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A powder neutron diffraction study of the pressure-induced phase transitions within silver iodide

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Abstract. Powder neutron diffraction measurements of silver iodide are described for pressures up to 5.5 kbar. Three phases have been observed, and the so called ‘intermediate’ phase which exists in the narrow pressure region from ~ 2.8 to ~ 3.8 kbar has been stabilized with no contamination from neighbouring phases. This phase is found to possess a tetragonal unit cell ($a = 4.570(1)$ Å and $c = 5.973(1)$ Å), with space group $P4/nmm$ and two formula units per cell. Isotopically enriched ^{107}AgI allows the distribution of the ions over the four sites to be determined. The intermediate phase has the ‘anti-litharge’ structure, with Ag^+ in 2(a) sites at $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$ and I^- in 2(c) sites at $(0, \frac{1}{2}, z)$ and $(\frac{1}{2}, 0, -z)$. The transformations between this phase and the neighbouring zincblende and rocksalt phases can be described by redistribution of the smaller silver ions, while the iodine sublattice remains largely unchanged.

1. Introduction

Silver iodide is a much studied material, largely as a result of its fast-ionic behaviour within the α phase (stable above $T = 420$ K), but also because it undergoes a number of phase transitions in a readily accessible temperature and pressure range (see figure 1). The phase diagram of silver iodide has been investigated using conductivity measurements [1,2] and there have been some attempts to deduce the structures associated with the various crystallographic phases [3,4]. At ambient temperature and pressure AgI usually exists as a mixture of two phases, β and γ . The β phase has the hexagonal wurtzite structure (space group $P6_3mc$) and the γ phase has the cubic zincblende structure (space group $F43m$). The former is believed to be the more stable phase [5]. As temperature is increased AgI undergoes a first-order phase transition to the fast-ionic α phase (space group $Im3m$) which has a body-centred cubic arrangement of I^- ions and a distribution of highly mobile Ag^+ ions which preferentially occupy tetrahedral sites [6]. As the pressure is increased at temperatures above ~ 310 K the β/γ phase changes to a rocksalt structure (space group $Fm3m$). At lower temperatures however, this transformation occurs via an intermediate phase which only exists in a narrow range of pressures between ~ 2.8 and ~ 3.8 kbar at room temperature (see figure 1). The transformations from the neighbouring zincblende or rocksalt phases to the intermediate phase are extremely sluggish, showing considerable hysteresis, whereas transformations from the intermediate phase occur instantaneously [1]. The structure of the intermediate phase has not been unambiguously determined, although hexagonal, orthorhombic and tetragonal unit cells have been proposed

[3, 7, 8]. These disparate assignments have resulted from the experimental problems involved, principally that of contamination from neighbouring phases. Molecular dynamics simulations which successfully reproduce the behaviour of AgI in other phases fail to stabilize the intermediate phase, observing instead sluggish distortions between unrecognizable structures close to the relevant region of p/T space [9].

This paper describes a neutron powder diffraction study of the phases of silver iodide which exist at pressures less than 5.5 kbar and close to room temperature with the aims of determining conclusively the structure of the intermediate phase and elucidating the mechanisms of the pressure-induced phase transformations.

2. Experimental details

Preliminary measurements were conducted using commercially available AgI powder, of approximately purity 99%, supplied by the Aldrich Chemical Company. The sample was found to be two phase, containing approximately 70% γ -AgI and 30% β -AgI. Naturally occurring Ag(^{nat}Ag) has a significant thermal neutron absorption cross-section ($\sigma_a = 63.3$ bn at $\gamma = 1.8$ Å) which can be reduced by using the ^{107}Ag isotope ($\sigma_a = 38$ bn). Such enrichment also enhances the contrast between the iodine and silver coherent neutron scattering lengths ($b_I = 0.528 \times 10^{-12}$ cm, $b_{Ag} = 0.597 \times 10^{-12}$ cm for ^{nat}Ag and $b_{Ag} \approx 0.764 \times 10^{-12}$ cm for ^{107}Ag). This allows differentiation between the two ions in neutron diffraction experiments which would be difficult using neutron diffraction from ^{nat}AgI and previously found to be impossible with x-ray diffraction because of the similarity of the form factors [3]. Subsequent experiments therefore used a sample of AgI enriched in ^{107}Ag to 99%.

High-pressure data were collected using a gas cell of approximately 1 cm³ sample volume, mounted inside a standard neutron scattering cryostat to provide a stable temperature environment. The pressure cell is constructed of 'null scattering' $\text{Ti}_{0.52}\text{Zr}_{0.48}$ alloy, so chosen because it contributes no coherent scattering. The sample was initially pressurized to 5.5 kbar, using compressed Ar gas, and the pressure was then released to perform measurements at 3.8 kbar, 3.0 kbar and 1 bar and temperatures between 270 K and 290 K.

The diffraction experiment was performed using the Polaris medium resolution diffractometer at the ISIS spallation neutron source, UK [10]. Diffraction data were collected by the time-of-flight method using detector banks situated at $15^\circ < 2\theta < 30^\circ$ and at $87^\circ < 2\theta < 93^\circ$. The former provides data in the d -spacing range $1 \text{ \AA} < d < 12 \text{ \AA}$ with resolution $\Delta d/d \sim 2\%$ and the latter $0.3 \text{ \AA} < d < 4.0 \text{ \AA}$ with $\Delta d/d \sim 0.5\%$. The diffraction data were corrected for the effects of absorption by the cell and by the sample itself. These were subsequently normalized to remove the wavelength dependence of the incident neutron flux using standard procedures [10]. Data of sufficient quality to monitor the kinetics of the sluggish transformation to the intermediate phase were collected in one hour and diffraction patterns suitable for full structural refinement were collected in approximately 24 hours. Rietveld profile refinements of the time-of-flight data measured at $2\theta \sim 90^\circ$ were performed using the computer program TF14LS [11], which is based upon the Cambridge Crystallographic Subroutine Library [12].

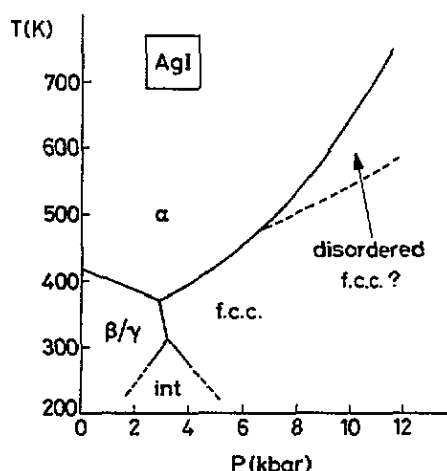


Figure 1. The phase diagram of AgI [1,2]. The β phase has the hexagonal wurtzite structure, the γ phase has the cubic zincblende structure and α is the fast-ion phase with a BCC arrangement of I^- and highly mobile Ag^+ . The approximate stability region of the intermediate phase and the proposed disordered phase of the high-pressure rocksalt phase are shown by broken lines.

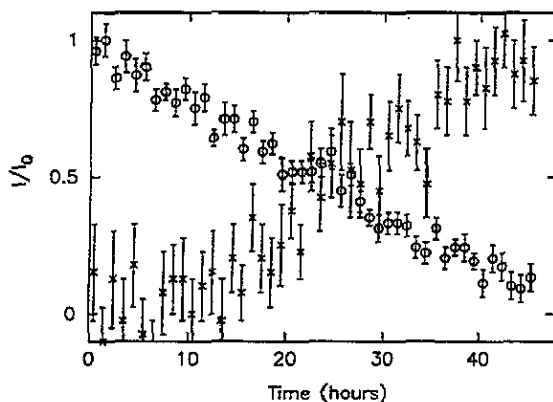


Figure 2. The intensity of the $(220)_{\text{rocksalt}}$ Bragg peak (O) and the $(112)_{\text{tetragonal}}$ Bragg peak (x) as a function of time during transformation to the intermediate phase at $p = 3$ kbar and $T = 290$ K. Intensities are given as a proportion of the peak intensity found for the respective pure phases.

3. Results

3.1. High-pressure phase

The diffraction peaks observed at pressures of 5.5 kbar and 3.8 kbar and at a temperature of 270 K were found to be consistent with $Fm\bar{3}m$ symmetry and confirm the presence of the rocksalt-structured high-pressure phase of AgI, with Ag^+ located in 4(a) sites at $(0, 0, 0)$ etc and I^- in 4(b) sites at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ etc (see table 1). The relatively high value of the isotropic thermal parameter for

Ag indicates that there is considerable thermal disorder of these ions. Indeed, conductivity measurements suggest that the high pressure rocksalt phase displays fast-ion behaviour at temperatures above 500 K [2]. It is likely, therefore, that AgI at $p > \sim 4$ kbar exhibits thermally induced disorder as observed in AgBr at ambient pressure, which has the same rocksalt structure [13]. It would be particularly interesting to perform temperature-dependent neutron diffraction measurements at pressures greater than 4 kbar to compare the nature and extent of thermally induced disorder within the rocksalt phases of AgI and AgBr.

Table 1. Summary of the results obtained by least-squares refinements of the diffraction data collected at each pressure. V/Z is the volume occupied by one formula unit of AgI, V/V_0 is the volume ratio compared to ambient and B is the isotropic thermal parameter for each ion. N_d and N_p are the number of data points and reflections, respectively. R_w and R_{exp} are the weighted and expected R -factors.

Pressure (kbar)		5.50	3.80	3.00	0.001
Temperature (K)		270	270	290	290
Phase		f.c.c.	f.c.c.	int.	γ
		rocksalt	rocksalt	anti-litharge	zinc-blende
Space Group		Fm3m	Fm3m	$P4/nmm$	F43m
a (Å)		6.067(1)	6.082(1)	4.570(1)	6.499(2)
b (Å)		(=a)	(=a)	(=a)	(=a)
c (Å)		(=a)	(=a)	5.973(1)	(=a)
V/Z (Å ³)		55.82(2)	56.25(2)	62.38(2)	68.82(3)
V/V_0		0.811	0.817	0.906	1.000
Ag	x	0	0	0	0
	y	0	0	0	0
	z	0	0	0	0
	B (Å ²)	2.5(2)	2.5(1)	2.9(1)	5.1(5)
I	x	1/2	1/2	0	1/4
	y	1/2	1/2	1/2	1/4
	z	1/2	1/2	0.292(1)	1/4
	B (Å ²)	0.9(1)	0.8(1)	0.8(1)	2.2(2)
N_d		1764	1729	1784	1387
N_p		45	45	232	91
R_w (%)		2.64	3.09	4.07	4.55
R_{exp} (%)		2.25	2.69	3.37	3.99

3.2. Intermediate phase

3.2.1. Kinetics of the rocksalt-intermediate phase transition. Following the phase boundary determination of Mellander *et al* [1, 2] formation of the intermediate phase of AgI was achieved by raising the temperature to 290 K and reducing the pressure to 3.0 kbar. Measurements were taken every one hour to monitor the progress of any observed transition at this temperature and pressure. A gradual decrease in intensity of the rocksalt reflections was observed and a slow increase in Bragg peak intensity from a new phase developed. Figure 2 shows the decrease of the (220) Bragg peak from the rocksalt phase ($d = 2.150$ Å) and the increase of the strong $d = 2.192$ Å peak from the intermediate phase with time. This indicates that at least two days are required for complete transformation to the intermediate phase.

3.2.2. *Determination of the structure of the intermediate phase.* Diffraction measurements performed seven days after annealing at 3.0 kbar and 290 K showed no evidence of the rocksalt phase. Table 2 lists the measured d -spacings together with those from previously published x-ray work which have indexed the diffraction pattern on the basis of several unit cells, hexagonal with $a = 9.20 \text{ \AA}$ and $c = 9.02 \text{ \AA}$ [7], tetragonal with $a = 9.14 \text{ \AA}$ and $c = 7.98 \text{ \AA}$ [7], orthorhombic with $a = 9.37 \text{ \AA}$, $b = 8.15 \text{ \AA}$ and $c = 9.20 \text{ \AA}$ [7], tetragonal with $a = 4.58 \text{ \AA}$ and $c = 6.00 \text{ \AA}$ [3] and tetragonal with $a = 12.99 \text{ \AA}$ and $c = 12.14 \text{ \AA}$ [8]. Overall the d -spacings obtained in this work agree best with those of Moore and Kasper [3]. The determination of the correct unit cell relies heavily on the presence of the longest d -spacing reflections. Figure 3 shows the data collected at 3.0 kbar in the low- 2θ detector banks. The reflections in the vicinity of 4 \AA found by the other workers are not observed here, even though these peaks are reported to be of comparable intensity to the highest d -spacing reflection at 6.0 \AA . It is concluded, therefore, that these reflections observed in some of the previous work are spurious, perhaps resulting from the neighbouring wurtzite phase, which has a (100) peak at $d \sim 3.97 \text{ \AA}$. Careful inspection of the diffraction pattern obtained at 3.0 kbar in this work indicated that none of the neighbouring phases were present.

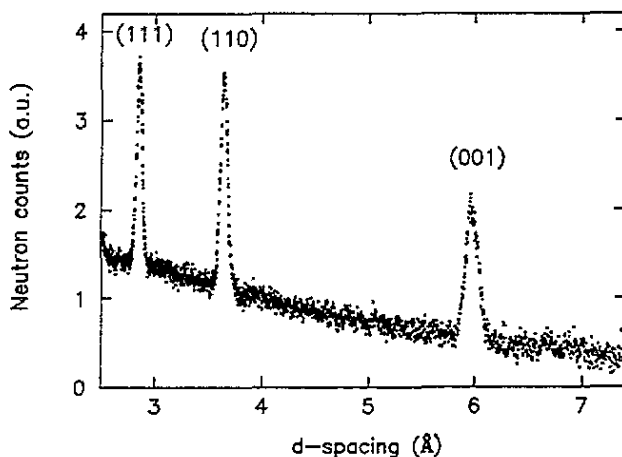


Figure 3. Diffraction data collected at $p = 3.0$ kbar using the low-angle detector bank. The reflection indices refer to the tetragonal cell with $a = 4.570 \text{ \AA}$ and $c = 5.973 \text{ \AA}$.

The observed d -spacings for the intermediate phase can be completely indexed on the basis of a tetragonal unit cell with $a = 4.570 \text{ \AA}$ and $c = 5.973 \text{ \AA}$, which is close to one proposed previously [3]. The reflection conditions, $(hk0)$ with $h + k = 2n$ and $(h00)$ with $h = 2n$, are consistent with $P4/n$ and $P4/nmm$ symmetry. The unit cell volume $v = 124.76 \text{ \AA}^3$ indicates that there are two formula units per unit cell and, since both space groups possess three identical twofold sites, the higher symmetry space group ($P4/nmm$) is adopted here. An acceptable structure of high symmetry has one pair of ions in 2(a) sites at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ and another pair in 2(c) sites at $(\frac{1}{2}, 0, \frac{1}{4})$ and $(0, \frac{1}{2}, \frac{3}{4})$. Refinements of the above structure produced a significantly better fit to the experimental data when Ag^+ ions were located on 2(a) sites and I^- ions in 2(c) sites rather than the reverse. The z coordinate of the

Table 2. Comparison of the observed d -spacings of the AgI reflections at 3.0 kbar and 290 K with those published previously on the basis of x-ray measurements [3, 6, 7] and those calculated for a tetragonal unit cell (space group $P4/nmm$) with $a = 4.570 \text{ \AA}$ and $c = 5.973 \text{ \AA}$.

$d_{\text{obs}}(\text{\AA})$ ref. [6]	$d_{\text{obs}}(\text{\AA})$ ref. [3]	$d_{\text{obs}}(\text{\AA})$ ref. [7]	$d_{\text{obs}}(\text{\AA})$ this work	$d_{\text{calc}}(\text{\AA})$ this work	hkl
6.04	5.98	6.05	5.970	5.973	0 0 1
-	-	4.12	-	-	-
3.97	-	-	-	-	-
-	-	3.71	-	-	-
3.66	3.65	3.68	3.632	3.630	0 1 1
-	-	3.47	-	-	-
-	-	3.23	-	3.232	1 1 0
-	3.06	3.05	-	2.987	0 0 2
2.86	2.852	2.86	2.839	2.842	1 1 1
-	-	2.60	-	-	-
2.50	2.496	-	2.500	2.500	1 0 2
-	2.289	2.30	2.286	2.285	2 0 0
2.20	2.193	2.19	2.193	2.193	1 1 2
-	2.154	-	-	2.134	2 0 1
1.995	1.994	-	1.992	1.991	0 0 3
1.949	-	1.942	-	-	-
-	1.937	-	1.934	1.934	2 1 1
1.829	1.827	-	1.823	1.825	0 1 3
-	-	1.816	-	1.815	2 0 2
-	-	-	-	1.695	1 1 3
-	1.686	-	1.688	1.687	2 1 2
-	-	1.662	-	-	-
1.624	1.618	1.613	1.616	1.616	2 2 0
-	-	1.574	1.560	1.560	2 2 1
1.503	1.498	1.492	1.502	1.501	0 2 3
-	-	-	-	1.493	0 0 4
-	-	1.470	1.475	1.476	0 3 1
-	-	-	-	1.445	3 1 0
-	-	-	1.423	1.426	1 2 3
-	1.411	-	-	1.421	2 2 2
-	-	-	-	1.419	1 0 4
1.409	-	1.398	1.405	1.405	1 3 1
1.380	-	-	-	-	-
-	1.368	-	-	1.357	3 0 2
-	-	-	-	1.356	1 1 4
1.304	1.304	-	1.302	1.301	3 1 2
1.258	-	-	1.253	1.255	2 2 3
1.246	1.244	-	-	1.250	2 0 4
-	-	-	1.242	1.240	2 3 1
-	-	-	1.210	1.210	0 3 3

iodine anion is not constrained by symmetry to lie at $z = \frac{1}{4}$ and refines to a value $z = 0.292(1)$. The full list of fitted parameters obtained by least-squares refinement of the 3.0 kbar data is given in table 1, and figure 4 shows the quality of the fit to the experimental data. The structure of the 3.0 kbar phase is, therefore, 'anti' that of litharge (red PbO) and can be described as a face-centred cubic (FCC) array of I^- ions swelled and distorted by the introduction of sheets of Ag^+ cations. Each Ag^+ ion has four nearest-neighbour Ag^+ ions in the (001) plane at a distance of 3.23 \AA and is approximately tetrahedrally coordinated to I^- at 2.88 \AA . In the twelvefold-coordinated I^- sublattice there are three I^- - I^- distances of 4.07 \AA , 4.57 \AA and 4.76 \AA .

3.3. Ambient pressure phase

Bragg peaks characteristic of the tetragonal phase were not present in the first one-

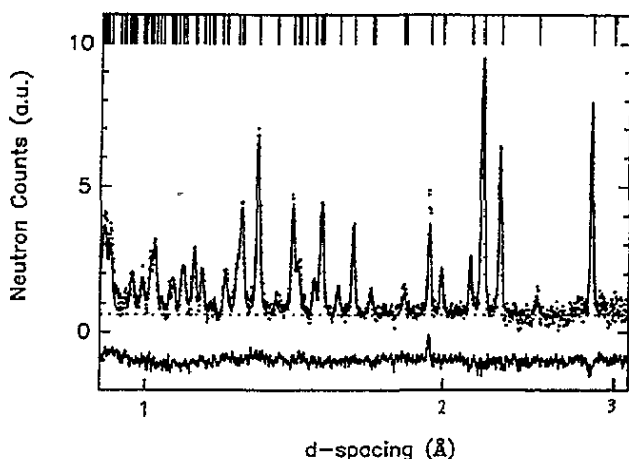


Figure 4. Comparison of the diffraction data (·) collected in the $2\theta \sim 90^\circ$ detector bank at $p = 3.00$ kbar with the fitted profile (—) using the anti-litharge structure described in the text. The tick marks at the top of the figure indicate the expected positions of the Bragg peaks, and the lowest trace gives the difference/experimental error, offset vertically by -1 . Note the log scale along the x -axis, emphasizing the constant $\Delta d/d$ resolution from time-of-flight neutron diffraction.

hour diffraction measurement following the complete removal of the applied pressure, in contrast to the sluggish formation of the intermediate phase. At ambient pressure the sample was found to be single-phase zincblende, with $a = 6.499(2)$ Å. It is well known that the conversion to the zincblende structure of AgI can be achieved by prolonged grinding of the wurtzite phase [3]. By contrast, quenching from the high-temperature phase produces a mixture of the β and γ phases largely dependent on the cooling rate [14]. It is likely therefore, that with increasing pressure wurtzite AgI transforms to its zincblende modification at a pressure lower than the β/γ -tetragonal phase boundary. Indirect support for this hypothesis is provided by the observation of anomalies in the ionic conductivity of AgI at $p \sim 1.0$ kbar [15].

4. Discussion

The mechanism of transformation between the zincblende and rocksalt structures, via the anti-litharge intermediary, is now considered. Both the zincblende and rocksalt structures contain interpenetrating FCC lattices of Ag and I, displaced by $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ respectively. To demonstrate the structural relationship between the three phases tetragonal sub-units of the two cubic structures with $a_{\text{tet}} = a_{\text{cub}}/\sqrt{2}$ and $c_{\text{tet}} = a_{\text{cub}}$ are taken. In this notation the three phases all possess two formula units per unit cell. The zincblende-tetragonal phase transition involves a reduction in the c -axis of the tetragonal cell, from 6.5 Å to 6.0 Å, with the a -axis essentially unchanged at 4.6 Å. The subsequent transition to the rocksalt structure at higher pressure causes a significant decrease in the a -axis from 4.6 Å to 4.2 Å whilst the c -axis shows a slight increase of 0.1 Å. Relative to the tetragonal axes, and with suitable choice of origin, the zincblende structure has two I^- at $(\frac{1}{2}, 0, \frac{3}{4})$ and $(0, \frac{1}{2}, \frac{1}{4})$ and two Ag^+ located at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. For the rocksalt structure the I^-

are at the same locations and are now sixfold coordinated to Ag^+ at $(\frac{1}{2}, 0, \frac{1}{4})$, $(0, \frac{1}{2}, \frac{3}{4})$ etc. These are illustrated in figures 5(a) and 5(d), respectively.

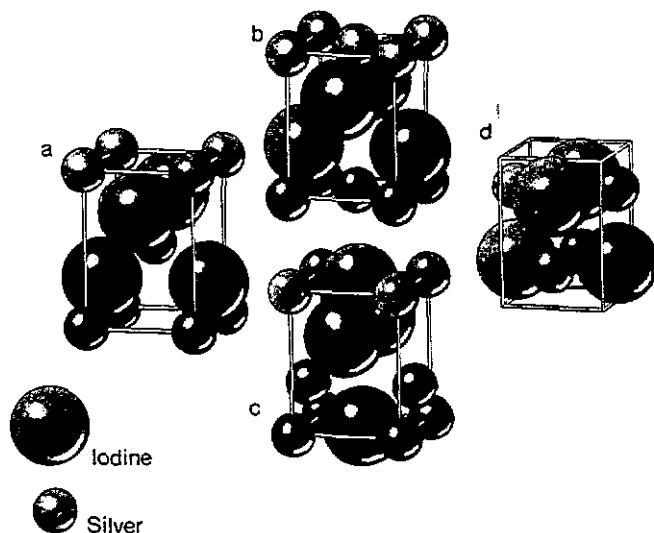


Figure 5. Schematic diagrams of the arrangements of ions in the cubic zincblende (a) and rocksalt (d) phases of AgI. (b) shows the anti-litharge structure determined by this work and (c) the orthorhombic structure proposed by Moore and Kasper [3].

The sequence of pressure induced transitions using the structure of the intermediate phase described in the previous section is illustrated in figures 5(a), 5(b) and 5(d). The transition to the tetragonal phase involves a compression along the c -axis and the repositioning of one of the Ag^+ from $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ to $(\frac{1}{2}, \frac{1}{2}, 0)$. The I^- distort slightly from their close-packed FCC sites at $(0, \frac{1}{2}, \frac{1}{4})$ to $(0, \frac{1}{2}, 0.292)$. The subsequent transformation to the rocksalt structure occurs by translations of all the Ag^+ by $\pm(\frac{1}{2}, 0, -\frac{1}{4})$ and the I^- sublattice returns to its close packed array. The transformations therefore involve an essentially rigid I^- lattice and two rearrangements of the Ag^+ cations, which are known to become more mobile than the I^- anions at elevated temperatures and diffuse rapidly in the fast-ionic phases.

Figure 2 demonstrates the sluggish nature of the transition. In some previous measurements an intermediate phase was not observed in this pressure and temperature range, presumably because equilibration times were not sufficiently long. The reason for the sluggish transitions into the anti-litharge tetragonal phase is not clear, but may be due to the distortion of the iodine sublattice away from its ideal close-packed FCC configuration.

An alternative model for the pressure induced transitions within AgI has been proposed by Moore and Kasper [3], who determine the same tetragonal cell but suggest a different ionic arrangement. In the tetragonal notation, the zincblende to tetragonal transition involves the displacement of alternate (010) planes by $(0, \frac{1}{2}, -\frac{1}{4})$, so the Ag^+ are located at $(0, 0, 0)$ and $(0, \frac{1}{2}, \frac{1}{4})$ whilst I^- are at $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, 0, \frac{3}{4})$. A subsequent small distortion results in the atoms at $(0, \frac{1}{2}, \frac{1}{4})$ moving to $(0, \frac{1}{2}, z)$ and those at $(\frac{1}{2}, 0, \frac{3}{4})$ moving to $(\frac{1}{2}, 0, -z)$, with $z \sim 0.3$. This arrangement

is illustrated in figure 5(c) and possess orthorhombic symmetry which, recalling the similarity in x-ray form factors for Ag and I, appears tetragonal if the a and b axes are sufficiently close. Attempts to refine the diffraction data collected in the $2\theta \sim 90^\circ$ detector banks ($0.3 \text{ \AA} < d < 4.0 \text{ \AA}$) at 3.0 kbar on the basis of an orthorhombic cell gave values for the a - and b -axes which differ by less than the estimated error on their values (0.001 \AA). The refinement produced a weighted R -factor of 5.72% (compared with 4.07% for the anti-litharge structure) and was only stable when the Ag^+ and I^- temperature factors were constrained to be the same. Furthermore, simulations based on this model of the expected neutron diffraction pattern from ^{107}AgI predicts a peak of measurable intensity at $d = 4.57 \text{ \AA}$ corresponding to the orthorhombic (100)/(010) reflection. As illustrated in figure 3, this peak is absent. For these reasons, and the anomalously short $\text{I}^- - \text{I}^-$ distances obtained for this structure (2.88 \AA), it is concluded that this model for the intermediate phase structure is incorrect.

It is interesting to note that the pressure-induced phase behaviour of copper iodide shows some similarities with that determined here for silver iodide. At ambient pressure, CuI has the zincblende structure. On increasing pressure at ambient temperature, CuI undergoes phase transitions at ~ 15 kbar to a phase which possibly has a rhombohedral unit cell, at ~ 42 kbar to a tetragonal cell with the anti-litharge structure and at ~ 90 kbar to a phase which may have the rocksalt structure [16]. In the anti-litharge phase of CuI the cell parameters have been determined to be $a = 4.02 \text{ \AA}$ and $c = 5.70 \text{ \AA}$, with the Cu^+ at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ and I^- at $(0, \frac{1}{2}, z)$ and $(\frac{1}{2}, 0, -z)$ with $z \sim 0.28$ [16]. Following the formalism of Liu [17] it is straightforward to show that the (anti-) litharge structure is indeed more densely packed than the zincblende (or wurtzite) structures if the single positional parameter z takes a value significantly greater than 0.25. This is in contrast to the case of the binary monoxides where, for example, red PbO has $z(\text{Pb}) = 0.2385$ and the litharge structure is the most loosely packed. The available experimental evidence suggests pressure induced transitions from litharge to the wurtzite structure (as in SnO [18]).

5. Conclusions

The pressure-induced phase transitions which occur within AgI at close to ambient temperature have been studied using powder neutron diffraction. The 'intermediate' phase has been stabilized at 3.0 kbar and 290 K for the first time without contamination from the neighbouring phases. The measured diffraction pattern gives a tetragonal unit cell with $a = 4.570(2) \text{ \AA}$ and $c = 5.973(1) \text{ \AA}$ and space group $P4nmm$. Using diffraction data from isotopically enriched ^{107}AgI this phase has been found to possess the anti-litharge structure with Ag^+ in 2(a) sites at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ and I^- in 2(c) sites at $(0, \frac{1}{2}, z)$ and $(\frac{1}{2}, 0, -z)$ with $z = 0.292(1)$. As a consequence it has been shown that the pressure-induced modifications from zincblende to tetragonal to rocksalt structures involve an essentially rigid iodine sublattice and two rearrangements of the Ag^+ cations.

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