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Phase transformations and polytypism in silver iodide: A molecular-dynamics study

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Molecular-dynamics studies have been carried out to investigate structural phase transformations in AgI as the temperature is lowered below the superionic transition temperature of ≈420 K, while holding the pressure constant at selected values. Upon lowering the temperature for pressures below 0.27 GPa the system always transformed from the superionic phase α-AgI into the wurtzite phase β-AgI. Starting from the superionic phase and lowering the temperature at the pressures of 0.28, 0.29, 0.30, and 0.31 GPa we obtained various polytypes of the same hexagonality as has been reported experimentally. At pressures above 0.32 GPa the structure obtained upon temperature lowering was always the rocksalt form of AgI in agreement with previous simulations and experiments. At pressures between 0.31 and 0.32 GPa the system did not transform but underwent sluggish distortions among unrecognizable structures over the entire time of the simulation. This "frustration" of the system near the polytype-rocksalt phase boundary may be associated with the, so-called, intermediate phase mentioned in the literature. We also present results for nucleation from the liquid phase to the solid phase as a function of pressure in rapid-quench simulations.

I. INTRODUCTION

Superionic conductors such as AgI, Ag_2S, Ag_2Se, etc., are fascinating condensed matter systems in which solidlike and liquidlike properties are combined in an interesting manner.[1–7] In the superionic form of silver iodide, α-AgI, the iodine ions form a thermally agitated but stable bcc lattice through which the silver ions move with a diffusion constant of the same order of magnitude as liquid silver. The silver ions show fourfold coordination with the iodine ions.

Silver iodide has a rich phase diagram with several different solid phases existing. For example, at low pressure and below a temperature of ≈420 K, α-AgI undergoes a phase transformation to the nonsuperionic phase, β-AgI, where the iodine sublattice transforms from bcc to a close-packed lattice, hcp, with the silver ions retaining their fourfold coordination with the iodine ions. The different phases of AgI have been studied experimentally and the experimental phase diagram as given by Mellander, Bowling, and Baranowski[8] is shown in Fig. 1.

It is often stated[9] that, at low temperatures and pressures, AgI may exist in either of two phases, β-AgI or γ-AgI; this is indicated in Fig. 1 by the β/γ region. In β-AgI the iodine ions are arranged in a hcp lattice with the silver ions being tetrahedrally coordinated to each of the iodines. Thus, in β-AgI, the system is in a wurtzite structure. In γ-AgI, the iodine ions are arranged in a fcc lattice with the silver ions also tetrahedrally coordinated to the iodine ions. Silver positions may be obtained by translating the I^- lattice positions by $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ along the body diagonal of the fcc conventional unit cell of the iodine ions. Thus, in γ-AgI the system is in a sphalerite or zinc-blende structure. No diffusion is shown by either species of ions in these low-temperature phases. In the rocksalt structure the I^- ions are arranged in a fcc lattice with the silver ions sixfold coordinated with the iodines, e.g., this is the sodium chloride or rocksalt structure.

Majumdar and Roy,[10] in their x-ray powder studies, could not find evidence for the existence of the "pure" sphalerite (γ) form of AgI but did find evidence that the "pure" wurtzite (β) form of AgI exists. They also found evidence for several polytypes but did not give detailed identification of them. Davis and Peterson[11] discovered an AgI polytype and Davis and Johnson[12] carried out a careful study of the structure of the sample which they reported to be a seven-layer polytype of the hexagonal type, denoted *7H*. The notation *7H* indicates that this polytype has seven layers of close-packed planes before it repeats and has a primitive unit cell that is hexagonal. Other polytypes have rhombohedral unit cells and are denoted by *nR*, where *n* is the number of layers before repeating. Prager[13] identified four new polytypes, *4H*, *8H*, *12H*, and *16H*. Johnson and Schock[14] carried out a detailed study of the *4H* polytype found by Prager.[13] Later Prager[15] identified another distinct twelve-layer polytype.

The first detailed theoretical treatment of silver iodide was the molecular-dynamics calculations by Vashishta and Rahman[16] where they constructed model ionic potentials and used these potentials in molecular-dynamics calculations to determine the diffusion constant of the silver ions in α-AgI. They also studied the detailed microscopic motion of the silver ions during diffusion, determining the statistics for jumps between different

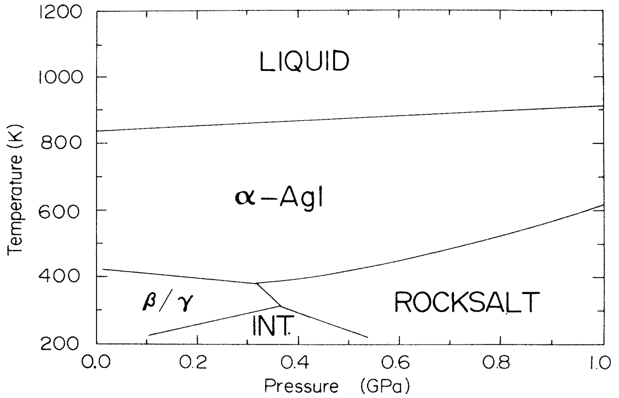

FIG. 1. Phase diagram of silver iodide from Ref. 8. In our simulations the β/γ region is made up of only the β phase below 0.27 GPa and various polytypes between 0.27 and 0.31 GPa and the rocksalt structure above 0.32 GPa. Between 0.31 and 0.32 GPa the system underwent long periods of distortion without transforming. We interpret this as the appearance of the intermediate phase.

tetrahedral sites of the bcc I^- lattice and the residence time at these sites. In a later paper Vashishta and Rahman[17] presented more details of their study of the diffusion of Ag^+ in α-AgI and extended this method of study to α-CuI. In the case of CuI they were able to study the superionic to nonsuperionic phase transition as a function of temperature since, in CuI, the iodine lattice retains the same structure for this transformation, fcc→fcc. Recall that, in AgI, the iodine sublattice is bcc in the superionic phase and hcp or fcc in the nonsuperionic phase. It was not possible to model the superionic to nonsuperionic phase transformations in AgI at the time of these studies since the only form of molecular dynamics known at that time was for fixed shape and size of the molecular-dynamics computational cell and it is not possible for the bcc→hcp phase transformation to take place in this version of molecular dynamics for the small systems employed in these studies.

Parrinello and Rahman[18] developed a method of carrying out molecular dynamics which allows the molecular-dynamics cell to vary in size and shape in response to the difference between the internal microscopic stress tensor and the applied external stress. Parrinello, Rahman, and Vashishta[19] showed that this form of molecular dynamics could be used to study the superionic to nonsuperionic phase transformations in AgI; that is, they were able to model the α-AgI to β-AgI phase transformations using the Parrinello-Rahman form of molecular dynamics and, in fact, used these phase transformations to refine the interionic potentials employed to model AgI. This method of studying solid→solid phase transformations is now standard and has been employed in several studies including further studies of AgI by Tallon.[20,21] For more examples of using the Parrinello-Rahman theory to study phase transformations, along with many references, we refer the reader to the study of the superionic to nonsuperionic phase transformations in Ag_2S by Ray and Vashishta,[22] and a study of pressure-induced bcc→hcp martensitic transformations by Lee and Ray.[23]

In this paper we report on further detailed studies of the phase transformations in AgI using the Parrinello-Rahman form of molecular dynamics. As we shall show, the polytypism that is observed experimentally emerges directly from these studies. We also report on studies of homogeneous nucleation which involve the rapid cooling of liquid AgI at constant pressure. In these studies one nucleates different phases depending on the final system temperature and the value of the constant pressure applied to the system during the simulation.

II. INTERACTION POTENTIALS AND VARIABLE SHAPE MOLECULAR DYNAMICS

The interaction potentials that we use in this paper have the form[19]

$$U_{\text{Ag-Ag}} = H_{\text{Ag-Ag}}/r^{11} + 0.36/r \ , \tag{2.1}$$

$$U_{\text{Ag-I}} = H_{\text{Ag-I}}/r^{9} - 0.36/r - 1.1736/r^{4} \ , \tag{2.2}$$

$$U_{\text{I-I}} = H_{\text{I-I}}/r^{7} + 0.36/r - 2.472/r^{4} - 6.933/r^{6} \ , \tag{2.3}$$

where $H_{\text{Ag-Ag}} = 0.014\,804$, $H_{\text{Ag-I}} = 114.48$, and $H_{\text{I-I}} = 446.64$. The unit of length is the angstrom and the unit of energy is $1e^2/1\ \text{Å} = 14.40$ eV. The Coulomb interactions are calculated by using the Ewald summation method, while the other terms are evaluated directly.

For details of the Parrinello-Rahman form of molecular dynamics, see Parrinello and Rahman[18] and Ray and Rahman.[24] This latter paper shows how the Parrinello-Rahman theory can be made consistent with the finite theory of elasticity. The Parrinello-Rahman molecular-dynamics equations of motion have the form[18,24]

$$m_a \ddot{s}_{ai} = -\sum_b \chi_{ab} s_{abi} - m_a G^{-1} \dot{G} \dot{s}_{ai} \ , \tag{2.4}$$

$$W\ddot{h} = (\mathcal{P} - P)A - h\Gamma \ , \tag{2.5}$$

where the overdot represents time differentiation.

III. POLYTYPISM

Polymorphism refers to different crystal structures that a substance may exist in at different thermodynamic conditions. Polytypism is a special kind of one-dimensional polymorphism which is physically quite different than ordinary polymorphism; one difference being that the energy differences between polytypic structures are quite small, while another is that polytypism is associated with the stacking of close-packed planes of particles in sequences different than in fcc and hcp. The fcc and hcp structures are made up of close-packed planes of particles that differ only in the stacking sequence of the planes. In fcc this stacking is along the [111] direction of the conventional unit cell while in hcp it is along the [0001] direction of the hexagonal unit cell. In fcc the planes are stacked in the sequence $ABCABCABC \cdots$, while in hcp the planes are stacked in the sequence $ABABAB \cdots$. Polytypes are characterized by stacking sequences of close-packed planes different from fcc or hcp. For example, the four-layer polytype denoted 4*H* has the stacking sequence *ABCBABCB* $\cdots$. In the 4*H* structure there are four independent close-packed planes and the primitive unit cell is hexagonal and contains four lattice sites, one in each of the layers.

Polytypes were first reported in molecular dynamics by Moody, Ray, and Rahman[25] and Moody[26] and we refer to these two papers for many of the details of polytypes in molecular dynamics. It should be pointed out that polytypes are not associated with stacking fault defects but are distinct crystal structures. A comprehensive and readable discussion of polytypism is contained in the book by Verma and Krishna.[27] In molecular-dynamics studies of structural properties of systems one often uses the pair-distribution functions and the corresponding particle coordination numbers to obtain a classification of structures. For simple structures, such as fcc, hcp, bcc, etc., the particle coordination numbers have well-known integer values and the pair-distribution functions exhibits a specific shape for these structures. Polytypes exhibit noninteger particle coordination numbers and a complete classification of the polytypes by coordination numbers alone is not so easy or useful.[25,26] Two polytypes with large numbers of layers can have structures in which most of the atoms have identical environments up to very distant coordinations. The differences in energies are therefore very small compared to the energy barriers separating the two structures.

In order to facilitate the study of polytypism in molecular dynamics, Moody, Ray, and Rahman[25] developed a method of graphically displaying particle positions within the molecular-dynamics cell. The method consists of projecting the positions of all the atoms in the molecular-dynamics cell onto a $(11\bar{2}0)$ plane and drawing lines connecting all nearest neighbors. The Zhdanov sequence and *ABC* stacking sequence for the given polytype can then be found from this projection by inspection.[25] The Zhdanov sequence of numbers represent the zigzag sequence of I^- ions in the $(11\bar{2}0)$ planes. If a particular ion is in close-packed plane *A*, then the nearest ion in the next close-packed plane and in the same $(11\bar{2}0)$ plane must either be to the right on, say, a *B*-type plane or to the left on a *C*-type plane. If to the left, then the third next layer can again either go to the right or to the left. Because of the repeated possibility of changes in direction, in general, a zigzag pattern results. Such a pattern can be represented by a sequence of numbers describing how many layers are traversed with a given shift before the shift changes to the other direction. The direction changes are denoted by dashed lines between the numbers. For the 4*H* structure, the Zhdanov symbol is [2—2—]. The Zhdanov sequence uniquely characterizes the crystal structure of the polytype. The structure of closed-packed polytypes can also be completely described by specifying the *ABC* stacking sequence of the successive close-packed planes in the hexagonal unit cell. For other notations used to describe polytypes, see the comprehensive treatment by Verma and Krishna.[27] Note that when using the *ABC* notation, *A*, *B*, and *C* do not necessarily represent single-plane layers of atoms. The unit of structure may be polyatomic, and in such cases *A*, *B*, and *C* define the positions of one kind of ion in the layer, the positions of the other ions being fixed relative to these positions. For convenience in the following *A*, *B*, and *C* will denote the planes formed by the I^- ions in the given polytypes. Each Ag^+ ion is tetrahedrally coordinated to I^- and giving the I^- planes completely defines the structure.

IV. AgI PHASE TRANSFORMATIONS

A. Preparation of the initial sample

In most of our simulations of the AgI phase diagram, a system of 512 particles (256 Ag^+, and 256 I^-) was employed. These particles were programmed to interact with the interionic potential, Eqs. (2.1)–(2.3) and we imposed periodic boundary conditions as is usual in studies of such small-particle number. The calculations were, for the most part, carried out in the HtN form of molecular dynamics using Eq. (2.4) for the particles and Eq. (2.5) for the *h* matrix defining the molecular-dynamics cell. The Coulomb potential was evaluated using the Ewald procedure and the other potentials were truncated at 10 Å. A time step of 2.458×10^{-14} s was employed in all the simulations. To begin we arranged the 512 particles in a cubic cell to form γ-AgI at a temperature of 350 K and a pressure of 0.2 GPa. In Fig. 2 we show the I-I partial pair-distribution function and coordination number divided by five for the γ-AgI system cooled to a low temperature. A study of this figure shows that the iodine sublattice is in the fcc structure.

In a calculation extending over 6000 time steps, or 147 ps, the temperature and pressure of the equilibrated γ phase were raised in a controlled manner to 700 K and 0.8 GPa, respectively. This calculation was carried out in the HtN form of molecular dynamics in which the size and shape of the molecular-dynamics cell were allowed to

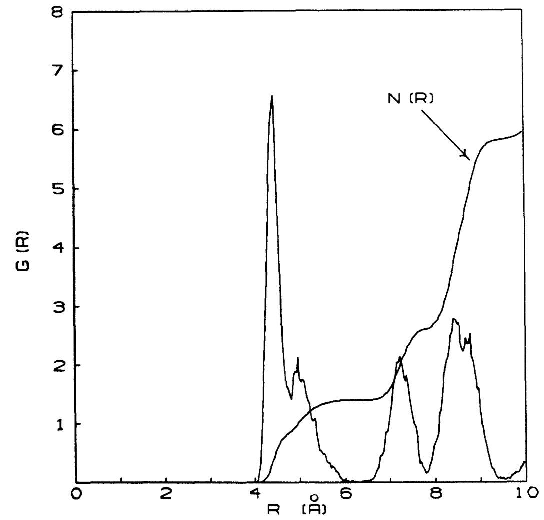

FIG. 2. Partial pair-distribution function and coordination number divided by five for I-I in the quenched sample of γ-AgI constructed to begin the study.

change in time according to Eq. (2.5). At the end of this calculation it was found that the molecular-dynamics cell had changed to a noncubic shape and the γ-AgI$\rightarrow\alpha$-AgI transition had occurred. This newly formed α-AgI was equilibrated and used as the starting point for further studies of structural phase transformations. A detailed study of the I-I partial pair-distribution function for the system quenched to a low temperature is shown in Fig. 3 and confirms the I^- sublattice has transformed to the bcc structure. The silver ions had the correct diffusion constant $D \approx 10^{-5}$ cm^2/s for the superionic phase.

B. Phase transformations

From the prepared α-AgI, a sequence of experiments were performed in which the pressure was reduced to a definite value and then the temperature was lowered back to 350 K while holding the pressure at this value. It was found that, as a function of pressure, the α phase underwent structural phase transformations into the β and rocksalt phases at the extreme ends of the range of pressures investigated. At pressures intermediate between these extremes, α-AgI transformed from the α phase into a number of distinct polytypes which were analyzed by the graphical methods mentioned above. In each experiment the final temperature was near 350 K while the densities and pressures of the final structures are given in Table I along with the Zhdanov sequence and the percent hexagonality of the polytypes. The percent hexagonality is the fraction of the independent close-packed planes that have locally a hcp-type stacking; plane B has locally hcp-type stacking if it appears as $\cdots ABA \cdots$ or $\cdots CBC \cdots$ in the ABC stacking sequence. In Figs. 4 and 5 we show the $(11\bar{2}0)$ projections of the polytypes formed at pressures of 0.28 and 0.3 GPa, respectively. The polytype form at 0.28 GPa has eight independent close-packed planes, the Zhdanov sequence $[3-1-1-1-1-1-]_3$, an ABC stacking sequence of 24 planes, and 50% hexagonality. The 0.30-GPa polytype has four independent close-packed planes, the Zhdanov sequence $[3-1-]_3$, an ABC stacking sequence of 12 planes, and 50% hexagonality. The subscript 3 on the Zhdanov sequence symbol $[\cdots]_3$ indicates that one must go through the independent planes three times to complete the ABC stacking sequence. Figures such as this were made for all the low-temperature structures in order to obtain the Zhdanov sequence and ABC stacking sequence. For a more detailed discussion of the $(11\bar{2}0)$ figures and their use in arriving at the Zhdanov sequence, we refer the reader to Refs. 25 and 26.

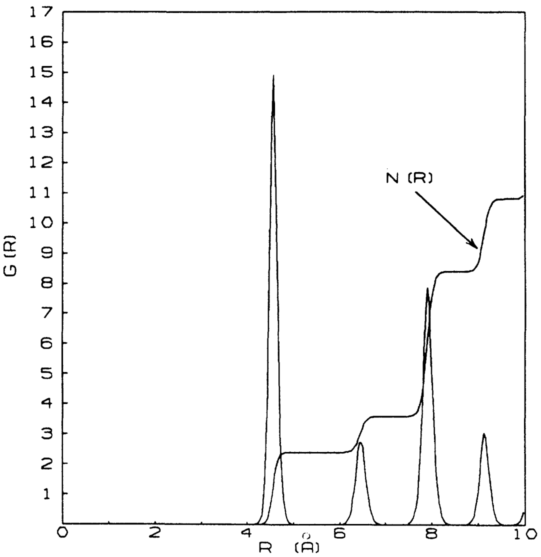

FIG. 3. Partial pair-distribution function and coordination number divided by ten for I-I in the quenched sample of α-AgI produced by heating the γ phase in Fig. 2.

All the transformations into definite structures took approximately the same length of time. Approximately 2000 time steps after lowering the temperature to 350 K, while holding the pressure at the desired value it was

TABLE I. Properties of the low-temperature structures obtained from α-AgI upon lowering the temperature and pressure. Below 0.27 GPa we always obtained the β phase while above 0.32 GPa we obtained the rocksalt phase. The rocksalt structure is not a close-packed polytype of the same type as the other members of the table since it does not have fourfold coordination. The ABC stacking orders are given below the Zhdanov sequences. The / separators are used to tell when one has gone through one set of independent planes in the molecular-dynamics systems; these are polytypes that have rhombohedral primitive cells.

Pressure GPa	Density g/cm^3	Zhdanov sequence	% hexagonal
≤ 0.27	≤ 5.828	β-AgI, $[1-1-]$	100
		AB	
0.28	5.836	$[3-1-1-1-1-1-]_3$	75
		ABCBCBCB/CABABABA/BCACACAC	
0.29	5.849	$[3-2-2-1-]_3$	50
		ABACACBA/BCBABACB/CACBCBAC	
0.30	5.846	$[3-1-]_3$	50
		ABCA/CABC/BCAB	
0.31	5.855	$[3-2-1-2-]$	50
		ABCBACAB	50
≥ 0.32	≥ 6.158	NA (rocksalt)	NA

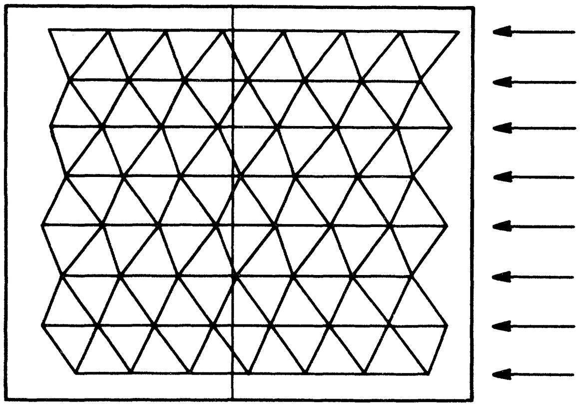

FIG. 4. The polytype formed at 0.28 GPa is shown in a $(11\bar{2}0)$ projection. Some of the close-packed planes are pointed to by the arrows. Properties of this polytype are shown in Table I. This polytype has eight independent close-packed planes.

found that the molecular-dynamics cell had altered its shape that it had in the α phase and that the I-I nearest-neighbor coordination number had changed from 14 back to 12. This indicates that a structural phase transformation had taken place changing the iodine bcc lattice characteristic of the α phase to a close-packed structure. By quenching these structures to low temperatures, one could see from the partial pair correlation functions that α-AgI had transformed into different structures at the pressures selected. From each of these quenched final structures, a $(11\bar{2}0)$ projection of the I^- sublattice was made from which the detailed structural information could be obtained by inspection.

At a pressure of 0.32 GPa, a check of the partial pair-distribution functions showed that the structure was rocksalt. In further studies where the pressure was greater than 0.32 GPa, the result of the structural phase transformation was always to give the rocksalt structure in agreement with the experimental phase diagram and other simulations using this potential by Tallon[20,21] and a report by Vashishta.[28] The fact that the rocksalt structure forms at elevated pressures is consistent with the cohesive energies of the different structures calculated with our model potential. In Fig. 6 we show the cohesive energy versus density for the rocksalt and close-packed structures. At low densities (pressures) the close-packed structures are more stable but at higher densities (pressures) the rocksalt structure becomes more stable.

With the external pressure now changed to 0.27 GPa, the temperature was now lowered carefully from 700 to 350 K. Again, the I-I coordination number dropped from 14 to 12 indicating that a structural transformation had occurred. This time the $(11\bar{2}0)$ projection showed that the system had transformed into β-AgI with the I sublattice being hcp and the Ag ions fourfold coordinated with the iodines. Interestingly, at all pressures lower than 0.27 GPa which were studied, the final structure was always β-AgI. Even returning to 0.2 GPa where the γ-AgI used to start the study had been prepared, the final structure was β-AgI via the transformation from α-AgI. In none of our simulations was the transformation $\alpha \rightarrow \gamma$ obtained; that is, we never saw the reappearance of the γ phase during any of our experiments. This is consistent with the experimental results of Majumdar and Roy,[10] and the studies of Davis and Johnson[12] and Prager[13,15] where no reports of the γ structure appear. The fact that only the β phase appears is consistent with the cohesive energies of the two structures as calculated using our model potential.

C. Comparison to known polytypes of AgI

As mentioned previously, various polytypes of AgI have been reported in the literature. In Table II we list polytypes reported by Prager[13,15] and Davis and Johnson.[12] Note that the densities of the systems found

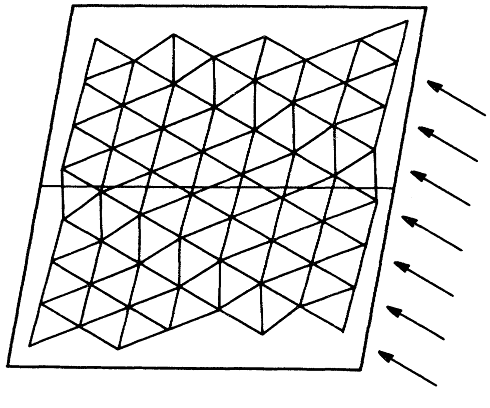

FIG. 5. The polytype formed at 0.3 GPa is shown in a $(11\bar{2}0)$ projection. Some of the close-packed planes are pointed to by the arrows. Properties of this polytype are shown in Table I. This polytype has four independent close-packed planes.

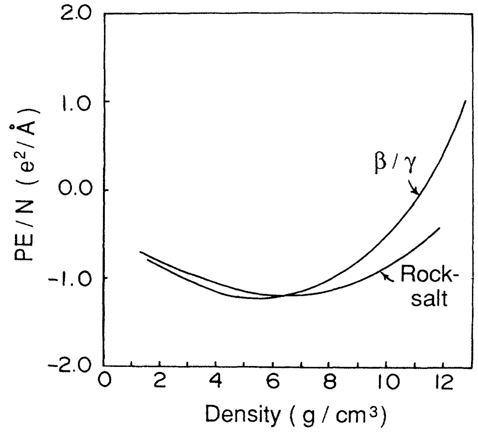

FIG. 6. Cohesive energies per particle in e^2/Å for the close-packed structures and the rocksalt structure using the model potential. The energy difference between the β and γ structures is not resolved in the figure so this represents the cohesive energy of all polytypes since they have intermediate energies.

TABLE II. Polytypes of AgI and their properties reported by Prager in Refs. 13 and 15 and Davis and Johnson in Ref. 12. The last entry is the seven-layer polytype reported by Davis and Johnson.

Density g/cm^3	Zhdanov sequence	% hexagonal
5.69	β-AgI, [1−1−] *AB*	100
5.69	[2−2−] *ABCB*	50
5.69	[2−1−1−1−1−2−] *ABCBCBCB*	75
5.69	[2−1−1−1−1−2−1−1−1−1−1−] *ABCBCBCB AB AB*	$83\frac{1}{3}$
5.69	[1−2−1−1−1−1−1−1−2−1−] *AB AC AC AC AC AB*	$83\frac{1}{3}$
5.69	[1−1−2−1−1−1−1−1−1−1−1−2−1−1−] *AB ABCBCBCBCBCB AB*	87.5
5.69	[1−2−1−3−] *ABCBCAC*	$57\frac{1}{7}$

in the molecular-dynamics study are somewhat different than the experimental densities. This is a problem with the potential employed in this study, Eqs. (2.1)–(2.3). No attempt was made to modify the potential to correct this problem in this study. The fact that the model potential employed gives polytypic structures of the same general type as observed experimentally is surprising given the simplicity of the potential being employed. Also, our study gives support that the pure sphalerite form of AgI probably does not exist but that polytypes have been incorrectly interpreted as mixed β and γ phases. More careful experiment on single crystal could perhaps shed light on this interesting question.

D. Fractional coordination numbers

As previously mentioned, polytypes show fractional coordination numbers. Interestingly, in the original Parrinello *et al.* study of AgI (Ref. 19), they reported fractional coordination numbers but did not recognize them as polytypes. An explanation of fractional coordination numbers in polytypes in AgI was first mentioned by Ray, Rahman, and Vashishta.[29]

In using the graphical method to study the closed-packed structures, one must keep in mind that not all of the close-packed planes within the molecular-dynamics cell are necessarily independent. The number of close-packed planes which are independent for a given polytype may be determined by finding the greatest common divisor of the number of planes intersecting each projected side of the molecular-dynamics cell in the $(11\bar{2}0)$ projection as discussed by Moody *et al.*[25,26] If the close-packed planes in the $(11\bar{2}0)$ projection are oriented parallel to one side of the projected molecular-dynamics cell, then all of the planes within the cell are independent. Let the number of independent close-packed planes be n. For the polytype formed at 0.28 GPa and shown in Fig. 4, all eight close-packed planes are independent, $n=8$. In contrast, the polytype formed at 0.30 GPa shown in Fig. 5 has $n=4$. An investigation of the other polytypes formed at 0.29 and 0.31 GPa shows that they also had eight independent close-packed planes. Once the number of independent close-packed planes is determined, it is a simple manner to determine which of these planes have locally hcp-type stacking. For $n=8$, as in the polytypes formed at 0.28, 0.29, and 0.31 GPa, there can be 0, 2, 4, 6, or 8 of the planes locally hcp. Denote by c the number of planes that are locally hcp. The restriction of nonzero c to even integers is due to the periodic boundary conditions used in the simulations. With this notation, the ratio c/n is the fraction hexagonality and $1-c/n$ is the fraction of the independent planes that have locally fcc-type stacking. Moody *et al.*[25,26] explain in detail how to calculate the coordination number of polytypes by studying the $(11\bar{2}0)$ projection. The details of this along with the exact method of finding coordination numbers of the polytypes are given in Refs. 25 and 26 along with detailed examples. For the polytype formed at 0.28 GPa which has 75% hexagonality, the coordination numbers start as 12, 18, 19.5, 39, 48, 55.5, ... The polytypes formed at the other pressures have 50% hexagonality and their coordination numbers start as 12, 18, 19, 40, 46, and 55; the coordination numbers for these polytypes would all differ at large enough distances since they are distinct structures.

E. Analysis of close-packed planes in polytypes

As mentioned above, the polytypes formed at 0.28, 0.29, and 0.31 GPa all had eight independent close-packed planes of iodine ions which were oriented parallel to one side of the molecular-dynamics cell as in Fig. 5. By looking perpendicular to these planes and studying the iodine positions, we were able to find similarities among the structures. It was found that each of the eight independent planes within the three structures contained 32 ions within the molecular-dynamics cell and the same ions occupied corresponding close-packed planes in all three structures. Also, the planes were always stacked in the same order except for cyclic rearrangement due to the periodic boundary conditions. By relating these planes back to the α-AgI structure, it was found that these close-packed planes were parallel (110) planes in the bcc iodine lattice. Thus, these three polytypes formed when parallel bcc (110) planes converted into close-packed planes. The mechanism is the same martensitic mechanism discussed by Lee and Ray[23] in investigating bcc$\rightarrow$hcp transformations in simple metals under pressure loading and is associated with a contraction in the [001] direction accompanied by relative plane sliding of parallel (110) planes in the bcc structure. The fact that three of the polytypes formed have $n=8$ is because all three of them were formed from the same (110) planes of the iodine sublattice of the α-AgI from which they were formed. The different stacking sequence of the close-packed planes in these polytypes arises from the different relative sliding directions taken by the planes during the phase transformation.

As for the polytype at 0.30 GPa, it could not be compared with the other polytypes quite so easily since its close-packed planes formed such that the normal to these planes is close to a body diagonal of the molecular-dynamics cell, see Fig. 4. Also, these planes do not all contain the same number of ions, if only ions inside the molecular-dynamics cell are counted, and the ions in the planes are different ones than those in the planes in the other three polytypes. These facts lead to the conclusion that the polytype at 0.30 GPa was formed when a different set of (110) bcc planes in the α-AgI structure were selected as the close-packed planes in the phase transformation. A detailed study confirms this to be the case. The mechanism is again the martensitic mechanism discussed by Lee and Ray.[23] As a result of different (110) planes in the bcc structure becoming the close-packed planes, the orientation of the planes within the molecular-dynamics cell is different and the number of independent planes is four instead of eight. It must be remembered that each of the different polytypes formed are distinct crystal structures; however, three of them have some similarities since they formed from the same (110) planes in the parent structure.

F. Transformation among polytypes

Having seen the formation of polytypes through structural phase transformations from α-AgI, the next step was to study the direct structural phase transformations between different polytypes. In this investigation the pressure was changed from, say, 0.28 to 0.29 GPa while holding the temperature near 350 K. In HtN molecular-dynamics runs extending over 25 000 time steps, no transformations were observed between any of the polytypes. The failure to observe direct transitions between polytypes is probably due to the small energy differences along with the large energy barriers. Such transformations might be observed at higher temperatures but no systematic search was carried out. Upon increasing the pressure above 0.32 GPa, all the polytypes converted into the rocksalt structure; however, upon lowering the pressure below 0.32 GPa in the rocksalt structure, we never observed the transformation to a polytype.

G. Reproducibility

We desired to know whether the transformation from α-AgI into a particular polytype would always occur at a given pressure. To study this point we went back to the original γ-AgI and again formed α-AgI by the transformation $\gamma\rightarrow\alpha$; however, this time we formed the α phase at 600 K rather than 700 K. After equilibration of the new α, we proceeded in the experiment as before. It was found that at the extreme ends of the pressure studied, $P\leq 0.27$ GPa and $P\geq 0.32$ GPa, the transition was into the β and rocksalt phases, respectively, as before. However, a return to a pressure at which a polytype was originally formed, while still forming a polytype, might result in a different one being formed. For example, starting from the α phase at 600 K and lowering the temperature to 350 K and the pressure to 0.29 GPa yielded the polytype which was earlier found at 0.28 GPa. In another study of this problem we returned to the original 700-K α phase and merely equilibrated it for a longer period of time. Using this to start the experiment we found the same polytypes as the first time at the same pressures. In still another change of initial conditions the polytype found originally at 0.29 GPa was converted into the α phase at 700 K and 0.8 GPa. After equilibration of this α phase, the temperature and pressure were lowered back to 350 K and 0.29 GPa. This time the polytype which formed originally at 0.28 GPa was formed. We conclude from this portion of the study that a given polytype will not always form at a given pressure and due to the small energy difference between polytypes the final state depends in a sensitive way on the initial conditions. Thus, which polytype is formed is more a matter of chance than energy difference. Note, however, at low enough pressures we always obtained β-AgI. It is interesting that Lee and Ray[23] always obtained the hcp structure when they carried out the pressure loading of bcc at low enough temperatures.

H. Accuracy of the model potential along the phase boundaries

As we have seen, the model potential of Parrinello, Rahman, and Vashishta[19] accurately models various phase transformations in AgI. An attempt was made to determine how accurately this model potential would map the boundary on the experimental phase diagram. In mapping, say, the $\alpha\rightarrow\beta$ transformation the temperature was lowered to a value near the experimental phase boundary for the chosen pressure. The system was allowed to run without interruption in HtN molecular dynamics until the expected transformation occurred.

Transitions were achieved within 5 K of the given experimental phase boundaries in the transformation $\alpha\rightarrow\beta$, rocksalt transformations. The same degree of accuracy was achieved in going in the other direction, from the β and rocksalt phases to the α phase. Typically these transformations occurred in 9000–12 000 time steps which is at least twice the time required when we studied the transformations further away from the phase boundary. While carrying out this part of the study we explored the region of the phase diagram that had been associated with the superionic rocksalt phase by Tallon.[20,21] No evidence of a superionic rocksalt phase was seen.

I. Frustration near polytype rocksalt boundary

In carrying out the temperature lowering experiments for pressures between 0.31 and 0.32 GPa, we observed that the system did not transform to any recognizable structure but underwent sluggish distortions over the entire time of the simulation. We suggest this "frustration" of the system near the polytype-rocksalt phase boundary may be associated with the so-called, intermediate phase mentioned in the literature.

V. NUCLEATION STUDIES OF AgI

A. Preparation of initial state

In the previous sections the structural phase transformations from one solid phase into another were discussed. Now, we ask if the different solid phases of AgI, as well as the polytypic structures, could be obtained by cooling molten AgI into the region of the phase diagram where the respective solid phases appear. Vashishta[28] has presented a preliminary discussion of this topic.

Nucleation studies were carried out on a system of 512 particles. To start this portion of the study we began with the equilibrated sample of γ-AgI which had been the starting point of the previous studies. Thus, we started from γ-AgI at a pressure of 0.2 GPa and 350 K. The temperature of the system was raised in a controlled manner to 1100 K, well above the melting point of 812 K and the sample was allowed to equilibrate. This part of the calculation was carried out in the HPN form of molecular dynamics where the molecular-dynamics cell is allowed to change in volume while remaining cubic. If one allows the freedom of the cell to change its shape, then in the liquid state one finds that the shape of cell "wanders" due to the lack of shear constants for the liquid state. After equilibration, the silver ions showed a diffusion constant of 11×10^{-5} cm^2/s, while the iodine ions gave 5×10^{-5} cm^2/s. After equilibration this liquid sample of AgI was used for all further nucleation studies. Thus, our starting point is liquid AgI at a temperature of 1100 K and a pressure of 0.2 GPa.

B. Nucleation of α-AgI

Starting from the prepared liquid, the velocities of all the ions were set to zero. This calculation was done while still using the HPN form of molecular dynamics. The constraints of the molecular-dynamics cell being cubic was then released and the cell was henceforth allowed to vary in both shape and size; that is, we use the HtN form of molecular dynamics. The reason to change to the HtN form of molecular dynamics is to allow for the fullest possible relaxation of the system. The system was then allowed to evolve for 20 time steps and then the velocities were again set to zero. After this the system was allowed to run undisturbed.

After approximately 3000 time steps, the iodine subsystem began to show a shell structure in its partial pair-distribution function, and after 6000 time steps the nucleation to the α phase was complete. The temperature of the system at the completion of nucleation was 660 K and, of course, the pressure was 0.2 GPa. A quench of the system to low temperature gives the I-I partial pair-distribution function very similar to that shown in Fig. 3. A study of this pair-distribution function along with that for Ag-I and Ag-Ag confirms that the structure formed is α-AgI. Thus, we have homogeneously nucleated α-AgI from molten AgI.

C. Temperature and pressure during nucleation

During the nucleation calculations various properties of the system were monitored in order to further quantify the nucleation process. We observed a slow increase in the temperature and a slow decrease in the pressure up to a time around 3700 time steps after the temperature was lowered, at which time the changes in the temperature and pressure are more rapid. As we shall show later, the phase transformation takes place starting around 3700 time steps and is essentially finished by 4200 time steps.

D. Structure factors during the phase transformation

One of the most useful quantities to monitor during a phase transformation involving an ordered structure is the geometrical structure factor, $S(\mathbf{k})$.[30] For the iodine sublattice this quantity is defined by

$$S(\mathbf{k})=\left|\sum_a \exp(\mathbf{k}\cdot\mathbf{r}_a)\right|^2/N \; , \tag{5.1}$$

where $\mathbf{k}$ is a reciprocal-lattice vector associated with the vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$, spanning the molecular-dynamics cell. In Eq. (5.1) the sum over a is over the iodine ions. The reciprocal-lattice vectors have the components $k_j=2\pi\sum(h)^{T-1}_{jk}n_k$, where $n_k=0,\pm1,\pm2,\ldots$. Note that we calculate the geometrical structure factor at various times t during the simulation to monitor the structure. For a perfect bcc lattice at zero temperature, the iodine structure factor would have a value of $N=256$ for our system; however, because of Debye-Waller factor at finite temperature, this value would be reduced. In our analysis we checked all integer triplets, apart from an overall change of sign such that $(n_1^2+n_2^2+n_3^2)\leq100$. From all the $\mathbf{k}$ vectors thus generated, we picked the seven which gave the largest values for $S(\mathbf{k})$. For the nucleation event under discussion, the results are shown in Table III. From Table III it is clear that ordering occurs between 3750 and 6000 time steps. By the latter time, the structure in $\mathbf{k}$ space and hence in $\mathbf{r}$ space is already established and only becomes sharper as time proceeds. The first 6 vectors shown at 6000 time steps together with their negatives form a complete set of 12 basis vectors of a fcc lattice in reciprocal space. In Table III these six vectors, in the order in which they occur from left to right, can be identified with the directions [110], [011], [101], $[01\bar{1}]$, $[10\bar{1}]$, and $[1\bar{1}0]$ of the fcc reciprocal lattice. From this structure in reciprocal space it is inferred that the ordered structure of the iodine sublattice is bcc in real space.

E. Three-body bond angles

Another way to identify structures is by using the three-body bond-angle distributions. There are six such distribution functions, however, we shall concentrate on the iodine sublattice. Let P be any of the 256 iodine ions and let P' and P'' be two of its neighbors that are within a certain distance R_3 of the first chosen. We then calculate the distribution of cosine of the angle subtended at P

TABLE III. The seven **k** vectors that give the largest value of the I-I structure factor as a function of time during the homogeneous nucleation of α-AgI. Here $\mathbf{k}_i$ denotes the integers (n_1, n_2, n_3) and S_i denotes the value of the structure factor for $\mathbf{k}_i$ at the various times listed. The time is the number of timesteps since the temperature was lowered.

Time	$\mathbf{k}_1$			S_1	$\mathbf{k}_2$			S_2	$\mathbf{k}_3$			S_3	$\mathbf{k}_4$			S_4
250	7	−1	0	18	6	2	3	17	6	1	−4	24	3	7	−1	28
500	6	1	−4	18	5	3	4	23	4	6	1	19	3	7	−1	18
750	7	−1	0	23	6	1	−4	20	6	−2	2	16	4	5	3	25
1000	7	−1	0	19	6	1	−4	17	6	−2	−2	17	5	4	−4	22
1250	7	−1	0	17	6	1	−4	15	6	−2	−2	17	5	4	−4	24
1500	7	0	0	16	7	−1	0	29	5	4	−4	29	3	4	5	18
1750	7	0	0	30	7	−1	0	31	4	5	3	16	3	6	−2	16
2000	7	0	0	33	7	−1	0	19	5	4	−4	18	4	−3	−6	20
2250	7	0	0	30	6	3	−3	21	5	2	4	27	4	−4	−5	28
2500	7	0	0	33	4	−5	−4	27	5	2	4	25	3	5	4	27
2750	7	−2	−2	24	5	4	−3	30	5	2	4	30	3	5	4	36
3000	7	−2	−2	38	5	4	−3	30	5	2	4	42	4	−5	−4	34
3250	7	−2	−2	58	7	0	0	21	5	2	4	47	4	5	−3	21
3500	7	−2	−2	48	7	0	0	23	5	2	4	51	4	5	−3	25
3750	7	−2	−2	100	5	5	−2	37	5	2	4	93	2	7	1	32
4000	7	−2	−2	165	5	5	−2	155	5	2	4	172	2	−4	−6	175
4250	7	−2	−2	189	5	5	−2	186	5	2	4	196	2	−4	−6	189
4500	7	−2	−2	192	5	5	−2	191	5	2	4	194	2	−4	−6	181
4750	7	−2	−2	179	5	5	−2	185	5	2	4	179	2	−4	−6	168
5000	7	−2	−2	181	5	5	−2	167	5	2	4	183	2	−4	−6	162
5250	7	−2	−2	168	5	5	−2	173	5	2	4	176	2	−4	−6	183
5500	7	−2	−2	159	5	5	−2	163	5	2	4	171	2	−4	−6	167
5750	7	−2	−2	185	5	5	−2	169	5	2	4	171	2	−4	−6	174
6000	7	−2	−2	168	5	5	−2	170	5	2	4	173	2	−4	−6	189

Time	k_5			S_5	$\mathbf{k}_6$			S_6	$\mathbf{k}_7$			S_7
250	3	−6	−3	18	1	−3	6	15	0	1	7	17
500	2	−5	−5	19	0	1	7	19	0	1	7	20
750	2	−5	−5	24	0	1	−7	16	0	0	7	18
1000	4	5	3	22	3	−6	−3	24	0	1	−7	15
1250	3	−6	−3	30	2	−5	4	23	1	−1	−7	18
1500	3	−6	−3	15	2	−5	−5	17	0	1	−7	16
1750	3	4	5	20	3	−6	−3	15	1	1	−7	15
2000	4	−5	−4	22	3	5	4	21	3	4	5	27
2250	4	−5	−4	27	3	4	5	24	1	1	−7	30
2500	3	−5	3	22	2	−4	−6	25	1	−3	6	22
2750	3	−5	3	23	2	−4	−6	26	1	0	−7	26
3000	3	−5	3	48	2	−4	−6	40	1	0	−7	26
3250	4	−5	−4	23	3	−5	−3	24	2	−4	−6	60
3500	4	−5	−4	28	3	−5	3	30	2	−4	−6	33
3750	2	−7	0	36	2	−4	−6	92	0	3	−6	35
4000	2	−7	0	168	0	−3	6	160	7	−5	4	106
4250	2	−7	0	185	0	−3	6	184	7	−5	4	140
4500	2	−7	0	185	0	−3	6	181	7	−5	4	141
4750	2	−7	0	175	0	−3	6	185	7	−5	4	130
5000	2	−7	0	175	0	−3	6	169	7	−5	4	140
5250	2	−7	0	173	0	−3	6	181	7	−5	4	115
5500	2	−7	0	162	0	−3	6	160	7	−5	4	104
5750	2	−7	0	160	0	−3	6	159	7	−5	4	110
6000	2	−7	0	182	0	−3	6	174	7	−5	4	116

by the lines connecting P to P' and P''. The distance R_3 was defined so as to include the first 14 neighbors of bcc and the first 12 neighbors of hcp and fcc structures. For the ideal bcc, hcp, and fcc lattices, we obtain the δ-function distributions shown in Figs. 7–9, respectively.

The distribution of iodine three-body angles was monitored during the nucleation events at selected times. A histogram of the distribution of three-body angles at 6000 time steps is shown in Fig. 10. The distance R_3 was taken to be the distance of the first minimum of the I-I partial pair-distribution function shown in Fig. 3. Comparison of the bond-angle distribution with the ideal distributions confirms again that the iodine lattice has nucleated into the bcc phase and that α-AgI has been nucleated from the liquid.

F. Nucleation into other phases

In another experiment we returned to the liquid at 1100 K and 0.2 GPa and again followed the same procedure for lowering the temperature. This time, however, we repeated the cycle of setting the velocities to zero one more time after running 20 time steps. After a short period of equilibration, the system temperature was around 300 K. We then allowed the system to run without interruption and noticed that the temperature steadily rose and had to be carefully lowered to keep from getting above the transition temperature to the α phase $\approx$420 K. If the system temperature reached 400 K, we scaled the velocities to bring the temperature back to near 300 K. This procedure had to be repeated three times during the course of the experiment to ensure that the system stayed below the transition temperature. After 8000 time steps a shell structure became noticeable in the iodine sublattice and grew sharper until the nucleation process was stopped after 10 000 time steps. The system temperature at the completion of the experiment was 385 K. Again the temperature, pressure, and structure factors were monitored during the nucleation process. A histogram showing the bond-angle distribution function at the completion of the nucleation is shown in Fig. 11. Comparison with the ideal distributions shows that the iodine sublattice has nucleated into the hcp structure and we have formed β-AgI by homogeneous nucleation from the liquid. A study of other properties of the system confirms that this is the case. A check shows that neither species of ion shows diffusion.

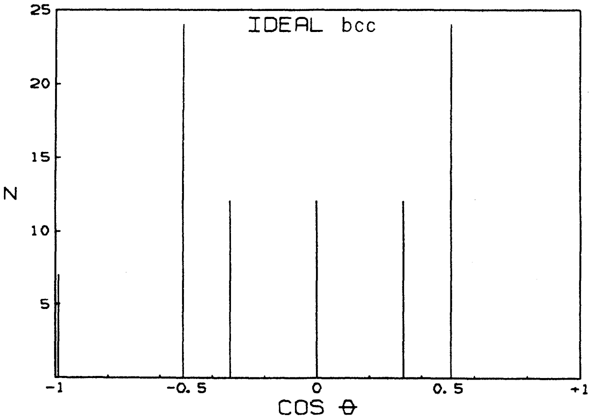

FIG. 8. Iodine three-body angular distribution function for the ideal hcp lattice.

Starting from the liquid again we next increased the pressure from 0.2 to 0.8 GPa while in the HPN form of molecular dynamics. The liquid was then quenched as before to 350 K and allowed to run undisturbed. After approximately 6000 time steps, a shell structure became evident and the nucleation was stopped after 8000 time steps. Again a check of the three-body bond-angle distribution was calculated and we obtained Fig. 12 which shows that the iodine lattice is fcc. A study of the Ag-Ag partial pair-distribution function shows that the silver sublattice is also fcc and a check of the Ag-I partial pair-distribution function shows that Ag has sixfold coordination with I. There was no diffusion of either species of ion in the nucleated structure and it is evident that we have formed the rocksalt phase by homogeneous nu-

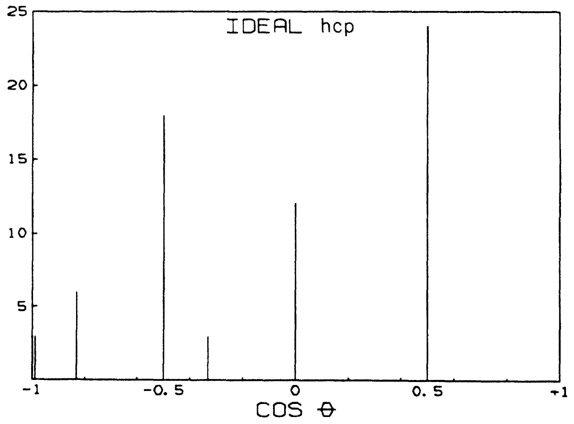

FIG. 7. Iodine three-body angular distribution function for the ideal bcc lattice.

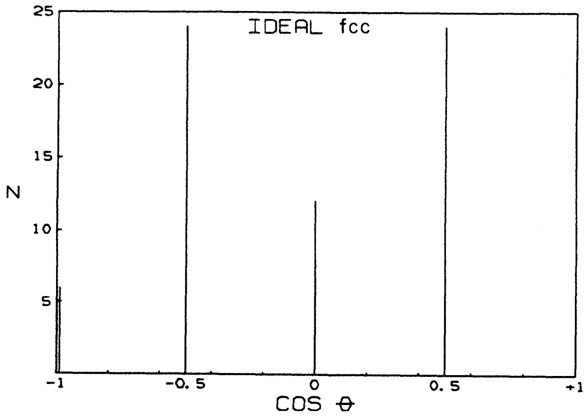

FIG. 9. Iodine three-body angular distribution function for the ideal fcc lattice.

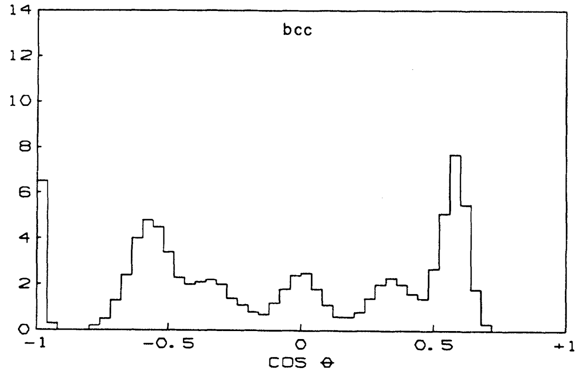

FIG. 10. Iodine three-body distribution function for the nucleated α phase.

cleation from the liquid. This result, at 0.8 GPa and 350 K, is entirely consistent with the experimental phase diagram and our studies described in previous sections.

Finally, several attempts were made to form a polytype at one of the pressures 0.27–0.31 GPa by lowering the temperature of the liquid at these pressures. None of these attmepts led to nucleation of a polytype over 25 000 time steps. In each instance an unrecognizable disordered structure is the end product. Since these pressures are near the rocksalt–close-packed phase boundary, the system is apparently frustrated from nucleating into either phase and again this may be associated with the intermediate phase in Fig. 1. It would be interesting to investigate this further.

G. Disorder in the nucleated structures

After nucleation into the α, β, and rocksalt phases just described, a low-temperature quench was made to determine more accurately the coordination numbers of the resulting structures. There was in each case a slight difference between the coordination numbers for the ideal structures and those formed in our experiments. For example, the I-I coordination second-nearest-neighbor coordination number in α-AgI was 13.94 instead of 14.00. An inspection of the positions of the particles indicated that the sample had vacancy and interstitial defects. This is not surprising given that these systems were formed from a disordered liquid phase. No such defects were detected in the phase transformations produced by temperature lowering from the α phase since these are simple displacive transformations.

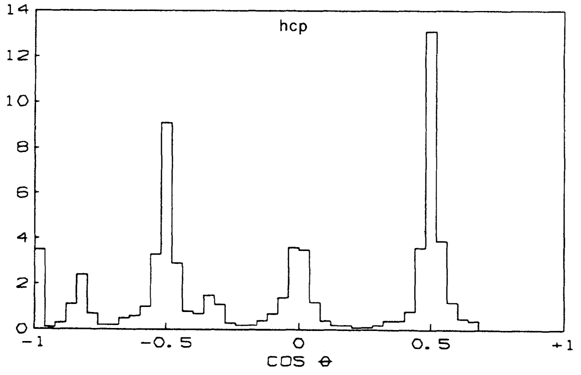

FIG. 11. Iodine three-body distribution function for the nucleated β phase.

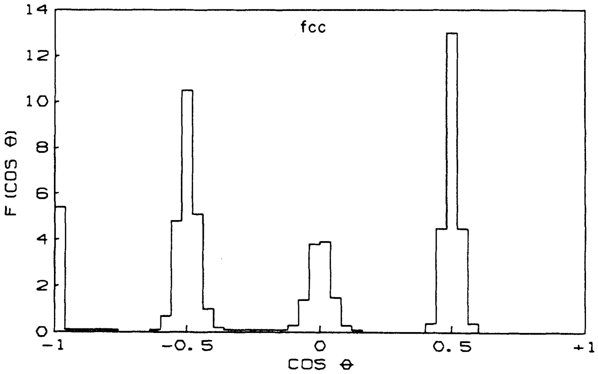

FIG. 12. Iodine three-body distribution function for the nucleated rocksalt phase.

VI. CONCLUSIONS

Molecular-dynamics simulations have been carried out on a system of 512 ions in careful studies of the AgI phase diagram and the homogeneous nucleation of different phases of AgI from the liquid.

Using the AgI model potential of Parrinello, Rahman, and Vashishta,[19] we accurately mapped the phase boundary in going from the high-temperature to the low-temperature phases. At a given pressure, the temperature of the phase transformations was found to be within 5 K of the experimental phase diagram. Mapping the boundaries of the experiental phase diagram is a very stringent test of the model potential. It is remarkable that such simple two-body potentials alone could so completely describe this rather complicated phase diagram. An attempt to see a rocksalt superionic phase was negative.

As a function of both temperature and density, silver iodide was found to undergo structural phase transformations from the superionic α phase into a number of interesting polytypes. These structures exhibit stacking of the close-packed planes which was different than that of fcc or hcp. Analysis of the four polytypes showed that three had formed from the same bcc (110) planes by the martensitic mechanism recently discussed by Lee and Ray.[23] The fourth polytype was not similar to these three and was formed when a different set of (110) planes in the bcc α phase were selected to become close-packed planes. Polytypes have been observed with the same hexagonality as the ones that we formed in our simulations. By picking different particle numbers it is possible to make an unlimited number of different polytypes and we would predict that a careful experimental study of AgI would find other polytypes besides those already reported.

In studying the reproducibility of these polytypes it was found that the formation of a given polytype depended on the initial conditions. The same structure would not always occur in the simulations at a given pressure. Our explanation for this is that the energy differences are small compared to the energy barriers separating the polytypes.

Our simulations support the conjectures in the literature that the pure γ phase does not exist. The x-ray data of polytypes has probably been incorrectly interpreted as mixed β and γ phases. At low pressure we found only the β phase even though our simulations started from the γ phase. Very near the polytype-rocksalt phase boundary the system did not transform from the α phase into a recognizable structure upon temperature lowering over the time of the simulation. The system underwent sluggish distortions between unrecognizable structures over the entire time of the simulation. We suggest that this is associated with what is called the intermediate phase in the literature; that is, the intermediate phase is a long-lived state that is frustrated from transforming into a polytype or rocksalt phase by the fact that these two phases have almost the same probability of forming near the phase boundary. Further, more detailed studies on this point would be of interest.

Homogeneous nucleation of three different phases was carried out and confirms the remarks of Vashishta[28] concerning the nucleation at different final temperatures and pressures. Attempts to nucleate into a polytype were not successful but led to slowly changing unrecognizable structures over the time of the simulations. This is another piece of evidence that, near the polytype-rocksalt phase boundary, the system is frustrated from transforming and this is the origin of the intermediate phase in Fig. 1. It is possible that nucleation into a polytype would occur on a longer scale than the 25 000 time steps used in this study.

It is interesting that, even with the extreme conditions of cooling employed in our nucleation experiments (cooling rates$\approx 10^{13}$ K/s), no appearance of an amorphous structure appears although there are interstitials and vacancies in the nucleated structures. This is important since large changes in the ionic conductivity may arise in going to the amorphous structure. Our results are consistent with experimental findings where no amorphous phase of AgI has been found.[31] It is probable that this difficulty in making amorphous structures in simple binary ionic systems is due to the strong tendency to maintain charge neutrality in these systems. Other temperature lowering, quenching strategies could, of course, lead to amorphous structures. We have observed in other systems that extreme cooling such as in the present study leads preferentially to homogeneous nucleation of the crystal structure, whereas an altered slower cooling strategy may significantly increase the probability of forming an amorphous structure.

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[1] *Superionic Solids and Solid Electrolytes: Recent Trends,* edited by A. L. Laskar and S. Chandra (Academic, New York, 1989).

[2] *Physics of Superionic Conductors and Electrode Materials,* edited by J. Perram (Plenum, New York, 1983).

[3] S. Chandra, *Superionic Solids: Principles and Applications* (North-Holland, Amsterdam, 1981).

[4] *Fast Ion Transport in Solids,* edited by P. Vashishta, J. N. Mundy, and G. K. Shenoy (North-Holland, Amsterdam, 1979).

[5] *Physics of Superionic Conductors,* edited by M. B. Salamon (Springer-Verlag, Berlin, 1979).

[6] *Solid Electrolytes,* edited by S. Geller (Springer-Verlag, Berlin, 1977).

[7] *Superionic Conductors,* edited by G. D. Mahan and W. L. Roth (Plenum, New York, 1976).

[8] B.-E. Mellander, J. E. Bowling, and B. Baranowski, Phys. Scr. **22**, 541 (1980).

[9] B.-E. Mellander, Phys. Rev. B **26**, 5886 (1982).

[10] A. J. Majumdar and R. Roy, J. Phys. Chem. **63**, 1858 (1959).

[11] B. L. Davis and R. L. Petersen, Cryst. Lattice Defects **1**, 275 (1970).

[12] B. L. Davis and L. R. Johnson, Cryst. Lattice Defects **5**, 235 (1974).

[13] P. R. Prager, Acta. Crystallogr. A **30**, 369 (1974).

[14] Q. Johnson and R. N. Schock, Acta. Crystallogr. B **31**, 1482 (1975).

[15] P. R. Prager, Acta Crystallogr. A **33**, 25 (1977).

[16] P. Vashishta and A. Rahman, Phys. Rev. Lett. **40**, 1337 (1978).

[17] P. Vashishta and A. Rahman, *Fast Ion Transport in Solids,* Ref. 4.

[18] M. Parrinello and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980); J. Appl. Phys. **52**, 7182 (1981).

[19] M. Parrinello, A. Rahman, and P. Vashishta, Phys. Rev. Lett. **50**, 1073 (1983).

[20] J. Tallon, Phys. Rev. Lett. **57**, 2427 (1986).

[21] J. L. Tallon, Phys. Rev. B **38**, 9069 (1988).

[22] J. R. Ray and P. Vashishta, J. Chem. Phys. **90**, 6580 (1989).

[23] K. Y. Lee and J. R. Ray, Phys. Rev. B **39**, 565 (1989).

[24] J. R. Ray and A. Rahman, J. Chem. Phys. **80**, 4423 (1984).

[25] M. Moody, J. R. Ray, and A. Rahman, Phys. Rev. B **35**, 557 (1987).

[26] M. C. Moody, Ph.D. thesis, Clemson University, 1985.

[27] A. R. Verma and P. Krishna, *Polymorphism and Polytypism in Crystals* (Wiley, New York, 1966).

[28] P. Vashishta, Solid State Ionics **18**, 3 (1986).

[29] J. R. Ray, A. Rahman, and P. Vashishta, *Superionic Solids and Solid Electrolytes: Recent Trends,* Ref. 1.

[30] C. S. Hsu and A. Rahman, J. Chem. Phys. **70**, 5234 (1979).

[31] T. Takahashi (private communication).