Structural Transitions in Superionic Conductors

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The $\alpha \rightleftarrows \beta$ phase transition in AgI is studied with use of the new molecular-dynamics technique which allows for a dynamical variation of the shape and size of the cell. In the present model, upon heating of β-AgI, the iodine ions undergo a hcp → bcc transformation and silver ions become mobile, whereas the reverse transformation is observed on cooling of α-AgI. The calculated $\alpha \rightleftarrows \beta$ transition temperature and structural and dynamical properties are in good agreement with experiments.

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Superionic conductors are a class of systems in which phenomena observed in fluids and solids come together in an interesting manner.[1] Silver iodide is a superionic conductor which, as a function of density and temperature, shows a number of structural transitions.[2] Of particular interest to us is the $\beta \rightleftarrows \alpha$ transition. The β phase has the wurtzite structure: Iodine ions form an hcp lattice and silver ions are tetrahedrally coordinated to each iodine and show no self-diffusion. At 420 K, the β-AgI undergoes a first-order phase transition into the superionic α phase in which iodine ions form a bcc lattice and silver ions are mobile, having a large constant of self-diffusion ($> 1\times10^{-5}$ cm^2/sec). Properties of α-AgI have been studied by a variety of experimental techniques by a number of workers.[1-3] A simple model for α-AgI was proposed[4] and the nature of ionic motions was studied by the usual molecular-dynamics (MD) technique in which both the shape and the size of the MD cell remain fixed.[4,5] Calculated results for the temperature dependence of the mean square displacement of iodine, the constant of self-diffusion of Ag, the density map of Ag in the unit cell, partial pair correlations, velocity autocorrelation functions, current-current correlation function, Haven's ratio, etc., were found to be in good agreement with experiments.[4-7]

However, a study of structural transitions is impossible within the framework of the usual MD technique in which both the shape and size of the cell are fixed. The iodine lattice, confined to a cubic cell and given a bcc structure, cannot undergo a structural transition; hence the $\alpha \rightleftarrows \beta$ transition in AgI will be prohibited. The MD technique can be generalized to include changes with time in the volume of the cell, $\Omega(t)$.[8] However, the bcc lattice in a cubic cell cannot transform into another lattice structure even though the volume of the cubic cell can change with time. Using an appropriate Lagrangian one can set up a molecular-dynamics calculation in which both the volume *and* shape of the periodically repeating cell change with time.[9]

In this Letter we report the result of our studies of the $\alpha \rightleftarrows \beta$ transition in AgI. Such studies have become possible because of the above-mentioned development in MD technique. Our aim is to construct a simple potential function for AgI which will make the iodines adopt a bcc structure at elevated temperatures with the silver ions jumping between the tetrahedral sites. On cooling of the system, the interaction potential, all on its own, should modify the bcc structure into a close-packed one, while at the same time the silver ions should settle down into a fourfold-coordinated nondiffusive configuration.

The problem of setting up a scheme to construct interaction potentials has been approached from a phenomenological point of view.[4] Since with the new MD technique we can study structural transitions, we are no longer confined to the α phase to determine the potential; hence we have used the true low-temperature structure of AgI to determine the constants in the potentials. This changes σ_{Ag} from 0.63 to 0.53 Å and leaves $\sigma_{\text{I}} = 2.2$ Å unchanged. It should be noted, however, that $\sigma_{\text{Ag}} = 0.53$ and the old exponents $n(\text{II}) = n(\text{AgI}) = n(\text{AgAg}) = n = 7$ produced unsatisfactory results. The potential functions are therefore refined by using different values of the exponents n_{ij} in the repulsive terms. It is our hope that a single set of potentials of the form given below, where the constants are determined from a low-temperature structure, will be adequate to describe not only the phase transition $\alpha \rightleftarrows \beta$, but also the high-pressure phases of AgI.[7] We take

$$V_{\text{AgAg}}(r) = H_{\text{AgAg}}/r^{n(\text{AgAg})} + 0.36/r,$$

$$V_{\text{AgI}}(r) = H_{\text{AgI}}/r^{n(\text{AgI})} - 0.36/r - 1.1736/r^4, \quad (1)$$

$$V_{\text{II}}(r) = \frac{H_{\text{II}}}{r^{n(\text{II})}} + \frac{0.36}{r} - \frac{2.3472}{r^4} - \frac{6.9331}{r^6},$$

where $H_{ij}=A(\sigma_i+\sigma_j)^{n(ij)}$, with angstroms and $e^2/(1\ \text{Å})=14.39$ eV as units. We kept $n(\text{II})=7$ and changed $n(\text{AgI})$ toward a higher value [$n(x)<7$ are uncommon and Pauling suggests $n(\text{Ag})>n(\text{I})$]. Since the Ag-Ag repulsion term $r^{-n(\text{AgAg})}$ does not play an important role, we took $n(\text{Ag})=11$, $n(\text{I})=7$ and constructed $n(\text{II})=7$, $n(\text{AgI})=9$, and $n(\text{AgAg})=11$. In brief, the changes from old to modified potential result from taking σ_{Ag} and σ_{I} from the low-temperature structure and changing $n(\text{AgI})$ to 9 from 7. Using these $n(ij)$, we get $A=0.010\,248$, $H_{\text{AgAg}}=0.014\,804$, $H_{\text{AgI}}=114.48$, and $H_{\text{II}}=446.64$. The value of charge, $Z=0.6$, and other constants were kept the same as in the earlier potential functions used to describe the α phase.[4,5] We shall refer to Eq. (1) as the "modified potential."

To study the structural transition of the iodine sublattice as well as the order-disorder transformation of silver ions, we take a neutral system of $N=500$ particles (250 I^- and 250 Ag^+) obeying $3N+9$ equations of motion.[9] Note that for a 500-particle system in a nonvarying cubic cell one can study only the properties of α-AgI and none of the other structures of AgI. Using the new MD method and the "modified potential," we made a calculation on α-AgI at 700 K. All the calculations reported here were carried out at a constant value of the pressure. After equilibration, a calculation extending over $\sim 5\times10^{-11}$ sec, i.e., 2500 MD steps, gave results in agreement with previous calculations.[4] The iodines form a thermally agitated, stable, bcc lattice; the Ag-I pair correlation gives a clear nearest-neighbor (nn) coordination of 4; the Ag ions diffuse with $D_{\text{Ag}}=4\times10^{-5}\ \text{cm}^2\ \text{sec}^{-1}$.

Having thus confirmed that we have a satisfactory model and method of calculation for α-AgI we proceeded to study the structural phase transitions in this system.

On cooling of the above system from 700 to 350 K, in only about 2×10^{-11} sec the apparent "nn" I-I coordination started to drop from 14 (8 + 6) to 12 while the nn Ag-I coordination remained 4 throughout. In addition the MD cell changed to a noncubic shape. This already was indicative of a structural change for the iodines from bcc to close packed. After these secular changes had stopped, a 2500-time-step run was made to calculate various average properties. *Both* iodine and silver ions showed no diffusion, the mean square displacments being $B_{\text{I}}=4.0\ \text{Å}^2$ and $B_{\text{Ag}}=6.3\ \text{Å}^2$. The $g_{ij}(r)$ are shown in Fig. 1(a). The nn coordination shows that on cooling to 350 K the α-AgI has been transformed to a zinc-blende or a wurtzite structure. From Fig. 1(a) by itself, one cannot resolve the situation unambiguously, but (i) the shoulder at 9 Å, and (ii) the value 55.6 of the number of I-I neighbors up to 9.8 Å indicate hcp character. Following the usual method in such cases, quenching the system to a very low temperature lifts the uncertainty. The result is shown in Fig. 1(b).

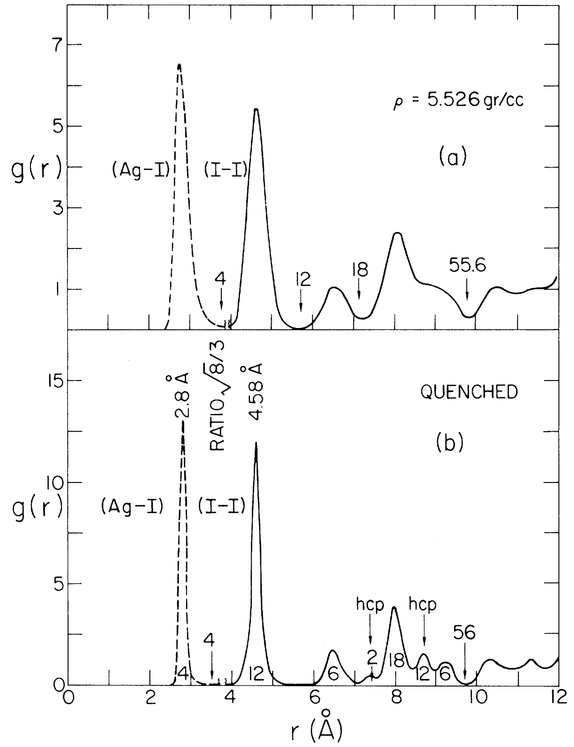

FIG. 1. (a) Partial pair correlation function, $g(r)$, after cooling from α phase at 700 K. The first peak for Ag-I shows a coordination of 4. Peaks for I-I are shown with coordination numbers. The first peak clearly shows a nn coordination of 12 and the arrow at 9.75 Å indicates a total coordination of 55.6 iodines. For a perfect fcc and hcp lattice this number is 54 and 56, respectively. (b) $g(r)$'s at 343.8 K on quenching to a very low temperature. The Ag-I peak at 2.8 Å is sharpened. The ratio between I-I and Ag-I nn distances is $(\frac{8}{3})^{1/2}$. The two peaks marked hcp containing two and twelve particles are clearly resolved. This shows that the pair correlations are for β-AgI with a wurtzite structure.

Ideally, for hcp structure, the $g_{\text{I-I}}$ should show 6 peaks and 56 neighbors up to 9.8 Å and 4 peaks and 56 neighbors for fcc. Figure 1(b) shows, firstly, an Ag-I and I-I coordination of 4 and 12, respectively, with a distance ratio of $\sqrt{\frac{8}{3}}$ between the peak positions. Secondly, 6 peaks in $g_{\text{I-I}}$, with 12, 6, 2, 18, 12, and 6 neighbors, are

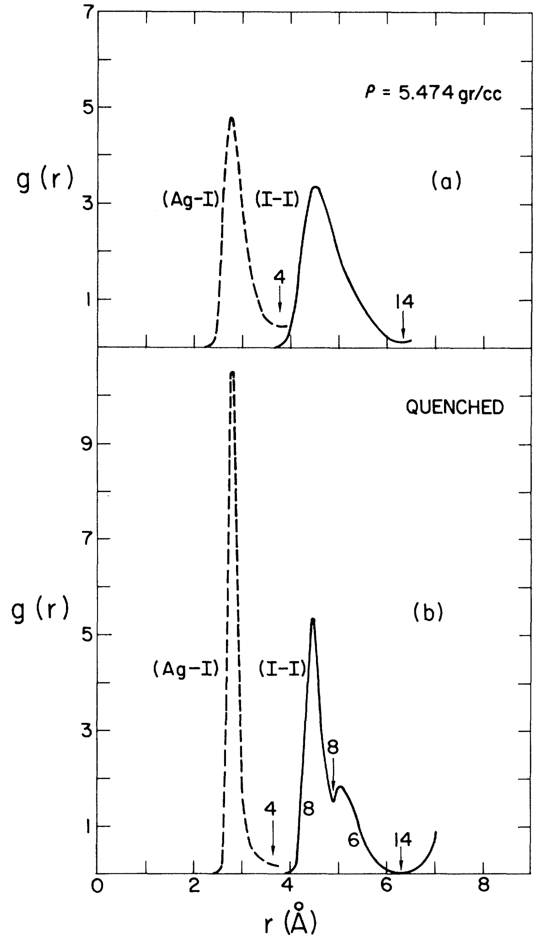

FIG. 2. (a) $g(r)$'s at 494.7 K obtained by heating from β-AgI at 343.8 K. The peaks for Ag-I and I-I show coordinations of 4 and 14, respectively. (b) $g(r)$'s at 494.7 K after quenching. The I-I correlation shows two peaks containing 8 and 6 iodines. This confirms that the figure described the pair correlation of α-AgI.

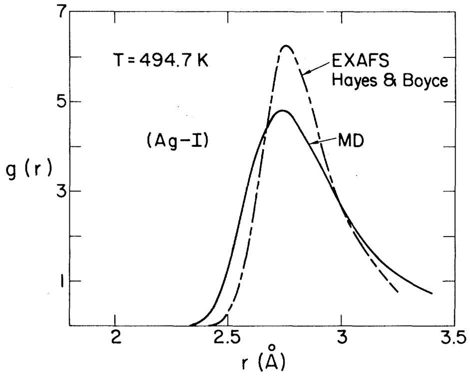

FIG. 3. The first peak of Ag-I pair correlation in α-AgI from MD calculations and EXAFS results (Ref. 10).

clearly seen. Thus α-AgI cooled from 700 to 350 K has transformed to β-AgI.

The $\beta \rightarrow \alpha$ transition was studied by heating of the β-AgI system from 343.8 to 495 K. After about 1000 time steps, the nn I-I coordination started to be more than 12. Pair correlation functions for a well thermalized system at 495 K are shown in Fig. 2(a). The first peak in $g(r)$ for I-I shows a nn coordination of 14—the characteristic value for a heated bcc lattice. Silver ions were found to be diffusing with $D_{\mathrm{Ag}} = 2 \times 10^{-5}$ cm^2/sec and nn Ag-I coordination was tetrahedral. The result of quenching to very low temperature is shown in Fig. 2(b). The first two shells of the bcc iodine lattice, containing eight and six particles, respectively, are clearly identified. This confirms that $\beta \rightarrow \alpha$ AgI transformation has been achieved.

By repetition of such calculations several times the $\alpha \rightleftharpoons \beta$ transition temperature was determined to lie between 472 and 495 K, in satisfactory agreement with the experimental value of 420 K.

The first peak of the Ag-I pair correlation function can be accurately measured by extended x-ray-absorption fine structure (EXAFS). In Fig. 3 we compare our MD results with the EXAFS results of Hayes and Boyce for α-AgI.[10] The agreement is indeed very good.

It is obvious that the "modified potential" given in Eq. (1), which has different exponents to describe Ag-Ag, Ag-I, and I-I repulsive terms, in conjunction with the MD technique which allows for a variation of the shape and size of the cell, successfully describes the $\alpha \rightleftharpoons \beta$ transition in AgI. Furthermore, the structural and dynamical properties of AgI in the superionic phase are in good agreement with experiments.

Very recently we have also studied structural transitions in AgI under hydrostatic pressure. In our computer model, AgI described by the potential function given in Eq. (1) successfully undergoes $\alpha \rightleftharpoons$ (rock salt) and $\beta \rightleftharpoons$ (rock salt) transitions. Results of this investigation will be reported elsewhere.

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