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Ordering of the silver ions in α-AgI: A mechanism for the α-β phase transition

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The disorder of the Ag^+ ions in the superionic conductor α-AgI has been studied with use of computer simulations in which reorganizations of the I^- lattice are inhibited. At high temperatures the ions are evenly distributed over the tetrahedral interstitial sites of the crystal but, as the temperature is lowered, the Ag^+ ions are found to condense onto particular sublattices. The condensation is associated with a loss of mobility. The possible occurrence of such order-disorder transitions in this system has been suggested by Szabó [J. Phys. C **19**, 3775 (1986)]. The structure of this phase was identified, using molecular-graphics methods. The Ag^+ ions are found to be in a locally crystalline (monoclinic) arrrangement, which is not one of the stable phases discussed by Szabó. From the geometric disposition of the ions at low temperature it is argued that the crystallites found in the simulated system would be unstable with respect to a hexagonal (wurtzite) structure if the boundary-condition-imposed stresses were to be relaxed. On this basis, it is argued that the ordering tendency of the Ag^+ ions in the α phase can be seen as the driving force for the α-to-β phase transition in this material.

I. INTRODUCTION

The α-phase of silver iodide has been a subject of interest since it was discovered by Tubandt and Lorentz[1] as part of their systematic study of the electrical conductivities of the silver halides. At low temperatures and normal pressure[2] AgI consists of a mixture of the β and γ phases, which have the wurtzite and zinc-blende structures. In these crystals the iodine ions form close-packed hexagonal and cubic lattices (respectively) and the silver ions occupy a sublattice of interstitial tetrahedral sites. Above 410 K, β is the more stable phase and, when the temperature is further raised, the $\beta \rightarrow \alpha$ transition is found at 420 K. In the α phase, the iodine ions form a bcc lattice, and the silver ions exhibit superionic or "fast-ion" conduction. Diffuse x-ray-scattering experiments[3] have established that the preferred locations of the Ag^+ ions are the tetrahedral (T_d) sites. In Fig. 1 we sketch the positions of these sites in one unit cell of α-AgI. We note that there are 12 such tetrahedral sites and 2 Ag^+ ions within this unit cell. Consequently, there is the potential for a considerable degree of disorder in the Ag^+ positions.

It has been shown[4] from thermodynamical calculations that the value of the β-to-α transition entropy is too low to be consistent with complete disorder of the Ag^+ ions over the tetrahedral sites in α-AgI. On the basis of experimentally observed anomalies in the heat-capacity data[5] in the 600–700-K temperature range, it was further suggested that an order-disorder transition occurs within the α phase. Marked changes have also been found in the (Raman) light-scattering spectrum of α-AgI in the same temperature regime. Experimentally,[6(a)] the light-scattering intensity is found to drop by an order of magnitude over the temperature range 600–600 K and the depolarization ratio also falls considerably. An order-disorder transition of the type suggested by the heat-

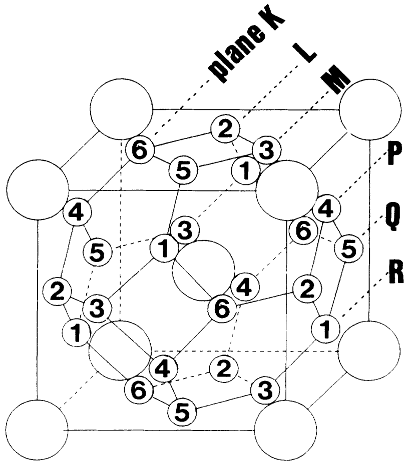

FIG. 1. A schematic diagram of the bcc unit cell indicating the positions of the I^- ions (large circles) and the T_d interstitial sites (small circles). As indicated by numbers, the T_d sites form six interpenetrating bcc lattices. Within the unit cell, they like in six (110) planes, as labeled by the letters.

capacity measurements could also be responsible for these effects.[6(b)]

The silver-ion disorder has also been the subject of theoretical models. Andreoni and Phillips[7] suggested a lattice liquid description, in which there is short-range order arising from the repulsion between the silver ions. More recently, Szabó[8] made use of a lattice-gas model incorporating nearest-neighbor and next-nearest-neighbor interactions to predict the occupancies of the T_d sites. He pointed out that the tetrahedral sites themselves form six interpenetrating bcc sublattices, indicated by the labeling scheme in Fig. 1. Note from Fig. 1 that a site on a given sublattice, say 1, has nearest neighbors of types 2, 3, 5, and 6 and has next-nearest neighbors of type 4. Within a mean-field analysis he showed that a variety of stable phases could exist within this description of the α phase. These phases are characterized by unequal sublattice occupancies, and Szabó argued that a transition between two such phases might explain the anomalies in the Raman intensity and heat-capacity data.

A good deal of progress has been made by studying AgI by use of computer simulations. Parrinello, Rahman, and Vashista[2,9] introduced a polynomial form for the short-range potential (RVP) and showed, in computer simulations with flexible boundary conditions, that this potential was capable of describing the α-to-β transition. More recently, Tallon,[10] using similar techniques, found that the potential gives a solid phase diagram in semiquantitative agreement with the experimental one. Remarkably, Tallon also found evidence for a heat-capacity anomaly in his simulations similar to that experimentally observed. Chiarotti, Jacucci, and Rahman[11] have shown that the RVP potential also gives a very good description of the dynamics of the Ag^+ ions. They calculated neutron dynamical structure factors in good agreement with experiment and proposed a mechanism for the motion of the Ag^+ ions through the I^- lattice. Overall, given its simplicity as a pair potential, the RVP potential has been found to give a remarkably accurate representation of the properties of AgI.

The present paper stems from a more general simulation study of α-AgI,[12] which was motivated by the wish to understand the experimental results described above and to test the theoretical suggestions which bear upon the degree of disorder of the Ag^+ ions in the α phase. We studied silver-ion disorder in molecular-dynamics computer simulations on a system of 864 ions which interact via the RVP potential and which are constrained to a cubic simulation cell by the use of fixed cubic periodic boundary conditions. The density was chosen to be that of the α phase close to the $\alpha \to \beta$ transition ($\sim$470 K) found in the constant stress simulations of RVP.[2] The unit-cell length was taken to be $a = 5.206$ Å^{-1} (Ref. 11) and simulations were performed over a wide temperature range. Because of the fixed density, the crystal cannot melt, and because of the boundary conditions,[13] the I^- ions are unable to reorganize into either the hexagonal or close-packed cubic structure so that the α-to-β transition is also prevented.

As part of this work we monitored the number, $n^i(t)$, of silver ions found on each sublattice i as the simulation progressed. An ion was assigned to a T_d site if it was located within a cube of side $a/4$ centered on that site. At high temperatures the occupancy of each sublattice fluctuates about a common mean value $\bar{n}$; we found no strange behavior at the temperature where the experimental heat-capacity anomaly is found (note, however, that the fixed density used in our calculations is considerably higher than the experimental density at this temperature at normal pressures[10]). At low temperatures (similar to the experimental α-to-β transition temperature) we found that two sublattices became unoccupied while the occupation numbers of the remaining four remained finite. Typical data are illustrated in Fig. 2 where we show the sublattice occupancies $n^i(t)$ for all six sublattices for a simulation at 400 K. To understand the significance of this data note that, although the sublattices are equivalent, particular pairs bear special relationships, sublattices 1 and 4, 2 and 5, and 3 and 6 are related in that they have sites which are next-nearest neighbors (Fig. 1), whereas all other pairings have sites which are nearest neighbors. The two sublattices that become zero occupied are related as next-near neighbors. With the way we have drawn Fig. 1, the reader will find it most convenient to think of 2 and 5 as the unoccupied pair. In several different runs, different pairs of sublattices were found to become the zero occupied set, but in all cases the two sublattices were related as next-near neighbors.

This observation suggests that the silver ions are undergoing some kind of ordering transition as the temperature is lowered below about 450 K. The present paper describes our efforts to characterize the ordered phase. We found that the iodine lattice remains bcc despite the silver ordering. This is almost certainly due to the fact that we maintained cubic periodic boundary conditions which prevent the rearrangement of the iodine ions into a hexagonal structure. As we noted above, in the RVP simulations at constant stress,[2,9] the RVP potential was found to give a transition of the iodine lattice from bcc to hexagonal at a temperature of $\sim$470 K (see footnote in Ref. 14). The silver-ion transition with which we are concerned is therefore unlikely to be directly observable in a real experiment since it will be masked, or preceded by,

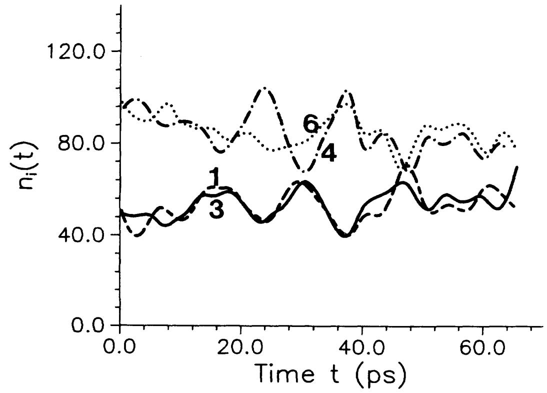

FIG. 2. The number, n^i, of Ag^+ ions found on T_d sublattice i is plotted as a function of time through the simulation at 400 K. Sublattices 2 and 5 were found to be unoccupied.

the α-to-β transition. We have studied it for its intrinsic interest and because, as we will argue below, we believe that it provides the driving force for the α-to-β transition under experimental conditions.

II. CHARACTERIZATION OF THE LOW-TEMPERATURE PHASE

The ordering of the silver ions detected as described is associated with a cessation of silver-ion diffusion at low temperatures. In Fig. 3 we show the mean-square displacement for the silver ions taken from a series of short runs at different temperatures. This sequence of runs was initiated from a very well-aged simulation at a temperature of 500 K. After scaling the ion kinetic energies by a small factor (corresponding to a temperature drop of 10–20 K), the system was equilibrated for 3000 steps ~20 ps and the statistics gathered for a further 3000 steps.

The transition to the low-temperature phase has a distinctly second-order character, as seen by a pretransitional slowing of the fluctuations in the sublattice occupation numbers. We monitored these fluctuations $[n^i(t)]$ by calculating the correlation function

$$C(t)=\tfrac{1}{6}\sum_i \langle [n^i(t)-\bar{n}^i][n^i(0)-\bar{n}^i]\rangle \qquad (1)$$

for the high-temperature runs where the average sublattice occupancies are equal. In Fig. 4 we show the normalized correlation functions from the runs at 900, 700, and 500 K which show a distinctive slowing of the relaxation rates. This slowing down seems to be reasonably well described by

$$\tau \propto (T-T^*)^{-1}\ , \qquad (2)$$

$1/\tau$ is plotted vs T in the inset to the figure; T^* comes out as 460 K, which is close to the $\alpha \rightarrow \beta$ transition temperature found in the constant stress simulations and to the temperature at which the ordered phase first appears in ours.

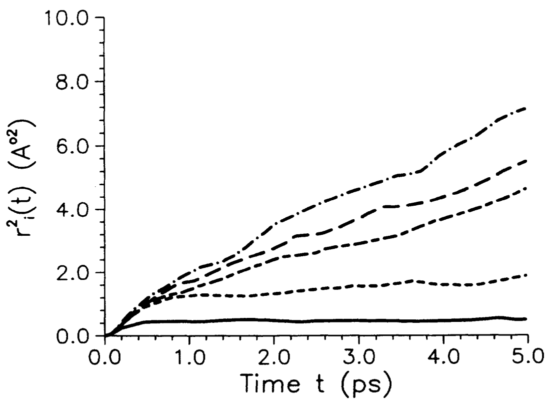

FIG. 3. The mean-square displacement (MSD) of the Ag^+ ions at several temperatures; from top to bottom: 450, 430, 410, and 400 K. The MSD for the I^- ions at 400 K is also shown by the solid line.

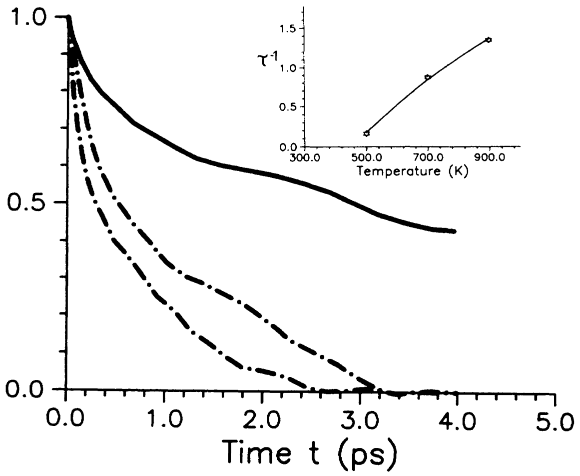

FIG. 4. The time correlation function [Eq. (1)] which characterizes the fluctuations in the sublattice occupation numbers vs time. The lines'(from top to bottom) show the data for 900, 700, and 500 K. A plot of the reciprocal of the relaxation time vs temperature is shown in the inset.

The ordering process seems to be driven by a tendency of the ions to occupy the same sublattice. We illustrated this tendency in an earlier paper where we showed the radial distribution functions for ions on the same sublattice, $G^{11}(r)$, for ions on the nearest-neighbor sublattice, $G^{12}(r)$, and for ions on the next-nearest-neighbor sublattice, $G^{14}(r)$. We showed that, at 500 K, for a given value of r, $G^{11}(r)$ was substantially larger than $G^{12}(r)$ and $G^{14}(r)$. In Fig. 5 we reproduce the data for $N^{ij}(r)$ which gives a measure of the excess population of sublattice j at a given distance from an occupied site on sublattice i, i.e.,

$$N^{ij}(r)=\frac{\sum_{r'\le r} G^{ij}(r')n^{ij}(r')}{\sum_{r'\le r} n^{ij}(r')}-1\ , \qquad (3)$$

where $n^{ij}(r)$ is the number of sites of type j at a given distance from a site of type i. This demonstrates the tendency for the silver ions to occupy the same sublattice. At high temperatures the excess function is short ranged, saturating within two unit cells. At 500 K the excess is still growing at the edges of the simulation cell.

To complete this picture, we show in Fig. 6 the radial

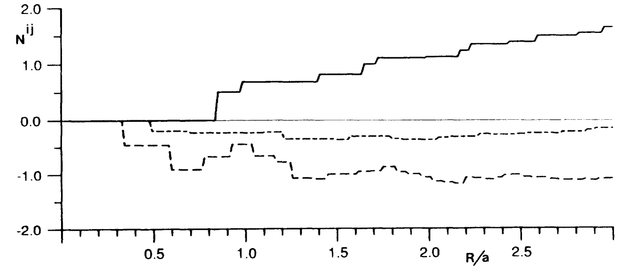

FIG. 5. The excess occupation of sublattice i, given an ion on sublattice j at the origin [Eq. (3)], as a function of distance, for the simulation at 500 K. The dash-dotted line is for i and j on the same sublattice, the dashed line when they refer to different sublattices with a nearest-neighbor relationship, and the solid line when they share a next-nearest-neighbor relationship.

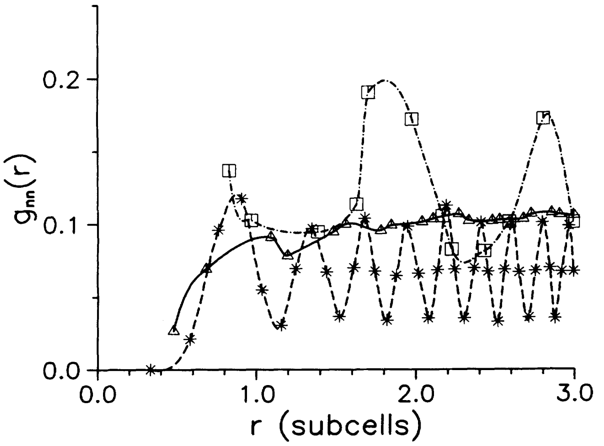

FIG. 6. The radial distribution function for the run at 400 K. The line types refer to different combinations of sublattices, as explained in the caption to Fig. 5. The symbols mark the points at which the actual lattice points occur.

distribution functions within the low-temperature phase. It is clear that there is now crystalline order in the silver-ion positions. We will attempt to interpret this pattern in the next section.

III. INTERPRETATION OF THE ORDERING

In order to characterize the positions of the silver ions in the low-temperature phase, we examined a typical ion configuration from the molecular-dynamics (MD) run at 400 K with a molecular-graphics computer. The Ag^+ ions were color-coded according to the particular T_d sublattice with which they were associated and their positions plotted according to their actual simulation coordinates (i.e., they were not forced onto the nearest T_d sites). A typical result is shown in Fig. 7; ions on sublattice 1 are colored green, those on sublattice 3 are blue, those on sublattice 4 are red, and those on sublattice 6 are yellow. No ions associated with sublattices 2 and 5 were found. In the figure, the simulation cell is viewed from the side, so that the atoms in a particular (110) plane are seen end on. The angle of view is close to that used in plotting the idealized cell in Fig. 1, which will be used to interpret the display.

First, we note that the simulation cell contains $6\times6\times6$ AgI unit cells, and since there are six planes of T_d sites in a single cell (Fig. 1: K, L, M, P, Q, and R), if all T_d sublattices were occupied there would be 36 planes of atoms visible across the cell. However, only 24 planes are to be seen, consistent with the finding that the 2 and 5 sublattices are unoccupied. Referring to Fig. 1, we see that if this is the case then planes L and Q are unoccupied.

The observation that only a single color shows in each plane (to a good approximation) means that (for the ions visible on the graphics display) only one of the two T_d sublattice sites in each of the K, M, P, and R planes is locally occupied. That is, within each plane, there are large patches in which all the silver ions are sitting on sites of the same T_d sublattice. This ordering is consistent with the observed tendency of the silver ions to occupy the same sublattice noted in the $N^{ij}(r)$ plot (Fig. 5) for the high-temperature runs; we now see that this preference is a local, in-plane effect.

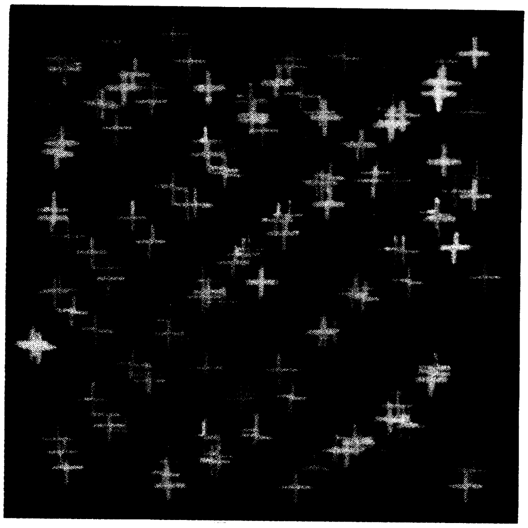

FIG. 7. A photograph showing a snapshot of the Ag^+ ion positions in the 400 K simulation. The ions have been color coded to specify which sublattice they occupy. Sublattice 1, green; 3, blue; 4, red; and 6, yellow. Sublattices 2 and 5 were not occupied.

We note that the pattern of colors repeats across the cell diagonal in the sequence yellow (sublattice 6)-green

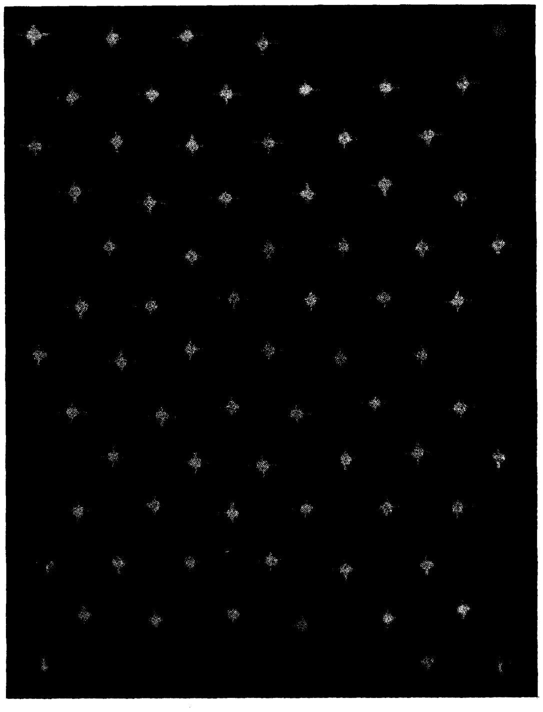

FIG. 8. A photograph of (part of) the same configuration as illustrated in Fig. 7. Included is a projection of the central (110) plane of I^- ions (light green) and those Ag^+ ions which are found within a rectangular slab which contains this central plane. The only Ag^+ ions found are of type 4 (red) and type 3 (blue)—which occur in nonoverlapping regions.

(sublattice 1)-red (sublattice 4)-blue (sublattice 3). At first sight this seems to imply that if sublattice 4, say, is occupied in plane P (which therefore appears red), then *nearby* occupied sites in plane M are of type 3 (and appear blue) and so on. However, this is not correct. In Fig. 8 we show in plan view the contents of a diagonally cut slab of the simulation cell. The iodine ions which make up a (110) plane (shown in green) and all the silver ions within the slab of thickness $a/\sqrt{2}$ containing this plane are displayed. Note that the silver ions in planes P and M should appear within this slab. The silver ions which appear belong to type 4 (red) in plane P and type 3 (blue) from plane M and we see that, in fact, these appear in nonoverlapping puddles. If sites 4 are occupied then *nearby* sites in plane P are *un*occupied. The red-blue alternation seen in Fig. 7 arises because the planes are viewed end on. The red plane is due to the puddle of occupied sites in plane P at the front of the cell, plane M at the front of the cell is unoccupied and we are therefore able to see the puddle of occupied type-3 sites on plane M from the rear of the cell.

There is one other aspect of the ordering phenomenon which can be learned from Fig. 8. This is that, within a given "puddle," *all* the T_d sites of a given type are occupied, i.e., within the red region of Fig. 8 there are as many red points as green (iodines) and these are disposed as on the (110) plane of a bcc lattice.

To reconcile these observations with the full yellow-green-red-blue color repetition across the cell diagonal (Fig. 7), we must postulate that, if a puddle of type-4 (red) sites is occupied on plane P, then plane K in the same region of space has to have type 6 (yellow) occupied. We therefore move to a complete picture of what is occurring. If there is a puddle of type-4 sites occupied in plane P then, locally, the two nearest planes in either direction are unoccupied (i.e., M and L above and Q and R below) and the type-6 sites are occupied in plane K. That type-6 sites are occupied in plane K means that type 4-sites are occupied in plane P in the next cell above, and so on—there is a tendency to long-range order on alternating sublattices perpendicular to the (110) plane as well as in-plane ordering on the same sublattice. The simulated system contains two such crystallites: the red-yellow crystallite, in which sublattices 4 and 6 are occupied as described above, and a blue-green (1-3) crystallite which occupies the remaining volume of the cell.

The crystal structure, identified in this way, does not belong to one of the phases identified as stable by Szabó.[8(a)] Our findings suggest that the cubic symmetry is broken and the silver ions condense to form a structure which is monoclinic. In Szabó's terms, this phase is characterized by equal average occupation numbers for two sublattices which have a nearest-neighbor relationship and zero occupancy for the others. Szabó's stable "intermediate" phase[8(b)] had equal occupancies for two sublattices with *next*-nearest-neighbor relationships. Note, however, that he did indicate that this phase had a lower symmetry than cubic as he found that "diffusion" (in the Monte Carlo sense) was anisotropic. Although we have described the results from a single simulation run, very similar observations were made in other runs. The lower-temperature simulations always quenched into *two* crystallites of this phase. The fact that two crystals are always found may be a consequence of the boundary conditions and the quench from the cubic phase.

With these observations we are able to rationalize some of the incidental features of the figures we have shown earlier. In Fig. 2, which shows the instantaneous occupation numbers of different T_d sublattices, the fluctuations in the sublattice occupancies are highly correlated. On the basis of our argument, a puddle of occupied type-4 sites on plane P should lead to a puddle of similar size of occupied type-6 sites in the nearest K plane, i.e., the fluctuations in the total number of type-6 ions should track the fluctuations in the number of type 4. Furthermore, this same puddle of occupied type-4 sites leads to a puddle of unoccupied type-1 and -3 sites on the adjacent plane M, therefore, the number of type-6 and -4 ions should be anticorrelated with the number of type 1 and 3. This is the behavior seen in Fig. 2. The fluctuations reflect the growth of one crystallite at the expense of the other.

It is also possible to rationalize the shape of the radial distribution functions $G^{ij}(r)$ for the low-temperature phase (Fig. 5) in terms of this same model of in-plane ordering on one sublattice and interplane ordering on a different (nearest-neighbor) sublattice.

IV. A MECHANISM FOR THE α-TO-β PHASE TRANSITION

We believe that the cation ordering phenomenon which we have identified in the simulations of the α phase is a driving force for the α (bcc) to β (hexagonal) reorganization of the iodine ions. We recall that the direct bcc to hexagonal transition is prevented in our calculations by the cubic periodic boundary conditions, we observe the cation ordering in a supercooled α crystal. However, as we noted above, the local ordering effects, which ultimately drive the Ag^+ to crystallize, are observable at higher temperatures well within the range of thermodynamic stability of the RVP α phase (which is known from Tallon's simulation[10]). In view of the tremendous success of the RVP potential in reproducing the properties of AgI, it seems not unreasonable to suggest that in the real material the silver ions becomes progressively more ordered, in the way that we have identified, as the temperature is lowered through the α phase. This tendency to increasing order could lead to the instability of the bcc I^- lattice with respect to the hexagonal form, as we will now attempt to explain.

In the Burgers mechanism[15] for a transition between a bcc and hexagonal crystal, a stack of parallel (110) planes of the original bcc crystal undergo a lateral compression so that they become close packed, adjacent (110) planes then glide across each other so as to place each atom in one plane above the center of a triangle of atoms in the adjacent planes. The latter motion carries the implication that a transverse, zone-boundary [110] phonon of the original bcc structure becomes soft.[16] We have not been able to confirm that the low-temperature simulated structure is indeed unstable with respect to the glide by calculating the phonon dispersion relationships in the simulation. Because of the large masses of the ions involved, the relatively high temperature, and the highly anharmonic nature of the crystal, the phonons appear overdamped at many points in the Brillouin zone (including the transverse [110] at the zone boundary)—so that our findings are compatible with the suggested mechanism but by no means compeling evidence for it. In the absence of such a demonstration, we resort to arguing for the plausibility of our suggestion on geometric grounds.

We begin by drawing attention to the close similarity of the positions of the ions in the wurtzite structure with the ion positions we have identified in (a single crystallite) of our low-temperature structure. Several cells of the wurtzite structure are shown in Fig. 9. The large particles represent the I^- ions which lie in hexagonal planes. (For clarity, we have exaggerated the interplane separation in the figure.) According to the Burgers mechanism we associate these planes with adjacent (110) planes in the bcc crystal. The smaller ions are the Ag^+ ions, which occupy tetrahedral interstitial sites. Note that the occupied interstitial sites also form a hexagonal lattice, i.e., only one set of interstitial sites is occupied.

In the original bcc structure (Fig. 1) there are three planes of tetrahedral sites between each of the (110) planes; in the low-temperature ordered phase only one of these planes is occupied—i.e., in common with the wurtzite-structure crystal, there is only a single plane of Ag^+ ions between an adjacent pair of I^- planes. Furthermore, since, in this plane, one sublattice is fully occupied and the other unoccupied (Fig. 8), the Ag^+ ions are arranged as in the (110) plane of a bcc structure, shifted with respect to the adjacent I^- plane—this relationship is very similar to that between adjacent Ag^+ and I^- planes in the wurtzite structure. To emphasize this connection, we have labeled the Ag^+ planes as R and M in Fig. 9 to make clear the suggested relationship with the occupied sites in the bcc structure (Fig. 1). Since, if type-1 sites are occupied in plane R, type-3 sites are occupied in M, the Ag^+ ions in *alternate* layers lie vertically above each other—as in the wurtzite structure.

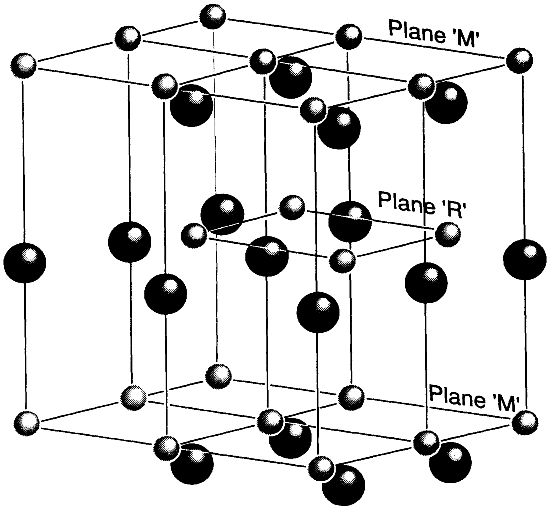

FIG. 9. A view of several cells of the wurtzite crystal. The relationship of the planes containing the Ag^+ ions to the T_d site planes of Fig. 1 is illustrated.

Alternatively, we can examine the relationship of ion positions in the two phases from a schematic diagram of the low-temperature bcc structure; this is illustrated in Fig. 10. The large solid circles represent the I^- ions in one of the (110) planes and the hatched circles the I^- plane immediately above the first. The small solid circles are the Ag^+ ions on the plane of tetrahedral sites above the first plane; i.e., in this plane, only one of the two sublattices is occupied and the Ag^+ ions also form a bcc (110) plane. In Fig. 10(a), the large solid circles and the small hatched circles are in idealized positions corresponding to those found in the red puddle of Fig. 8, and the open circles are the next plane of I^- ions in the bcc structure. In the Burgers transformation from this bcc structure to the hexagonal, the planes illustrated correspond to the central I^- plane (solid circles), the Ag^+

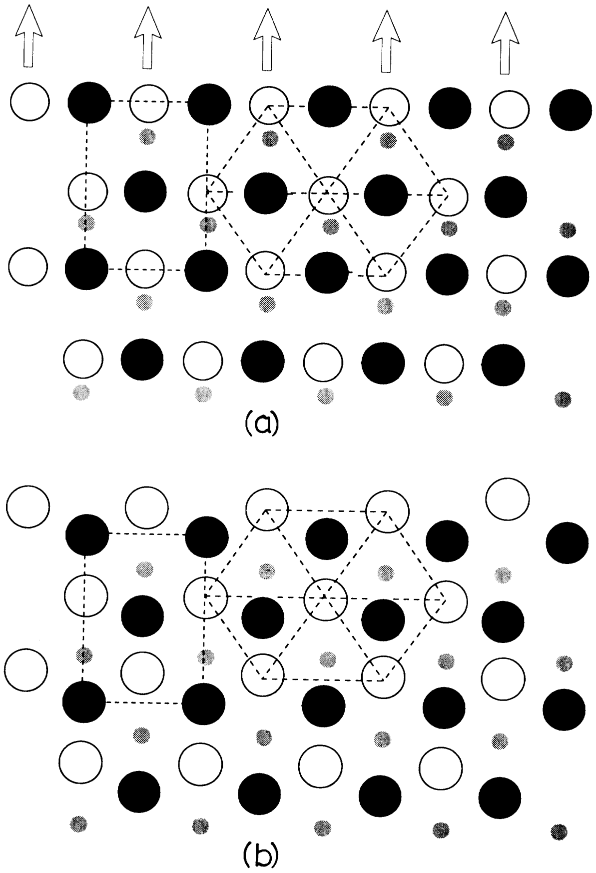

FIG. 10. (a) Idealized view of the ion positions in the low-temperature phase identified above. The larger circles show the I^- ions in two (110) planes of the bcc structure and the shaded circles show the positions of the occupied T_d sites between them. Note that the local coordination is unsymmetrical. The outlines of the rectangular 110 projection of the bcc cell and of the hexagon which will become regular in the transformed structure are shown by dashed lines. (b) The positions of the ions after a glide of adjacent I^- planes in order to relieve the strain gennerated by the asymmetric coordination.

plane above ("plane R"), and the upper I^- plane of the wurtzite structure in Fig. 9. Also indicated, by the dashed lines, are the outlines of the 110 projection of the bcc unit cell and the hexagon which must become a regular hexagon in the transformed structure. The necessary change in shape of the hexagon can be accomplished by a lateral contraction of the crystal.

What Fig. 10(a) shows is that the disposition of the Ag^+ ions about the I^- ions in the upper plane (open circles) is not symmetrical. The arrangement suggests that there should be a force on this upper plane [indicated by the arrows in Fig. 10(a)], which will tend to glide this upper plane until a symmetric site is found. The final state after this glide is indicated in Fig. 10(b). Now all the I^- ions sit in a triangle of Ag^+ ions and at the center of a triangle of I^- ions from the adjacent plane. That is, the final structure suggested by the consideration of the forces in the low-temperature bcc structure which spontaneously formed in the molecular-dynamics simulations is a hexagonal one.

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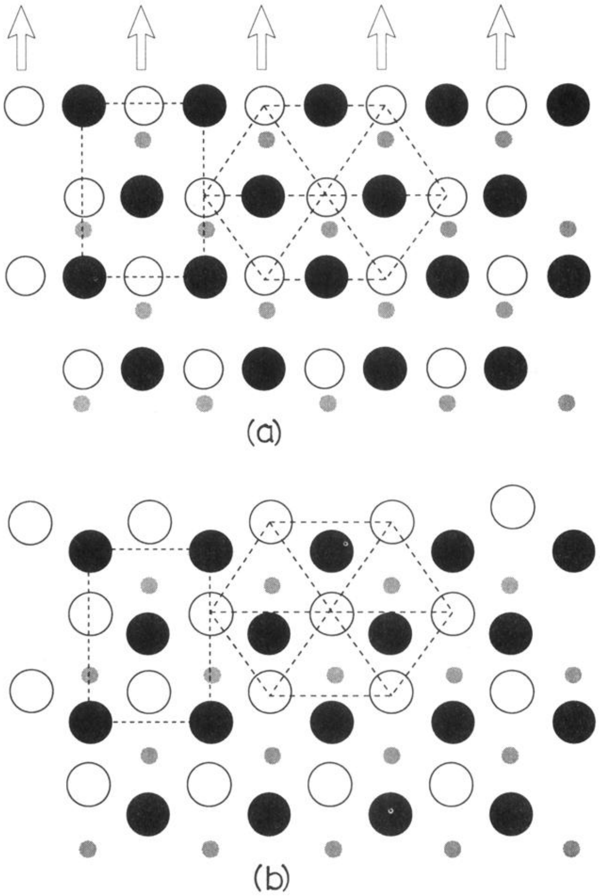

FIG. 10. (a) Idealized view of the ion positions in the low-temperature phase identified above. The larger circles show the I^- ions in two (110) planes of the bcc structure and the shaded circles show the positions of the occupied T_d sites between them. Note that the local coordination is unsymmetrical. The outlines of the rectangular 110 projection of the bcc cell and of the hexagon which will become regular in the transformed structure are shown by dashed lines. (b) The positions of the ions after a glide of adjacent I^- planes in order to relieve the strain gennerated by the asymmetric coordination.

FIG. 7. A photograph showing a snapshot of the Ag^+ ion positions in the 400 K simulation. The ions have been color coded to specify which sublattice they occupy. Sublattice 1, green; 3, blue; 4, red; and 6, yellow. Sublattices 2 and 5 were not occupied.

FIG. 8. A photograph of (part of) the same configuration as illustrated in Fig. 7. Included is a projection of the central (110) plane of I^- ions (light green) and those Ag^+ ions which are found within a rectangular slab which contains this central plane. The only Ag^+ ions found are of type 4 (red) and type 3 (blue)—which occur in nonoverlapping regions.

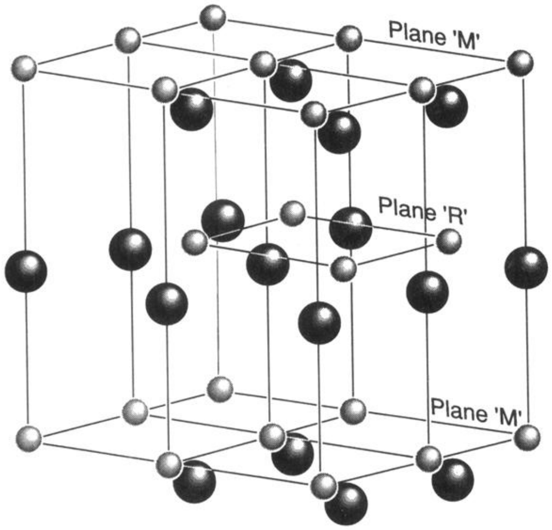

FIG. 9. A view of several cells of the wurtzite crystal. The relationship of the planes containing the Ag^+ ions to the T_d site planes of Fig. 1 is illustrated.