

Low-Temperature Phase Transitions in $(C_5H_5NH)Ag_5I_6$ *

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The solid electrolyte $(C_5H_5NH)Ag_5I_6$ undergoes two low-temperature transitions, probably associated with the ordering of the pyridinium ions. The two phases are monoclinic and have structures closely related to that of the hexagonal phase at 240°K. The transition to the γ -phase at 230°K is second order, and that from the γ - to the δ -phase at 180°K, first order. In the γ -phase, the monoclinic a and b axes correspond to the orthohexagonal B and A axes, respectively; in the δ -phase, the correspondence is reversed. If the pyridinium ions order in the γ -phase, its space group is most probably Cc . If the pyridinium ions are ordered in the δ -phase, the N atoms must lie on twofold axes in $C2/c$, but the space group Cc is also possible for this phase.

Introduction

In the course of an investigation of the conductivity and specific heat of the solid electrolyte $(C_5H_5NH)Ag_5I_6$ (where $(C_5H_5NH)^+$ is the pyridinium ion, for which we write Py^+), an additional transition was found at approximately 220°K (1). The specific heat measurements indicated that the transition is not first order. In the hexagonal phase, the Py^+ ions are statically disordered over six positions (2, 3) but at 240°K, the Ag^+ ions are ordered (2). One might expect, therefore, that the transition at approximately 220°K involves the ordering of the Py^+ ions.

Especially because of the very interesting behavior of this solid electrolyte (1, 3, 4), we decided that it would be worthwhile to investigate this transition. In the course of the investigation, we found that there are *two* low-temperature transitions in $PyAg_5I_6$, one of which must be first order.

Heat capacity data have also been obtained

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for PyI itself, and a first-order transition at 250°K was found (1). It is noteworthy that the crystal structure of PyI at room temperature has been determined (5) recently. In PyI , the Py^+ ions are also statically disordered similar to the disorder of the Py^+ ions in $PyAg_5I_6$. However, the iodide ion surroundings are different in the two structures.

Experimental

Crystals of $PyAg_5I_6$ used in this investigation were from among those obtained for the previous study (1). X-Ray diffraction photographs of reciprocal lattice planes perpendicular to the c -axis were taken with a Buerger precession camera. For increased resolution and also to obtain Bragg reflections in the "blind region" of the precession camera, oscillation photographs were taken. In this case, the flat plate cassette from the Buerger precession camera was set up where the telescope of the Supper Weissenberg camera is usually mounted. The track for the telescope was used as the track for the cassette holder. This allowed variation of the film-to-crystal distance; we used a film-to-crystal distance of 7.5 cm, close to the shortest distance possible with this

arrangement. For the oscillation photographs, the rotation axis was the hexagonal [110] direction.

To minimize absorption and to keep the spot size small, platelike crystals were selected of thickness ≤ 0.1 and less than 0.2 mm in cross-sectional dimension. The method used to obtain the various low temperatures ($\pm 5^\circ\text{K}$) at which photographs were taken is similar to that first described by Post, *et al.* (6). The radiation used was $\text{MoK}\alpha$.

Results and Discussion

The specific heat data of the previous study (7) showed that there is a transition at approximately 220°K , and rotation photographs taken at 160°K during the course of that study showed that a monoclinic phase existed at that temperature. However, in the present study, we found that there are, in fact, two different monoclinic phases of PyAg_5I_6 that are stable in different temperature regions below 230°K : one between 230 and 180°K , the other below 180°K .

In both phases, two types of twinning occur: one is the sixfold twinning associated with the 6-mm point group symmetry, the other with the symmetry plane perpendicular to the sixfold axis. The first could also be just sixfold rotational twinning, which is not distinguishable from 6-mm twinning for these monoclinic cases. In the first case the c -axes of the twins are coincident, while in the second case the c^* -axes are coincident. (We use an * to designate the reciprocal vectors.) The dominant twinning is of the former type. The multiple twinning makes definitive analysis of the crystal structures very difficult, to say the least; it virtually precludes obtaining data by a counter technique. Further, it is clear from the photographs that the twin volumes are not equal.

To simplify the discussion in what follows, we consider *only* the reflections resulting from the 6-mm or sixfold rotational twinning. Because the six twins have the same c -axis all the reflections for a given l lie in the same reciprocal lattice plane. In both phases, the monoclinic unit cell has the unique axis b_m coincident with the (former) hexagonal (001) plane. Each

reflection of the hexagonal crystal splits into six reflections in a hexagonal arrangement in the reciprocal lattice planes $l = 1, 2, 3, \dots$. At each temperature, the sizes of the hexagons of spots increase with increasing l and are essentially zero for $l = 0$ (i.e., no splitting is actually observed).

At temperatures away from the transition temperatures, the six reflections are fairly well resolved for reciprocal lattice planes with $l \geq 2$. Actually we concentrated on the plane with $l = 2$; larger l gave larger blind areas in the Buerger precession camera photographs.

Precession camera photographs (precession angle = 12°) of the $l = 2$ reciprocal lattice plane at 190°K (the higher-temperature monoclinic γ -phase) and at 77°K (the lower-temperature monoclinic δ -phase) are shown in Figs. 1 and 2. The principal difference between the two photographs is that each hexagon of spots in the δ -phase is rotated 30° with respect to its analogous hexagon in the γ -phase. This means that the monoclinic axes in the two phases are at an angle of either 30 or 90° to each other.

The unit cells of the two monoclinic phases are obtained mathematically first by a transformation from the hexagonal to an orthohexagonal cell as follows:

$$\mathbf{A} = 2\mathbf{a} + \mathbf{b},$$

$$\mathbf{B} = \mathbf{b},$$

$$\mathbf{C} = \mathbf{c},$$

where the lowercase letters refer to the hexagonal and the capital letters to the orthohexagonal cell. The unit cell of the higher-temperature monoclinic phase is obtained by the transformation

$$\mathbf{a}_m \approx \mathbf{B},$$

$$\mathbf{b}_m \approx \mathbf{A},$$

$$\mathbf{c}_m \approx -\mathbf{C}.$$

(The minus sign is to retain a right-handed system.) Thus in the γ -phase, the magnitude of a_m is close to that of the hexagonal a , and the magnitude of b_m is close to that of $a^{3/2}$; in the δ -phase, the magnitudes are reversed. In both cases, the monoclinic (001) plane is inclined to the hexagonal (001) plane by the angle $(\beta_m(T) - 90^\circ)$, where $\beta_m(T)$ is the

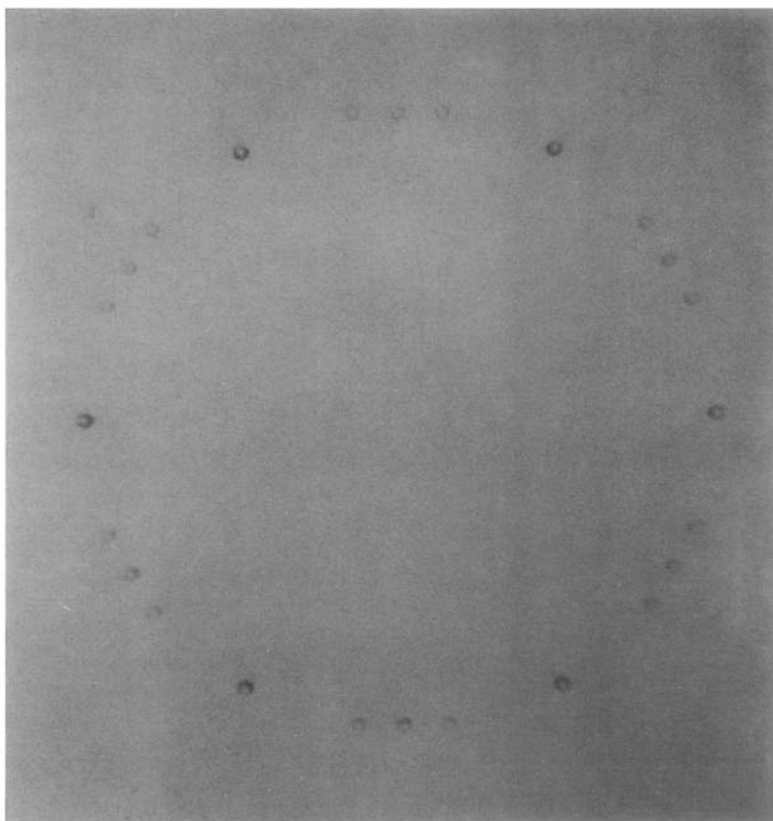


FIG. 1. Buerger precession camera photograph of the $l = 2$ level of the γ -phase at $193^\circ K$. Each former hexagonal reflection has split into six arranged in a hexagonal way, because of the sixfold rotational twinning. (Precession angle = 12° , $MoK\alpha$ radiation.)

monoclinic angle which changes with temperature.

The most intense groups of reflections in Figs. 1 and 2 are those that originate from the hexagonal 702 and equivalent reflections. The geometry (see Appendix) of the 702 group of reflections is drawn to scale in Fig. 3. Each member of the group of six reflections originates from one of the six twins. (It should be mentioned that we use "six twins" to simplify the discussion. There may actually be a large number of domains in the crystal itself with the six twins as resultant.) The reflections in the figure are indexed according to the two monoclinic cells (see below). The three distances between two opposite reflections in the hexagon are equal and directly related to β_m (Eq. (A4)). The distortion from an ideal hexa-

gon is caused by the deviation of a_m and b_m from the ideal orthohexagonal relation mentioned earlier (see Appendix).

Buerger precession camera photographs of the reciprocal lattice plane with $l = 2$ were taken at various temperatures. From these we determined the temperature dependence of the monoclinic a_m - and b_m -axes. Although it is possible to obtain β_m from these photographs, the oscillation photographs gave much more accurate values for this parameter from measurements on the groups corresponding to the hexagonal 004 reflection. The value of c_m was also estimated from these photographs. Because the rotation axis for these photographs was the $[110]$ direction, the hexagonal array of spots is projected onto the hexagonal (100) reciprocal lattice plane. Figure 4 shows

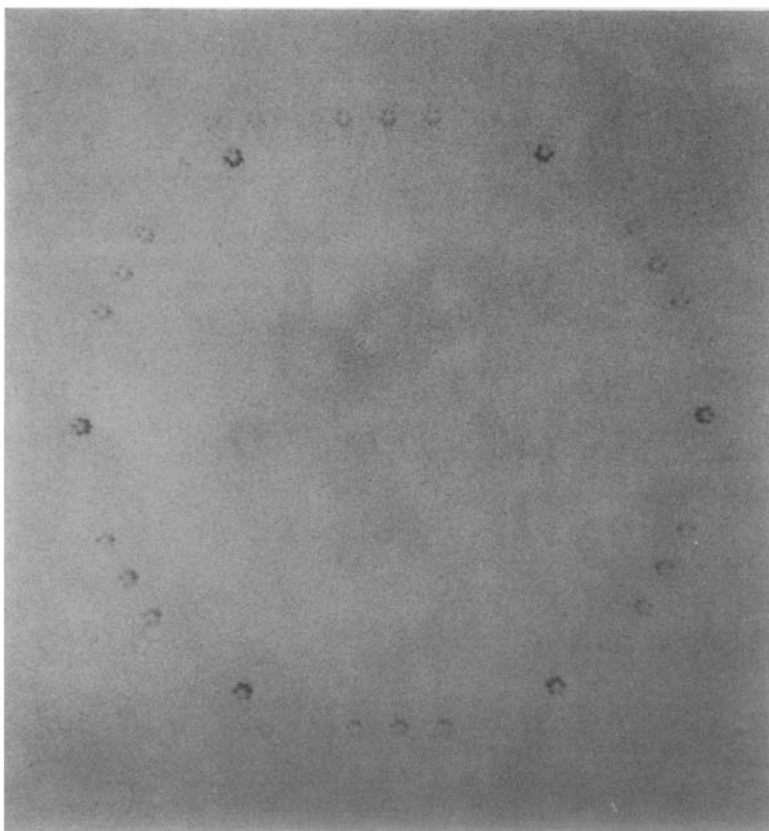


FIG. 2. Buerger precession camera photograph of the $l = 2$ level of the δ -phase at 77°K. The hexagons of spots are rotated 30° (or 90°) with respect to those of the γ -phase, showing that the monoclinic a_m and b_m axes have been reversed. (Precession angle = 12°, MoK α radiation.)

some of these photographs in a sequence of decreasing temperature—top to bottom.

The hexagon of spots from the original hexagonal $\{00l\}$ form remain $\{00l\}$ in the monoclinic case. Thus (see Table II) because the positions of these spots are independent of h and k , they form a regular hexagon. In the γ -phase, the projection of the hexagon gives four spots, the inner two being approximately twice as intense as the outer two. The spot in the center in this case is caused by the mirror twinning perpendicular to the hexagonal c -axis. In the δ -phase, on the other hand, the hexagon of spots projects into three spots of very nearly equal intensity.

The lattice constants of the two phases at various temperatures are given in Table I. (The values of β_m and c_m at specific temperatures for

which a_m and b_m were determined were obtained by interpolation.) The length of the c_m -axis remains constant within ± 0.02 Å over the whole temperature range in which the study was made. Lattice parameters vs temperature are shown in Fig. 5. For both phases, the values of the longest axis were divided by $3^{1/2}$ to show more clearly its relation to the corresponding hexagonal cell parameter as well as to the monoclinic axis of intermediate length.

The figure clearly shows that the transition at 230°K is second order, in agreement with the conclusion drawn from the specific heat data (J). The β angle decreases with increasing temperature and approaches 90° at the transition temperature; the a_m and $b_m/3^{1/2}$ values of the γ -phase change smoothly into the

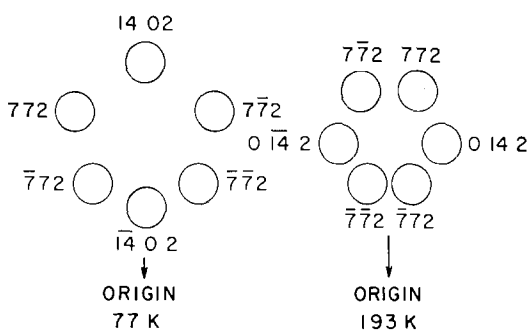


FIG. 3. Schematic drawing of the most intense hexagonal arrays of reflections of Figs. 1 and 2, which derive from the hexagonal $\{702\}$ reflections. Each spot originates from a different twin (monoclinic indices).

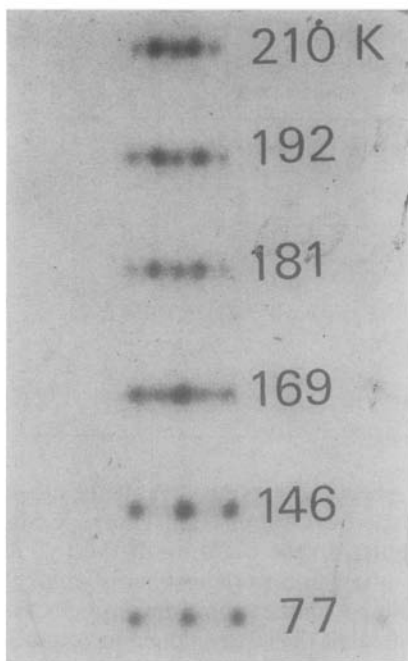


FIG. 4. Oscillation photographs showing the 004 reflections as a function of temperature; the temperature decreases from top to bottom. The rotation axis is the $[110]$ direction. The hexagon of spots projects onto the 100 plane giving four spots in the γ -phase and three in the δ -phase because in the latter phase the hexagons are rotated 30° with respect to the former. The center spot in the γ -phase is right at the center of the hexagon and comes from the mirror twinning perpendicular to the hexagonal c -axis.

hexagonal a value. The second-order transition requires (7) that the space group to which the monoclinic phase belongs be a subgroup of

$P6/mcc$. For the cases where b_m lies in the hexagonal (001) plane, there are three possibilities: $C2/c$, Cc , and $C2$. It should be possible to distinguish between the space groups containing the glide plane and $C2$; in the former, reflections $h0l$ with $h = 2n$ and l odd should have identically zero intensities.

Reflections $h0l$ (monoclinic indices) in the δ -phase originate from reflections belonging to the hexagonal $\{hhl\}$ form, in particular from the hexagonal $\pm(h, 2\bar{h}, l)$ and $\pm(\bar{h}, 2h, l)$ reflections. The hexagonal $\{hhl\}$ form transforms into the following for the γ -phase:

$$\pm(h, 3h, l; 2\bar{h}, 0, l; h, 3\bar{h}, l; \bar{h}, 3h, l; 2h, 0, l; \bar{h}, 3h, l).$$

In the hexagonal phase, reflections $\{hhl\}$ and $\{h0l\}$ with l odd have identically zero intensities. However, at most, only one true glide plane can remain in the monoclinic phase, so that only those reflections originating from the hexagonal forms with monoclinic indices $\pm(2h, 0, l)$ and $\pm(2h, 0, l)$ (in terms of the original hexagonal indices) with l odd might have identically zero intensities if the space group were $C2/c$ or Cc .

In fact, a number of the reflections deriving from the original $\{hhl\}$ and $\{h0l\}$, l odd forms do appear in photographs of the γ -phase. Again there should be a hexagon of spots for each of these also, unless the pair $2\bar{h}, 0, l$ and $2h, 0, l$ is missing. Unfortunately, the particular hexagons of reflections that do appear are very weak and the resolution is poor. Thus, for the γ -phase we cannot eliminate any of the three groups on the basis of space group absences.

The nature of the transition between the two monoclinic phases is less clear. Because the monoclinic b -axis must rotate either 30 or 90° , the transition is either first order or there is an intermediate triclinic phase in which there is a continuous rotation from one structure to another. The latter type of transition has been observed in the cases of the rotation of the magnetic moment systems of $ErFeO_3$ (8) and of $Ca_2Fe_{2-x}Al_xO_5$ (9). In both cases the boundaries of the temperature range in which this occurs are characterized by second-order transitions, and the space groups of the phases in the reorientation region are subgroups of the groups at the beginnings and ends

TABLE I
LATTICE CONSTANTS OF PyAg_5I_6 AT VARIOUS TEMPERATURES

| Phase | T (°K) | a (Å) | b (Å) | c (Å) | β (°) | V (Å ³) |
|-------------------------|----------|------------------|------------------|-----------------|----------------|-----------------------|
| Hexagonal (β) | 238 | 11.96 ± 0.02 | — | 7.40 ± 0.02 | — | 917 ± 6 |
| Monoclinic (γ) | 215 | 11.90 | 20.65 ± 0.04 | 7.38 | 92.1 ± 0.1 | 1812 ± 12 |
| | 206 | 11.87 | 20.65 | 7.38 | 92.25 | 1808 |
| | 193 | 11.92 | 20.68 | 7.38 | 92.4 | 1818 |
| | 191 | 12.01 | 20.87 | 7.38 | 92.5 | 1848 |
| Monoclinic (δ) | 173 | 20.58 ± 0.04 | 11.93 ± 0.02 | 7.38 | 92.9 | 1810 |
| | 168 | 20.46 | 11.85 | 7.38 | 92.95 | 1787 |
| | 77 | 20.51 | 11.89 | 7.38 | 93.3 | 1797 |

TABLE II

DISPLACEMENTS OF THE REFLECTIONS FROM SIXFOLD ROTATIONAL TWINNING IN A MONOCLINIC CRYSTAL RELATIVE TO THE POSITION OF THE CORRESPONDING HEXAGONAL hkl REFLECTION; $\Delta = l c_m^* \cos \beta^*$ AND $\epsilon = a_m^* 3^{1/2} - b_m^*$.

| Monoclinic, in terms of hexagonal, indices | Displacement in the direction of | |
|--|---|---|
| | a_m^* | b_m^* |
| $2h + k, k, l$ | Δ | $-k\epsilon$ |
| $2k + h, \bar{h}, l$ | $\Delta/2 - h\epsilon 3^{1/2}/2$ | $\Delta 3^{1/2}/2 + h\epsilon/2$ |
| $k - h, \bar{h} + k, l$ | $-\Delta/2 - (h + k)\epsilon 3^{1/2}/2$ | $\Delta 3^{1/2}/2 - (h + k)\epsilon/2$ |
| $\bar{2}h + k, \bar{k}, l$ | $-\Delta$ | $-k\epsilon$ |
| $2k + \bar{h}, h, l$ | $-\Delta/2 - h\epsilon 3^{1/2}/2$ | $-\Delta 3^{1/2}/2 + h\epsilon/2$ |
| $h - k, h + k, l$ | $\Delta/2 - (h + k)\epsilon 3^{1/2}/2$ | $-\Delta 3^{1/2}/2 - (h + k)\epsilon/2$ |

of the transitions. We therefore searched for this kind of transition in the PyAg_5I_6 case, but we did not find one.

At all temperatures between 230 and 77°K at which photographs were taken, the diffraction data indicated one monoclinic phase or the other. This is illustrated in Fig. 5 by the results for β_m obtained from the oscillation photographs as well as by the results from the Buerger precession camera photographs. In the region between 188 and 173°K, one can expect difficulty in obtaining sufficient resolution from the Buerger precession camera photographs, but there was no difficulty in discerning the phases with the oscillation photography. There is some unreliability in the temperature, however, and we can only conclude that the transition lies somewhere between 188 and 173°K.

In specific heat measurements, no strong anomaly was found. This may possibly be attributed to the ordering of the Py^+ ions in the γ -phase and to the probably small change in volume *right* at the transition. In Fig. 5 it appears that the large changes in volume occur *away* from the transition, rather than at it, then settling to more reasonable values as compared with the extension of the plot for the hexagonal phase.

In the case of the δ -phase, the monoclinic $h0l$ reciprocal lattice points derive from members of the hexagonal $\{h0l\}$ form, in particular $\pm(h0l)$ and $\pm(\bar{h}0l)$. The hexagonal $\{h0l\}$ form transforms to the following for the monoclinic cell (in terms of the hexagonal indices):

$$\pm(h, h, l; \bar{2}h, 0, l; h, \bar{h}, l; \bar{h}, h, l; 2h, 0, l; \bar{h}, h, l).$$

In the hexagonal structure these reflections

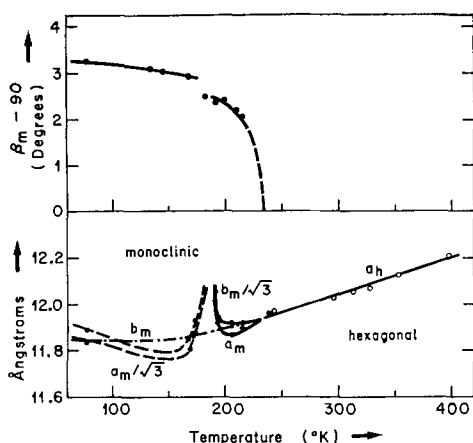


FIG. 5. The lattice parameters of $PyAg_5I_6$ as a function of temperature. The data for the hexagonal phases were taken from Ref. (3). The long monoclinic axes were divided by $3^{1/2}$ to compare them with the monoclinic axes of intermediate length and with the hexagonal a axis. The c_m parameters are constant and equal to $7.38 \pm 0.02 \text{ \AA}$ in the monoclinic phases. (See also Table I.) The figure demonstrates that the phase transition at about 230°K is second order and the transition at about 180°K is first order.

would all be absent when l is odd. However, reflections occurred corresponding to hexagonal 203 and 303 reflections. Only four spots were present instead of six, the absent ones being the monoclinic $\bar{4}03$ and 403 in the first case and the 603 and $\bar{6}03$ in the second. Although these are only a very small number of data, it is possible to suggest that the space group of this phase contains a c -glide plane. The diffraction data are also compatible with C -face centering (monoclinic $h + k = 2n$ for all hkl). Thus the probable space groups are $C2/c$ or Cc .

It should be emphasized that the a_m and b_m -axis orientations in the γ - and δ -structures are interchanged. Thus even if the space group of one of these phases were a subgroup of the other, the transition must still be first order, unless as in the cases mentioned earlier, there exists an intermediate (temperature) phase which belongs to a subgroup of space groups of both the γ - and δ -phase. This does not appear to be the case.

If the space group of either of these phases were Cc , the total number of structural para-

eters, excluding those for H atoms, requiring refinement would be 153: 50 positional and 102 anisotropic thermal parameters. In the space group $C2/c$, the total number would be close to half the number for Cc .

At -30°C , the Ag^+ ions are essentially ordered in the hexagonal structure (2, 3), but the pyridinium ions are statically disordered with the C,N atoms lying on the hexagonal axes and in planes $z = \pm \frac{1}{4}$. The transitions almost surely involve the ordering of the Py^+ ions, but it is very difficult to determine from the data we have just what is involved. It is very unlikely that in either of the monoclinic structures there is a very large change in the relative positions of the iodides, so that we expect that the orientation of the Py^+ ions relative to the iodide ions will also not be *drastically* different from one of the six orientations in the hexagonal phases. There is one remark that can be made with certainty: If the space group of the δ -phase is $C2/c$, then because there are only four N atoms in the unit cell, they *must* lie on twofold axes. (They cannot, of course, lie at the symmetry centers.) In that case, excluding the difference between N and C, the orientation of the Py^+ ions would be essentially the same as in the hexagonal phase.

It may also be said that if the Py^+ ions are ordered in the γ -phase, it is unlikely that the space group is $C2/c$, because this would require a 30° rotation of the pyridinium ring with respect to any of the six orientations in the hexagonal phases. Further, $C2$ would also be ruled out, because this would require a $c/4$ shift of the twofold axis relative to the hexagonal phase.

Preliminary X-ray work has been done on PyI itself. The first-order transition appears to cause disintegration of the crystals. Powder patterns have been taken at 77°K . The result thus far indicates a relation of the two phases bearing some similarity to that of the relation of γ - and δ -phases to the hexagonal phases of $PyAg_5I_6$. The work on PyI will be pursued at a later date.

Appendix

Geometric relations among the reflections of the positive reciprocal lattice levels from

sixfold rotation twinning about the c -axis of a monoclinic crystal, closely related to one of hexagonal symmetry.

In a hexagonal crystal, there are six equivalent (weighted) reciprocal lattice points for a particular (hkl) related by the sixfold axis for all positive (or all negative) l . In terms of the hexagonal indices, the orthohexagonal indices are $(2h+k), k, l$; in the l level, these give coordinates $(2h+k)|A^*|, k|B^*|$ in the orthohexagonal reciprocal lattice. Because $|A^*| = |B^*|3^{1/2}$, we may write the above coordinates as $(2h+k)|A^*|, k|3^{1/2}A^*|$. Then to obtain the coordinates of the five other reciprocal lattice vectors in the particular level, we have

$$\begin{pmatrix} H_n \\ 3^{1/2} K_n \end{pmatrix} |A^*| = \begin{pmatrix} \frac{1}{2} & -\frac{3^{1/2}}{2} \\ \frac{3^{1/2}}{2} & \frac{1}{2} \end{pmatrix} n \begin{pmatrix} 2h+k \\ 3^{1/2}k \end{pmatrix} |A^*|, \quad (\text{A1})$$

or briefly, $\mathbf{r}_n = \mathbf{R}^n \mathbf{r}$, $n = 0, 1, 2, 3, 4, 5$.

We assume first that $\mathbf{a}_m^* = \mathbf{A}^*$, $\mathbf{b}_m^* = \mathbf{B}^*$, and $\mathbf{c}_m^* = \mathbf{C}^*$. A monoclinic distortion of the orthohexagonal lattice causes the above vectors to change: (a) the center of the reciprocal lattice layer will shift along the \mathbf{a}_m^* axis by the amount $lc_m^* \cos \beta^*$; (b) the ratio of b_m^* to a_m^* will deviate from $3^{1/2}$. The modified vectors then are

$$\mathbf{r}_n' = (\mathbf{E} + \mathbf{D}) \mathbf{R}^n \mathbf{r} + \mathbf{d} \quad n = 0, 1, 2, 3, 4, 5, \quad (\text{A2})$$

where \mathbf{E} is the identity matrix and \mathbf{d} is the translation $lc_m^* \cos \beta$ along \mathbf{a}_m^* , and

$$\mathbf{D} = \begin{pmatrix} 0 & 0 \\ 0 & \frac{b_m^*}{a_m^* 3^{1/2}} - 1 \end{pmatrix},$$

which corrects for the change in b_m^*/a_m^* from $3^{1/2}$.

If the crystal has sixfold rotational twinning about the c -axis and the distortions are small, in general a group of six reflections will occur around each of the reciprocal lattice points of the formerly hexagonal reciprocal lattice. The coordinates of each of these groups may

be obtained by rotating the six vectors \mathbf{r}_n , by the correct multiple of 60° to bring them all to surround the particular one of the original hexagonal lattice points. For the particular case in which all are rotated to surround the point $(2h+k)|A^*|, k|3^{1/2}A^*|$, we have, operating on $n = 1, 2, 3, 4, 5$,

$$\mathbf{r}_n'' = \mathbf{R}^{-n} \mathbf{r}_n' = \mathbf{r} + \mathbf{R}^{-n} \mathbf{D} \mathbf{R}^n \mathbf{r} + \mathbf{R}^{-n} \mathbf{d}. \quad (\text{A3})$$

The components of the coordinate shifts calculated from (A3) are given in Table II.

If the second term on the right of (A3) is zero, the six reflections are arranged in a regular hexagon regardless of the b_m^*/a_m^* ratio. Table II shows that this occurs for the $00l$ reflections. For all others, the hexagon is distorted by the contribution of the second term. The distance between any two opposite spots in the hexagon is given by

$$|\mathbf{r}_{n+3}'' - \mathbf{r}_n''| = 2lc^* \cos \beta^*. \quad (\text{A4})$$

The above derivation applies to the δ -phase for which the a_m and b_m axes correspond to the orthohexagonal A and B axes, respectively. The calculation of the reciprocal lattice coordinates of the γ -phase can be done in a similar way.

Note added in proof: $|A^*|$ should be replaced by $|a_m^*|$ in \mathbf{r} of Eq. (A2).

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