

## Study of a Mixed-Polytype Crystal of Silver Iodide Containing a New 12H Polytype

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A mixed-polytype crystal of AgI is studied by X-ray diffraction. The constituent polytypes are found to be the common 2H and 4H varieties plus a new 12H polytype, and their proportions are determined. The stacking sequence of the 12H polytype is 1211111121 (Zhdanov notation). Disorder-diffuse scattering observed in the diffraction pattern is attributed to intrinsic-2h stacking faults in 2H regions of the crystal. The degree of disorder corresponds to a fault probability  $\alpha = 0.15$ .

### Introduction

It is now well established that polytypism is exhibited by silver iodide in common with several other adamantine compounds such as silicon carbide and zinc sulphide. The stable form of low-temperature AgI is the hexagonal wurtzite-type structure designated  $\beta$ -AgI. There is some dispute over the evidence for a cubic modification with the sphalerite structure,  $\gamma$ -AgI. Majumdar & Roy (1959) disputed the existence of the low-temperature cubic structure in pure form, but found in their X-ray powder studies evidence of several complex polytypes which, however, they did not specify further.

Prager (1974) reported four new AgI polytypes with stacking sequences intermediate between the hexagonal close-packed sequence of  $\beta$ -AgI [2H in the Ramsdell notation for polytypes: see Verma & Krishna (1966)] and the cubic close-packed sequence of  $\gamma$ -AgI (3C). Polytypes 4H, 8H, 12H and 16H were identified on the basis of precession studies of single crystals, and their detailed stacking sequences were reported. A 7H polytype was observed in a powder diffraction study by Davis & Johnson (1974). Johnson & Schock (1975) reported a complete structure analysis of the 4H polytype, confirming the stacking sequence determined by Prager (1974).

A second 12H polytype of AgI has since been found, and the determination of its stacking sequence is reported below. The previous determinations by Prager (1974) of the structures of AgI polytypes relied on visual estimation of intensities of selected Bragg reflexions recorded by X-ray precession photography. In the present work a more detailed quantitative study was made of a single crystal in which the 12H polytype occurred in syntactic coalescence with the common 2H and 4H polytypes. It confirms the structure tentatively assigned in a previous qualitative study of the same crystal, and supports the results of our previous work (Prager, 1974) in which some of the long-period polytypes were also in syntactic coalescence with 2H and 4H polytypes.

An account is given for the diffuse scattering ob-

served along certain reciprocal lattice rows of the diffraction pattern.

### Experimental details

Crystals were grown from KI solution by the method of Cochrane (1967). Cleavage parallel to the basal plane of a long, regular hexagonal prism yielded the subject crystal. Its prismatic faces were  $\sim 80 \mu\text{m}$  wide and  $145 \mu\text{m}$  long.

Optical examination of the crystal between crossed Nicol prisms revealed birefringent striae parallel to the basal plane. Uniformly birefringent sections were of the order of only  $1 \mu\text{m}$  wide.

Zero-level ( $H0.L$ ) precession photographs were taken with filtered Cu and Mo radiation. Integrated precession photographs (Mo  $K\alpha$  radiation) were used for the quantitative determination of intensities. Integrated intensities of Bragg reflexions were obtained by microphotometry using the plateau method (Buerger, 1964). In general the mean intensity was taken over four equivalent reflexions. Anomalous dispersion corrections and absorption corrections were omitted ( $\mu R = 1.4$ ). Lorentz-polarization factors appropriate to the precession method were calculated according to the formulae given by Buerger (1964) following the work of Waser (1951). The values chosen for the AgI structural parameter (conventionally also denoted by  $\mu$ ) and the overall isotropic temperature factors for Ag and I atoms were essentially those established by Burley (1963) in his study of wurtzite-type AgI:  $\mu = 0.3747$ ;  $B_{\text{Ag}} = 6.8$ ,  $B_{\text{I}} = 3.6$  ( $\text{\AA}^2$ ). [We note that there is a mistake in the presentation of Table 1 in Burley's (1963) paper. His isotropic temperature factors are labelled  $2B$  instead of  $B$ . We had not noticed this mistake previously (Prager, 1974), and had therefore used temperature factors too small by a factor of two. We have since checked our results, and they are unaffected by this oversight.]

### Determination of polytypic composition and stacking sequence

We assume that the various AgI polytypes differ only in the stacking sequence of Ag-I layers along the  $c$  axis

of an hexagonal lattice. The structure factor for a given  $n$ -layered polytype can therefore be written as

$$F(hkl) = [f_{Ag} + f_I \exp(4\pi i \mu l/n)] \times \sum_{j=1}^n \exp[2\pi i(hx_j + ky_j + lz_j)]$$

where  $\mu$  is the wurtzite structural parameter ( $\mu \approx \frac{2}{3}$ ) and the other symbols have their usual meaning. The three possible stacking positions of atoms within a layer  $j$  are  $A(0,0,z_j)$ ,  $B(\frac{1}{3}, \frac{2}{3}, z_j)$ ,  $C(\frac{2}{3}, \frac{1}{3}, z_j)$ , with  $z_j = (j-1)/n$ . Only reflexions with  $h-k = \pm 1 \pmod{3}$  are dependent on the stacking scheme.

The diffraction pattern, Fig. 1, showed that the periodicity of the highest-order polytype in the crystal was six times the wurtzite periodicity. The pattern was therefore indexed on the basis of a twelve-layered cell (12H).

Information on composition and stacking is contained in the 10.l and 20.l rows. Reflexions with  $l=0 \pmod{6}$  were extremely strong for these rows, suggesting that the 2H polytype was present. Comparison of Fig. 1 with a precession photograph taken 26 months earlier revealed an unmistakable decrease in the intensities of reflexions with  $l=3 [1 \pmod{2}]$  relative to reflexions with  $l=1 \pmod{3}$ . Table 1 shows that 4H and 12H polytypes can contribute to the class of reflexions with  $l=3 [1 \pmod{2}]$ , whereas only a 12H polytype can contribute to the class with  $l=\pm 1 \pmod{3}$ . The observed change in the relative intensities therefore indicated that the 4H polytype was originally present and that its proportion had declined relative to the proportion of 12H polytype. It seemed reasonable to assume, however, that the 4H polytype was still represented in the crystal.

Table 1. Classes of reflexions and the polytypes which contribute to their total intensity

$h-k$	$l$	Polytypes contributing to total intensity		
0(mod 3)	0(mod 6)	12H	4H	2H
	$\pm(1,2,3)$ (mod 6)	-	-	-
$\pm 1 \pmod{3}$	0(mod 6)	12H	4H	2H
	3[1(mod 2)]	[12H]*	4H	-
	$\pm 1 \pmod{3}$	12H	-	-

\* The 12H polytype we finally identified in fact contributed zero intensity to these reflexions. This is a peculiarity of the particular stacking sequence.

We proceeded on the assumption that the total diffracted intensity was the sum of intensities separately contributed by the 12H, 4H and 2H polytypes. Table 1 shows the polytypes which contribute to different classes of reflexions.

The stacking sequences of the 2H and 4H polytypes need not concern us here, since there is only one possibility in each case. To determine the stacking sequence of the 12H polytype we consider firstly those reflexions

which receive no contributions from the 2H and 4H polytypes – reflexions with  $l = \pm 1 \pmod{3}$ . From the observed equality of  $h0.l$  and  $h0.\bar{l}$  reflexions we deduce, following Ramsdell & Kohn (1951), that either the polytype falls in space group  $P6_3mc$ , or it falls in space group  $P3m1$  and has a symmetrical zigzag sequence. In the former case the Zhdanov symbol can be written as  $(a_1 a_2 \dots a_k)_2$  and in the latter case as  $(a_1 a_2 \dots a_k)_2^-$ ; in either case the stacking sequence of the entire unit cell is determined by the sequence of half the unit cell (Prager, 1974). This greatly simplifies the determination, since there are only 17 different 12H polytypes of this type to be considered. [They are termed 'symmetric' polytypes. Two of them,  $(123)_2$  and  $(321)_2$ , constitute a homometric pair and are therefore indistinguishable by their diffraction patterns: Prager (1976).]

Fig. 2 provides a comparison between observed and calculated intensities of this class of reflexions for  $h=1$ ,  $k=0$ . Only the eight 12H polytypes with calculated diffraction patterns remotely resembling the observed pattern are included in this figure. Calculated intensities were normalized so that  $I_{\text{calc}}(10.1) = 100$ . We note that the relative intensities  $I_{\text{calc}}(10.1):I_{\text{calc}}(10.11):I_{\text{calc}}(10.13)$  are the same for all seventeen 'symmetric' 12H polytypes. For the purposes of Fig. 2 the observed intensities were scaled so that there was approximate agreement with calculated intensities for reflexions 10.11 and 10.13. It is obvious that intensities for polytype  $(12111)_2^-$  agree very well with the observed data. Polytype  $(21111)_2$  shows a reasonable but inferior fit, while the other polytypes can be confidently rejected. Because the diffraction patterns of polytypes  $(12111)_2^-$  and  $(21111)_2$  show marked similarities we cannot discount the possibility that both are present. (Indeed, the overall fit in Fig. 2 would be improved if we considered a combination of the two.) The proportion of  $(21111)_2$  to  $(12111)_2^-$  is certainly less than 1:4, and we simplify the subsequent analysis by assuming that the predominant  $(12111)_2^-$  polytype is the only 12H polytype present. It remains to account for the intensities of other measured reflexions.

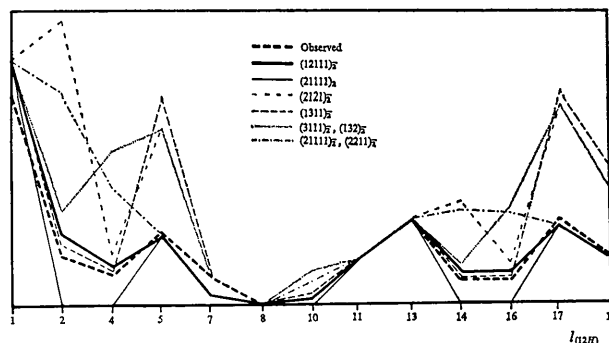


Fig. 2. Comparison of observed intensities with intensities calculated for several 'symmetric' 12H polytypes. Reflexions 10.l with  $l = \pm 1 \pmod{3}$ .

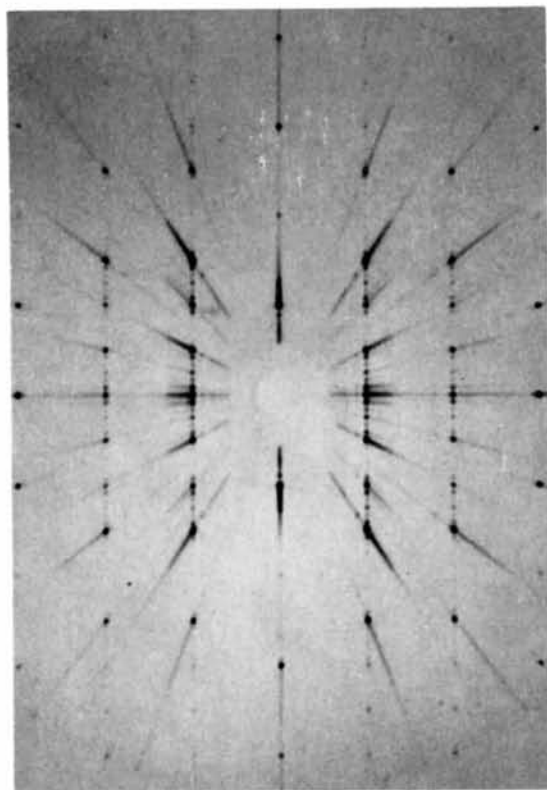


Fig. 1. Zero-level ( $H0.L$ ) integrated precession photograph of AgI mixed-polytype crystal. Zr-filtered Mo radiation.

The next class of reflexions to be considered is that contributed to in principle by the  $4H$  and  $12H$  polytypes:  $h-k = \pm 1 \pmod{3}$ ,  $l=3 [1 \pmod{2}]$ . It happens that the  $12H$  polytype ( $12111$ )<sub>2</sub> identified above contributes zero intensity to this class. There is only one possible  $4H$  polytype, namely (22). Very satisfactory agreement between  $I_{\text{obs}}$  and  $I_{\text{calc}}$  was obtained for the five observed reflexions in this class. The only free parameter used to obtain this agreement was a different scale factor from the one used in scaling the previous class of reflexions. The ratio of these two scale factors determines the relative volumes of  $12H$  polytype to  $4H$  polytype in the mixed crystal, due account being taken of the difference in unit-cell volumes. This ratio was found to be 100:16.

The final two classes of reflexions in Table 1 are those with  $l=0 \pmod{6}$ ; they receive contributions from the  $12H$ ,  $4H$  and  $2H$  polytypes. The intensities of reflexions with  $h-k=0 \pmod{3}$  are independent of the relative proportions of the polytypes, and indeed are unaffected by any stacking disorder, whereas the intensities of reflexions with  $h-k = \pm 1 \pmod{3}$  are dependent on the proportions of the contributing polytypes. We were able to obtain satisfactory agreement between observed and calculated intensities of the remaining reflexions (numbering eight in all) by introducing a third scale factor – one related to the proportion of  $2H$  polytype. The three strongest reflexions (10.6, 20.18 and 30.0) were ignored in obtaining this scale factor, since it was felt that their measured intensities were

underestimated. This procedure determined the ratio (by volume) of  $12H:4H:2H$  polytype as 100:16:35.

Table 2 presents the observed and calculated intensities of all the measured reflexions, indexed on the basis of a  $12H$  unit-cell. The contributions of the different polytypes to the calculated intensities are listed in addition to the total intensities. As an indication of the satisfactory overall agreement,  $R = \sum(I_{\text{obs}} - I_{\text{calc}})^2 / \sum I_{\text{obs}}^2$  was found to be 0.038.

### Diffuse scattering

A feature of the diffraction pattern (though one not apparent in the reproduction of Fig. 1) is the diffuse intensity along the  $10.l$  and  $20.l$  reciprocal lattice rows. Diffuse intensity distributed along rows with  $h-k = \pm 1 \pmod{3}$  but not along rows with  $h-k=0 \pmod{3}$ , together perhaps with the broadening of Bragg reflexions on the former rows, is characteristic of disorder in the stacking sequence of basal planes. From measurements of the diffuse intensity taken at half-integral values of  $l$  along the  $10.l$  and  $20.l$  rods, we have concluded that the intensity distribution is consistent with a small degree of random stacking disorder in regions of the crystal that have basically the  $2H$  polytype structure. From the restricted set of measurements we cannot specify with certainty which of several alternative types of stacking fault is responsible. Diffraction effects due to stacking faults in hexagonal close-packed ( $2H$ ) and double hexagonal close-packed ( $4H$ ) crystals have been discussed by many authors, including Wilson (1942), Jagodzinski (1949), Gevers (1954), Christian (1954), Lele, Anantharaman & Johnson (1967), Lele, Prasad & Anantharaman (1969); and Prasad & Lele (1971). Prasad & Lele (1971) have discussed the effects due to nine different stacking faults in the d.h.c.p. ( $4H$ ) structure. One of these faults, the intrinsic- $2h$  stacking fault, we have recently investigated in detail (Prager, 1976), believing it to be important in the understanding of ordered and disordered polytypes of AgI.

Table 2. Calculated and observed intensities of all measured reflexions

The indexing is based on a  $12H$  unit cell.

$hk.l$	$I_{\text{calc}}$ (12H)	$I_{\text{calc}}$ (4H)	$I_{\text{calc}}$ (2H)	$I_{\text{calc}}$	$I_{\text{obs}}$
10.1	100			100	86
10.2	29			29	20
10.3	0	33		33	31
10.4	16			16	12
10.5	29			29	30
10.6	124	19	56	199	156
10.7	4			4	6
10.8	<1			<1	<1
10.9	0	2		2	2
10.10	3			3	3
10.11	19			19	21
10.12	36	4	39	79	78
10.13	35			35	34
10.14	13			13	10
10.15	0	19		19	20
10.16	13			13	9
10.17	33			33	35
10.19	19			19	20
10.30	59	9	27	95	89
20.0	31	4	33	68	71
20.1	22			22	24
20.3	0	8		8	9
20.6	34	5	15	54	53
20.12	11	1	12	24	28
20.15	0	6		6	6
20.18	86	13	39	138	114
30.0	89	14	32	135	114

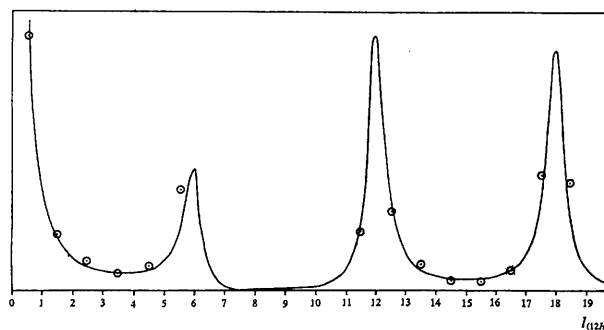


Fig 3. Diffuse intensity along  $10.l$  reciprocal lattice row.  $\odot$  Observed intensity. — Calculated intensity for intrinsic- $2h$  stacking faults occurring with a probability  $\alpha' = 0.85$  in a parent  $4H$  structure. (This is equivalent to a fault probability  $\alpha = 1 - \alpha' = 0.15$  in a parent  $2H$  structure.)

Fig. 3 shows the observed diffuse intensity from the mixed crystal, together with the intensity calculated on the basis of randomly distributed intrinsic- $2h$  faults in a parent  $4H$  structure. The best fit, as shown in Fig. 3, was obtained for a value of the random fault probability  $\alpha' = 0.85$ . Since  $\alpha' = 1$  corresponds to the ordered  $2H$  structure, this is equivalent to a slightly faulted  $2H$  parent structure (fault probability  $\alpha = 1 - \alpha' = 0.15$ ). A marginally inferior match between observed and calculated diffuse intensity was obtained using Wilson's (1942) model for faulting in the  $2H$  structure. Again, the best value obtained for the fault probability was  $\alpha = 0.15$ . These results indicate that the  $4H$  regions of the crystals are well ordered and that the disorder is associated with  $2H$  regions.

### Discussion

Ram & Singh (1976) have recently examined mixed-polytype SiC crystals which showed one-dimensional disorder. They found by a combination of etching and diffraction experiments that  $6H$ ,  $15R$  and completely disordered regions occurred in syntactic coalescence and were completely segregated; that is, the continuous disorder-diffuse scattering and the sharp Bragg reflexions originated from distinct regions of the crystal. They estimated that the thickness of regions giving rise to the continuous streaks was a few microns. Our results for AgI lead to similar conclusions except that the degree of disorder is smaller and we cannot preclude the existence of ordered (in addition to disordered)  $2H$  regions.

Palosz & Przedmojski (1975) have analysed mixed-polytype crystals obtained from  $Zn_xCd_{1-x}S$  and  $ZnS_xSe_{1-x}$  solid solutions. They found these crystals to be mixtures of  $10H$ ,  $6H$  and disordered  $3C$  structures. They assumed, from the appearance of a mirror plane perpendicular to the  $c^*$  axis, that the polytypes must all be characterized by Zhdanov symbols of the form  $m$ . This assumption is not essential, since all 'symmetric' polytypes produce a real or apparent mirror plane (Ramsdell & Kohn, 1951; Prager, 1974). Why polytypes of AgI (and these other materials) should be almost always 'symmetric' is not known.

### Summary

A new  $12H$  polytype of AgI has been observed and its

stacking sequence has been determined. Structural details are:

space group  $P3m1$ ,  
Zhdanov symbol  $1211111121 \equiv (12111)_2$ ,  
stacking sequence  $ABACACACACAB$ ,  
unit-cell dimensions  $a = 4.590$  (11),  $c = 45.08$  (10) Å.

The polytype was identified from its occurrence in a mixed-polytype crystal which showed evidence of stacking disorder. Systematic analysis of the intensities allowed the proportions of the various polytypes to be determined. The disorder was associated with  $2H$  regions of the crystal and the fault probability for these regions was estimated to be  $\alpha \approx 0.15$ .

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