can be explained by small domains of Ag$_2$S which are included in the Ag$_3$IS crystals.

2. Crystal growth and X-ray measurements

Single crystals of Ag$_3$IS were grown by the Bridgeman technique. Stoichiometric amounts of Ag$_2$S and AgI were sealed in a quartz ampoule, melted and then slowly pulled through a temperature gradient centered at 973 K. The result was a polycrystalline product containing various phases from which samples of single-crystal Ag$_3$IS some mm^3 in size could be separated.

Data collection was carried out with one crystal at room temperature on a Philips PW 1100 four-circle diffractometer and with another at 170 and 135 K on a Syntex $P2_1$ diffractometer; cooling was performed with nitrogen. All measurements were made with graphite-monochromatized Mo $K\alpha$ radiation.

For both crystals the orientation matrices for the cubic Ag$_3$IS structure were determined first. Then, by trying the possible transformations, the orientation of the tetragonal cell (describing the additional reflections) could easily be found. Up to a scattering angle of $\theta = 30°$, Ag$_3$IS and additional reflections were measured simultaneously. At 170 K Ag$_3$IS reflections were also measured in the θ range 30–40°. At room temperature the data were collected in one octant of reciprocal space plus the Friedel reflections. The ω scan mode was used with a scan width of $2 \cdot 8°$ and background measurement was made at each extremity for half the scan time. The low-temperature data sets were measured in two neighboring octants of reciprocal space in the ω–2θ scan mode, with a scan width of $3 \cdot 0°$, and with background measurement at each extremity for a quarter of the scan time. Absorption was corrected with the $ABSORB$ program of the $XRAY$ 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). With this correction the internal R value for symmetry-equivalent reflection intensities of the β phase of Ag$_3$IS could be reduced from $0 \cdot 29$ to $0 \cdot 12$ for the first and from $0 \cdot 16$ to $0 \cdot 06$ for the second crystal. According to symmetry $m3m$, the intensities of Ag$_3$IS reflections were averaged to 49 observed and 5 unobserved $[I < 3\sigma(I)]$ reflections at room temperature, to 76 observed and 28 unobserved reflections at 170 K, and to 54 observed reflections at 135 K.*

3. Structure refinement of the β phase

3.1. Results

According to the crystal structure reported by Reuter & Hardel (1965), the refinement was carried out in space group $Pm3m$ with I and S located at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ respectively and three Ag distributed on the 12-fold position $x,\frac{1}{2},0$ $[12(h)]$. Owing to the symmetry restrictions, I and S were refined with isotropic temperature factors, whereas the Ag$^+$ ions were refined anisotropically.

In addition, another structure model was tested: The Ag$^+$ ions were sited on the three face-centered positions $\frac{1}{2},\frac{1}{2},0$ with an occupation probability of one. With harmonic (anisotropic) temperature factors only, this model was clearly worse than that described above $[R(w) = 0 \cdot 087]$. Then, anharmonic temperature factors up to the sixth order based on the Gram–Charlier expansion were applied using the program system $PROMETHEUS$ (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1981). The agreement between observed

and calculated structure factors now became as good as for the disordered-structure model with harmonic temperature factors [$R(w) = 0.042$]. The room-temperature data do not allow a decision as to which of the two models is physically more meaningful. From a chemical point of view the disordered model with Ag in a tetrahedral position is more reliable and therefore this is used in the following discussion. No significant influence of anharmonic temperature factors could be found in this model and so we only used harmonic ones.

An extinction correction has been applied using Zachariasen's (1967) model as well as that of Becker & Coppens (1975); no significant influence could be found and extinction was subsequently neglected.

Furthermore, the populations of Ag and S were refined by fixing PP(I) = 1.0. We then obtained PP(S) = 1.13 (4) and PP(Ag) = 0.239 (4). In the next refinement step a disorder between I and S positions was allowed with the restrictions PP(0,0,0) = PP($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) = 1, and PP(Ag) = 0.239. This model takes into account the fact that in the β phase some I and S may be frozen at their disordered α-phase positions. In fact, the refinement led to the same amount of S positions occupied by I as vice versa but the degree of this occupational disorder seems to depend on the crystal history (Table 1).

The final refinements were carried out with scattering curves for uncharged atoms, because they gave significantly better agreement for the inner reflections than those for ions without changing any structure parameters. All calculations were performed with the program system *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1981). In Table 1 the final parameters for β-Ag$_3$IS are listed. The weighted R

Table 1. *Structure parameters of β-Ag$_3$IS*

The refinements were carried out with two different crystals. The β_{ij} were defined by the temperature factor $\exp(-\beta_{ij} h^i h^j)$. B is the usual isotropic temperature factor in Å^2.

	295 K	170 K
x(Ag)	0.405 (2)	0.395 (1)
PP(Ag)	0.239 (4)	0.239 (4)
β_{11}(Ag)	0.121 (8)	0.117 (5)
β_{22}(Ag)	0.084 (4)	0.077 (3)
β_{33}(Ag)	0.029 (1)	0.024 (1)
Position $\frac{1}{2},\frac{1}{2},\frac{1}{2}$		
PP(S)	0.97 (1)	0.95 (1)
PP(I)	0.03 (1)	0.05 (1)
B	2.7 (2)	2.9 (1)
Position 0,0,0		
PP(I)	0.97 (2)	0.95 (1)
PP(S)	0.03 (2)	0.05 (1)
B	3.27 (6)	2.94 (4)
Number of reflections	49	76
$R(w)$	0.041	0.041
Goodness of fit	1.69	1.83

value was $R(w) = 0.041$ for 295 K and for 170 K data. The weighting was $\sigma^{-2}(F_o)$. To calculate $\sigma(F_o)$ we used a modified $\sigma(I)$. In addition to the standard deviation $\sigma_c(I)$ calculated from the counting rate, an estimated error of $0.02I_o$ was considered: $\sigma(I) = \sigma_c(I) + 0.02I_o$.

3.2. *Discussion*

An interesting aspect of this refinement is the underoccupation of the Ag sites [0.239 (4) instead of 0.25]. Refinement of the mixed I/S population on 0,0,0 with PP(Ag) fixed at 0.25 led to the unphysical values of PP(I) = 1.03 (1) and PP(S) = −0.03 (1), which shows the significance of the underoccupation. We have measured the density of a single crystal. With the lattice constant of a = 4.897 (5) Å the calculated density of a stoichiometric crystal is 6.82 (4) Mg m^{-3}, whereas the density with only 96% Ag should be 6.60 (4) Mg m^{-3}. By weighing a crystal of about 0.3 g first in air, then in toluol with a density of 0.864 (1) Mg m^{-3}, the density of the Ag$_3$IS single crystal was determined to be 6.86 (5) Mg m^{-3}. Thus, we can conclude that we have investigated stoichiometric Ag$_3$IS. The fact that the refinement of X-ray intensities leads to an underoccupation of the Ag sites may be discussed in the following way.

The crystal contains small domains of the quenched α-phase structure, as can be deduced from the mixed I/S population. The distribution of the Ag$^+$ ions within these domains (Reuter & Hardel, 1965) is only partially described by the occupation of $x,\frac{1}{2},0$ in the β phase. A refinement of the Ag$^+$ ions in the α-phase positions is not possible, because the occupation probabilities are too small. Only the resulting underoccupation of the β-phase position can be seen.

The temperature factors of the Ag$^+$ ions are so large that the ellipsoids of thermal vibration overlap considerably (Fig. 1). This structural evidence for low potential barriers between the quadruplet of Ag states is in good agreement with the interpretation of far-infrared reflectivity data for Ag$_3$IS where evidence was found for a Debye-type relaxational hopping motion of
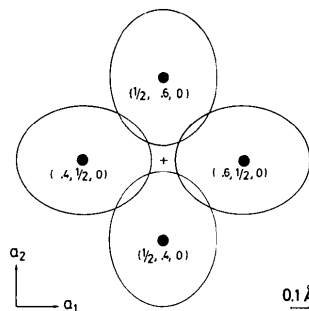

Fig. 1. Ellipsoids of thermal vibration for Ag at 295 K. The probability of finding the Ag inside the ellipsoid is 20%. + marks $\frac{1}{2},\frac{1}{2},0$.
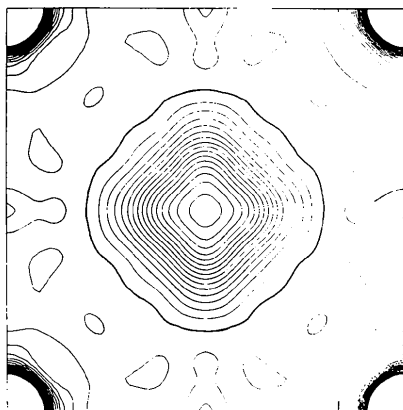
Fig. 2. Fourier map of the $z = 0$ section. Contours start at 1 e Å^{-3} and are at intervals of 2 e Å^{-3}. At the origin all densities above 35 e Å^{-3} are suppressed. At the origin the density is 176 e Å^{-3}.

the Ag$^+$ ions between these states. The infrared data suggest a barrier height of the order of $0\cdot06$ eV (Beyeler & Brüesch, 1977; Brüesch & Beyeler, 1978).

The large temperature factors are not in agreement with the much smaller ones reported by Hoshino *et al.* (1979) ($B_{Ag} = 3\cdot7$ Å^2 at room temperature) but this may result from the smaller range of $\sin(\theta)/\lambda$ which they measured [$\sin(\theta)/\lambda = 0\cdot51$ Å^{-1}, compared to our measurement of $\sin(\theta)/\lambda = 0\cdot9$ Å^{-1}]. the third-order refinement published by Hoshino & Sakuma (1980) is physically meaningless. For $z \to +\infty$ their potential $V(x,y,z)$ goes to $-\infty$. Two of the third-order parameters are negative. For this potential the probability density function $\exp[-V(x,y,z)/kT]$ (k = Boltzmann's constant, T = temperature) is not integrable. From the direction of the largest thermal vibration the direction of ionic conductivity may be deduced. The Ag$^+$ ion at $0\cdot4,\frac{1}{2},0$ has its largest amplitude along the x direction. This indicates that it probably jumps to $-0\cdot4,\frac{1}{2},0$ as well as to $0,\frac{1}{2},\pm0\cdot4$. This deduction is confirmed by a positive electron density around $0,\frac{1}{2},0$ in the Fourier map (Fig. 2), and will be the subject of further studies at higher temperatures.

4. Structure determination of the γ phase

4.1. Symmetry

At the transition temperature a non-linear decrease of the lattice constants was observed (Fig. 3), but the elementary cell remained exactly cubic. In addition, the reflection intensities showed the symmetry $m3m$, as was present above the phase transition. A refinement with the β-phase structure was therefore carried out. This resulted in $R(w) = 0\cdot17$ and physically meaningless large thermal vibrations (*e.g.* $u = 0\cdot57$ Å for Ag), so the intensities were used to calculate a Patterson synthesis (Fig. 4b). The comparison with the corre-

sponding Patterson section of the β phase (Fig. 4a) shows the striking similarities between both syntheses. There exists only one substantial difference between them: Compared to the origin peak the Patterson density at the center of the face is much lower in the γ phase than in the β phase. This can only be understood with a change in the occupancy of the Ag sites, combined with a lowering of the space-group symmetry. To do this by fixing the reflection symmetry is only possible with the assumption of a domain crystal.

4.2. Multi-domain crystal

If it is assumed that the transition from the β to the γ phase is caused by partial or complete ordering of the Ag$^+$ ions, the space groups with the highest possible symmetries are $Pm3$ or $R3$. In $Pm3$ the 12-fold atomic position of the Ag$^+$ ions is divided into two independent sixfold positions allowing now only one of these sixfold atomic positions to be occupied with an occupation probability of $\frac{1}{2}$ for each site (Fig. 5b). In $R3$ the 12-fold position is divided into four threefold atomic positions. Therefore, $R3$ allows a completely ordered structure with three Ag$^+$ ions arranged around one threefold axis
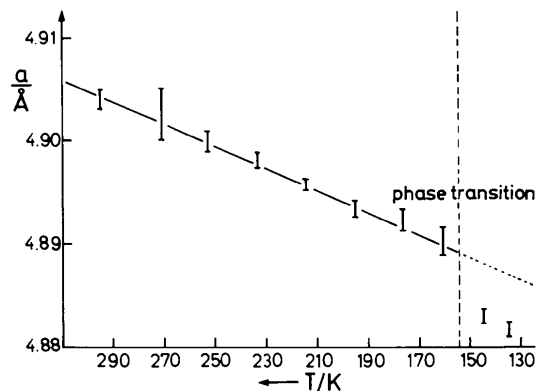

Fig. 3. Temperature dependence of the lattice constants. The 'error bars' are calculated from the measured deviations between a_1, a_2, and a_3. (The calculated standard deviation for a single value is $0\cdot005$ Å.)
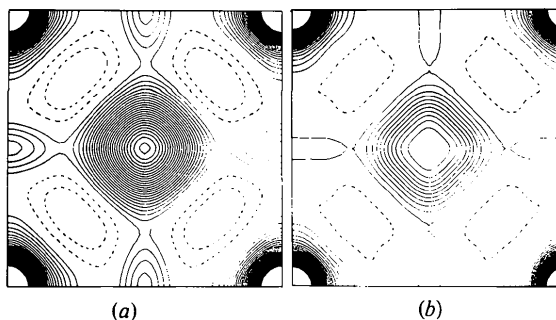

(a) (b)

Fig. 4. Patterson synthesis for atoms with $\Delta z = 0$. (a) 170 K (β phase). (b) 135 K (γ phase). Both are plotted with the same height for the origin peak.
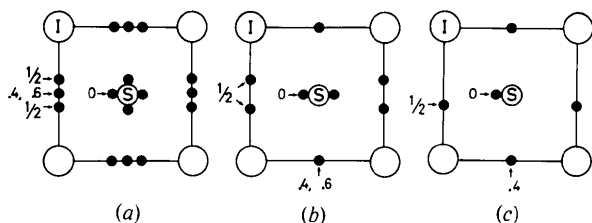
Fig. 5. Projection of the structure models into the $z = 0$ plane. (a) $Pm3m$, (b) and (c) one of the possible orientations of $Pm3$ and $R3$ respectively. Black circles mark the Ag sites, the numbers their z coordinates. I is at 0,0,0, S at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.

(Fig. 5c). This $R3$ domain can be realized in 16 different ways when starting from $Pm3m$. In general, the structure amplitude of an hkl reflection is different for each orientation when anomalous scattering is included.

The Patterson section of Fig. 4(b) allows an easy selection of the correct domain symmetry to be made. One has to keep in mind that the Patterson density of a multi-domain crystal is generated by the superposition of the Patterson densities of the different domains. Recalling that a peak $P(\mathbf{r}_p)$ in a Patterson synthesis is proportional to the product of the electron densities of the atoms having the distance $\mathbf{r}_p$, we can make an estimation of the heights of some peaks in the different space groups. For $Pm3m$, $Pm3$ and $R3$ the number of domains is $N = 1$, 2 and 16 respectively. The electron density can be approximated by the total number of electrons of each ion (Table 2).

A decrease of the I—Ag and S—Ag peaks to 66% or 51% depending on the symmetry $Pm3$ or $R3$ should be observable when these Patterson peaks of the γ phase are compared with those of the β phase and the origin is scaled to the same height. A decrease to 50% for I—Ag and to 52% for S—Ag was found. It follows that the symmetry of a single domain should be $R3$, which is in agreement with the assumption of Hoshino et al. (1979). The crystal has changed to a multi-domain crystal where all 16 possible orientations are occupying equal parts of the volume.

4.3. Refinement of the γ phase

A special program has been written in order to refine the structure parameters of a single domain from the superimposed intensities. Similar to the refinement of structure amplitudes, the expression $R(w) = \sum w(I_o - I_c)^2/\sum wI_o^2$ was minimized, where: I_o is the observed, I_c the calculated intensity; w is a weighting factor which has been chosen to be $\sigma^{-2}(I_o)$; and $\sigma(I_o)$ was calculated as described in § 3.1. According to the crystal model discussed above, the calculated intensities are given by:

$$I_c = S \sum_{i=1}^{16} |F_i(h,k,l)|^2,$$

where S is a scale factor. Intensity data averaged in the symmetry $m3m$ were used.

For this refinement the final parameters are given in Table 3. In order to compare the agreement between I_o and I_c with that of a usual structure refinement, the value $R_F(w) = \sum w_F(\sqrt{I_o} - \sqrt{I_c})^2/\sum w_F I_o$, with $w_F = \sigma^{-2} (\sqrt{I_o})$, was calculated. The result $R_F = 0.08$ indicates quite good agreement for such an unusual structure problem.

A further confirmation of this structure model is given by the agreement of I_o and I_c for those reflections which show the strongest intensity increases at the phase transition. They are listed in Table 4. The R value for these reflections based on $\sqrt{I}$ is $R_F(w) = $

Table 2. *Estimated Patterson peaks* (e^2) *for the three possible structure models*

The element symbols represent the electrons per atom (Ag = 47 e, S = 16 e, and I = 53 e).

	$Pm3m$	$Pm3$	$R3$
Origin:	$I^2 + S^2 + 12\left(\dfrac{Ag}{4}\right)^2$	$I^2 + S^2 + 6\left(\dfrac{Ag}{2}\right)^2$	$I^2 + S^2 + 3(Ag)^2$
	$= 4722$	$= 6379$	$= 9692$
I–Ag:	$I \times \dfrac{Ag}{4}$	$I \times \dfrac{Ag}{2} \times \frac{1}{2}$	$I \times Ag \times \frac{1}{4}$
	$= 623$	$= 623$	$= 623$
S–Ag:	$S \times \dfrac{Ag}{4}$	$S \times \dfrac{Ag}{2} \times \frac{1}{2}$	$S \times Ag \times \frac{1}{4}$
	$= 188$	$= 188$	$= 188$

Table 3. *Final structure parameters of the γ phase*

B (Å^2) are the isotropic temperature factors.

Ag: 3(b), (x,y,z)	x	0·515 (1)
	y	0·399 (1)
	z	0·016 (1)
	B	4·21 (4)
S: 1(a), (x,x,x)	x	0·536 (1)
	B	1·3 (1)
I: (0,0,0)	B	1·29 (2)

Table 4. *Observed and calculated intensities for the reflections which increase more than a factor of* 10 *at the transition from the β to the γ phase*

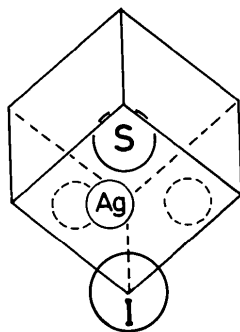|	$\dfrac{I(135\ K)}{I(170\ K)}$		
h k l		I_o (135 K)	I_c
0 1 2	157	183 000	176 000
0 1 4	76	92 000	83 000
0 1 6	58	30 000	19 000
1 2 2	43	101 000	112 000
0 0 1	34	40 000	46 000
3 3 5	34	14 000	12 000
1 2 6	21	19 300	14 800
1 2 4	20	37 800	40 600
3 3 3	19	41 700	43 400
0 3 6	16	16 900	16 300

Fig. 6. Atomic arrangement of the γ phase of Ag$_3$IS.

0·06. Structure refinements in space groups $Pm3$ or $Pm3m$ lead to deviations of up to 400% for these reflections. A perspective drawing of the final structure model is shown in Fig. 6.

4.4. Discussion

The γ phase of Ag$_3$IS is pyroelectric. This may be the reason why, when cooling a β-phase single crystal, a multi-domain γ-phase crystal results. The ordering process of the Ag$^+$ ions at the phase transition tends to make the macroscopic electric field zero. This can be reached by the formation of domains in all possible orientations and with the same size. The structure refinement has shown that this is realized very well. It will probably not be possible to obtain single crystals by applying an electric field as is done with ferro-electrics because the mobile Ag$^+$ ions will neutralize the external field in a very short time.

The thermal parameters are reduced to 50% at the phase transition. This indicates the deeper potentials in the ordered γ phase.

Our results for the structure parameters of the γ phase are in fair agreement with those reported by Hoshino *et al.* (1979). The directions of the coordinate shifts are the same in both investigations but we found smaller deviations from the atomic coordinates of the β phase. This may be caused by the higher investigation temperature of our measurements. This different temperature may partly account for the differences in the temperature factors but the deviations are so large that systematic errors are probably responsible for the main part of the deviations (*cf.* § 3.2).

5. Explanation of additional reflections

As mentioned above, at room temperature our single crystals of β-Ag$_3$IS show additional weak reflections. The relation between the tetragonal cell describing these reflections and the cubic unit cell is shown in Fig. 7. The observable reflections show the following index restrictions: (1) $h + k + l = 2n$, (2) for $l = 2n$: $h = 2n$ ($k = 2n$) and (3) for $h00$: $h = 4n$. All other reflections are absent. The reflection symmetry is $4/mmm$.

By detailed investigations we found that small domains of Ag$_2$S included in the Ag$_3$IS crystals are the reason for the additional reflections. These domains are probably generated during crystal growth.

Below 450 K, Ag$_2$S is monoclinic (α-Ag$_2$S) with space group $P2_1/c$ and $a = 4\cdot231$, $b = 6\cdot930$, $c = 9\cdot526$ Å and $\beta = 125°\,29'$ (Sadanaga & Sueno, 1967). With the transformation matrix $020/40\bar{1}/00\bar{1}$ one obtains a pseudotetragonal cell with $a = 13\cdot86$, $b = 13\cdot78$, $c = 9\cdot525$ Å and $\alpha = 88°\,45'$, which is nearly identical with the tetragonal cell of Fig. 7. All pseudotetragonal indices created by this transformation obey the observed extinction restrictions described above. The tetragonal symmetry is caused by different orientations of the Ag$_2$S domains which can be transformed into each other by fourfold rotation
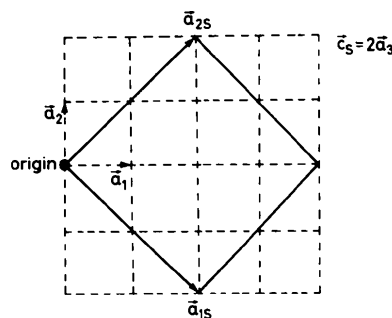

Fig. 7. Tetragonal cell describing the additional weak reflections.

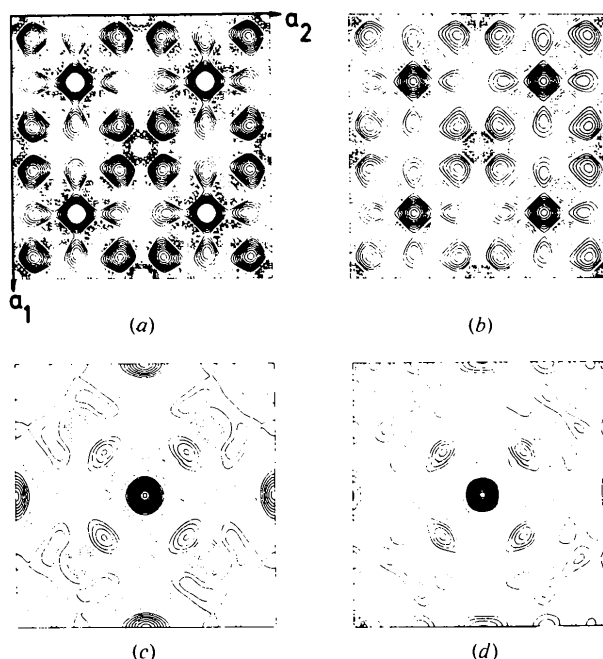Fig. 8. Two sections of the partial Patterson syntheses calculated with the observed additional reflections of an Ag$_3$IS crystal (a, c) and with the calculated intensities of the multiply twinned α-Ag$_2$S (b, d). (a) and (b) are calculated for $\Delta z = \frac{1}{4}a_3$ of the tetragonal cell, (c) and (d) for $\Delta z = \frac{1}{2}a_3$.

around the c axis. Such multiple twinning of α-Ag$_2$S has been observed when crystals were cooled through the transition from the high-temperature (β) phase to the α phase (Frueh, 1958).

A final confirmation of Ag$_2$S domains in our Ag$_3$IS crystals could be given by a Patterson synthesis (Fig. 8). We have calculated the reflection intensities according to the multiple-twin model using the atomic positions reported by Sadanaga & Sueno (1967). With these intensities we calculated the Patterson synthesis of the subset of reflections for which we could measure intensities higher than three standard deviations. The good agreement of this synthesis with that calculated with the observed additional intensities shows that the interpretations are correct.

Two other observations can now be understood: At the phase transition from β- to γ-Ag$_3$IS no change in the intensities of the additional reflections could be seen. It follows that the Ag$_2$S domains are not affected by the transition of Ag$_3$IS. Above about 400 K the additional reflections disappear. A transition from α-Ag$_2$S to the cubic β-Ag$_2$S occurs and the remaining reflections coincide with the Ag$_3$IS reflections due to the close agreement of the lattice constant within 0·01 Å. The disappearance of the additional reflections is accompanied by a specific-heat anomaly (Beyeler & Brüesch, 1977), indicating that the Ag$_2$S inclusions really undergo a phase transition and do not merely dissolve in the Ag$_3$IS lattice.

The structure refinement of Ag$_3$IS is hardly affected by those reflections of Ag$_2$S which coincide with Ag$_3$IS reflections. The intensities of the Ag$_2$S reflections are

about 100 times smaller than the intensities of the Ag$_3$IS reflections.

References

BECKER, P. & COPPENS, P. (1975). *Acta Cryst.* A31, 417–425.
BEYELER, H. U. & BRÜESCH, P. (1977). *Bull. Am. Phys. Soc.* 22, 369.
BRÜESCH, P. & BEYELER, H. U. (1978). *Helv. Phys. Acta,* 50, 593.
FRUEH, A. J. (1958). *Z. Kristallogr.* 110, 136–144.
HOSHINO, S. & SAKUMA, T. (1980). *J. Phys. Soc. Jpn,* 48(3), 1036.
HOSHINO, S., SAKUMA, T. & FUJII, Y. (1978). *J. Phys. Soc. Jpn,* 45(2), 705–706.
HOSHINO, S., SAKUMA, T. & FUJII, Y. (1979). *J. Phys. Soc. Jpn,* 47(4), 1252–1259.
MAGISTRIS, A., CHIODELLI, G. & SCHIRALDI, A. (1978). *Z. Phys. Chem.* 112, 251–253.
REUTER, B. & HARDEL, K. (1961). *Naturwissenschaften,* 48, 161.
REUTER, B. & HARDEL, K. (1965). *Z. Anorg. Allg. Chem.* 340, 168–180.
REUTER, B. & HARDEL, K. (1966). *Ber. Bunsenges. Phys. Chem.* 70, 82–86.
SADANAGA, R. & SUENO, S. (1967). *Mineral. J.* 5(2), 124–148.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* 23, 558–564.
ZUCKER, U. H., PERENTHALER, E., KUHS, W., BACHMANN, R. & SCHULZ, H. (1981). To be published.

Structure d'un Phosphate Acide de Potassium, K$_2$H$_5$(PO$_4$,P$_2$O$_7$)

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Abstract

K$_2$H$_5$(PO$_4$,P$_2$O$_7$), monoclinic, $C2/c$, $a = 31·272$ (7), $b = 7·428$ (1), $c = 9·253$ (1) Å, $\beta = 99·85$ (1)°, $V = 2117·7$ Å^3, $Z = 8$, $d_m = 2·21$ (1), $d_x = 2·211$ Mg m^{-3}. The crystal structure was refined anisotropically to $R = 0·075$, using 526 independent reflexions measured on an automatic diffractometer (Cu $K\bar{\alpha}$ radiation). In H$_2$PO$_4^-$ the mean value of P–O is $1·53$ (2) Å. In H$_3$P$_2$O$_7^-$, the angle P–O–P is 139 (1)°; the P–O distances of the bridge are $1·56$ (3) and $1·57$ (3) Å and the mean value of P–O in terminal PO$_3$ is $1·52$ (2) Å. The potassium cation K(3)$^+$ is responsible for the ionic conductivity.

Introduction

La structure cristalline de K$_2$H$_5$(PO$_4$,P$_2$O$_7$) s'inscrit dans le cadre de l'étude systématique des sels à anion