

## Mechanism of $\text{Ag}^+$ ordering in $\text{AgI}$

Chaok Seok and David W. Oxtoby

Department of Chemistry and James Franck Institute, The University of Chicago, 5640 South Ellis Avenue, Chicago, Illinois 60637

(Received 24 November 1997)

We performed lattice Monte Carlo simulations to explore the suggestion made in our previous study of phase transitions in  $\text{AgI}$  using a lattice version of the density-functional theory [Phys. Rev. B **56**, 11485 (1997)] that the phase transition from the high-temperature  $\alpha$  phase to the low-temperature  $\beta$  phase is not driven by the ordering of  $\text{Ag}^+$  ions alone, but that instead ordering of  $\text{Ag}^+$  is correlated with a structural change of the  $\text{I}^-$  lattice. The results of our calculation are consistent with this proposal.

[S0163-1829(98)04734-1]

$\alpha$ - $\text{AgI}$  is a superionic conductor where the number of available interstitial sites formed by the bcc  $\text{I}^-$  lattice is larger than the number of  $\text{Ag}^+$  ions. It undergoes a first-order phase transition to nonconducting  $\beta$ - $\text{AgI}$  with the wurtzite structure at about 420 K and ambient pressure, where the  $\text{Ag}^+$  ions occupy particular tetrahedral sites in the hcp  $\text{I}^-$  lattice. The  $\alpha$  to  $\beta$  transition was reproduced using a constant-stress molecular-dynamics simulation.<sup>1</sup>

Szabó<sup>2</sup> applied a mean-field theory to the ordering transition of  $\text{Ag}^+$  ions in a fixed bcc  $\text{I}^-$  lattice. He considered only tetrahedral sites (where a majority of the  $\text{Ag}^+$  ions are found) and divided them into six sublattices, as shown in Fig. 1. In the low-temperature ordered phase ( $D$  phase), most  $\text{Ag}^+$  ions occupy only one particular sublattice, giving bcc symmetry. Partially ordered intermediate phases were found depending on the ratio of second- to first-nearest-neighbor interactions.

In a molecular-dynamics simulation, Madden *et al.*<sup>3</sup> observed a phase transition involving ordering of  $\text{Ag}^+$  ions when the cubic periodic boundary condition prevents the  $\alpha$  to  $\beta$  transition because the  $\text{I}^-$  lattice cannot be transformed to hcp. However, the ordered phase they obtained ( $M$  phase) differed from Szabó's  $D$  phase. In the  $M$  phase, the sites in the Szabó sublattices are not all equivalent, and can be redivided into twelve sublattices grouping together the same type of Szabó sites on alternating equivalent planes parallel to (110), as in Fig. 1. We call these sublattices 1, 1', 2, 2', and so on. Sublattices 1 and 1' are then mainly occupied in the  $D$  phase, and 1 and 3' are occupied in  $M$  (because all the sublattices are equivalent, there are five more combinations of sublattices that correspond to the same  $D$  or  $M$  phases). Madden *et al.*<sup>3</sup> noted that the  $\text{Ag}^+$  positions in the  $M$  phase are such that this phase can be transformed to the actual low-temperature  $\beta$  phase simply by the Burgers mechanism<sup>4</sup> for a transition from bcc to hcp [gliding of alternate (110) planes of  $\text{I}^-$ ], and argued that the  $M$  phase would be transformed to the  $\beta$  phase if the boundary-condition-imposed stresses were relaxed. They therefore suggested that the ordering tendency of the  $\text{Ag}^+$  ions is the driving force for the  $\alpha$  to  $\beta$  transition.

We applied a lattice version of density-functional theory to the same problem.<sup>5</sup> Only tetrahedral  $\text{Ag}^+$  sites in a fixed  $\text{I}^-$  lattice were considered, following Szabó. We found that

the ordered phase is  $D$ , not  $M$ , although we used the same potential energy as in Madden's simulation, and the  $\text{I}^-$  lattice could not change to hcp just as in the simulation. A lattice Monte Carlo simulation gave similar results.<sup>5</sup> However, we showed that a gliding of alternating  $\text{I}^-$  (110) planes by about  $0.15a$ , keeping tetrahedral coordination of  $\text{Ag}^+$  ions, significantly lowers the energy of the  $M$  phase. Such a deformation was not allowed in our simple lattice approximation, but was allowed in Madden's simulation despite the periodic boundary condition. A glide by  $\sqrt{2}/8a=0.177a$  with a change in unit-cell shape (the latter is not allowed in Madden's simulation because of the boundary condition), leads to the  $\beta$  phase. Such a deformation may have occurred in Madden's ordered phase, which would mean that the ordering of  $\text{Ag}^+$  ions and deformation of  $\text{I}^-$  occur together rather than the former driving the latter.

In this paper, we present results of lattice Monte Carlo simulations where the gliding of the (110) planes is incorporated. We performed separate simulations for systems with different degrees of deformations of the  $\text{I}^-$  lattice, and found

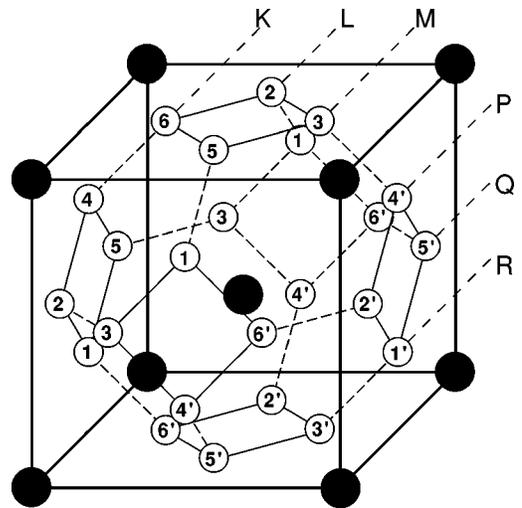


FIG. 1. Six sublattices of tetrahedral sites (with  $i=i'$ ) introduced by Szabó. Black circles represent  $\text{I}^-$  ions and white circles  $\text{Ag}^+$  sites. The twelve sublattices (with  $i \neq i'$ ) are discussed in the text.  $K$ ,  $L$ ,  $\dots$ , and  $R$  denote planes parallel to (110), and repeat in space.  $K$  planes consist of sublattices 4 and 6, and  $P$  of 4' and 6', etc.

a transition from a disordered state with no deformation to an ordered state in the  $M$ -phase symmetry with a deformation  $\delta$  of about  $0.155a$ .

We employ the same pair-potential model used in previous computer simulations,<sup>1,3</sup> and use the Ewald method, considering all periodic images of the ions in a background of opposite charge.<sup>6</sup>  $\text{Ag}^+ - \text{I}^-$  interaction energies are calculated to find site energies for the three types of sublattices ( $\{1,3',4,6'\}$ ,  $\{1',3,4',6\}$ , and  $\{2,2',5,5'\}$ ) that become inequivalent upon deformation.

A cubic simulation box with side length  $8a$  which contains 1024  $\text{Ag}^+$  ions was used. It is larger than the box used in Ref. 3 where the side length was  $6a$ . The side should be an even multiple of  $a$  in order for the periodic boundary condition to be consistent with the possible existence of an  $M$  phase. There is a size effect, the transition temperature for the system size  $(6a)^3$  being higher by about 100 K than for  $(8a)^3$  box, but the qualitative picture is not affected.

The Helmholtz free energy  $F$  is calculated by numerically integrating the potential energy  $E$  calculated for a series of temperatures using the following relation:

$$\beta F = \int_0^\beta E d\beta + \beta F(\beta=0), \quad (1)$$

that comes from

$$E = - \left( \frac{\partial \ln Q}{\partial \beta} \right)_{N,V} = \left( \frac{\partial \beta F}{\partial \beta} \right)_{N,V}, \quad (2)$$

where  $\beta = 1/kT$  and  $k$  is the Boltzmann constant, and  $Q$  is the canonical partition function.  $\beta F(\beta=0) = -S(\beta=0)/k$  must be the same for systems that differ only in the degree of deformation because the entropy  $S$  would then be just that of an ideal lattice gas.

For  $\delta \neq 0$  (the phase diagram is symmetric with respect to change in sign of  $\delta$ ), the high-temperature phase is a disordered state with the same occupation numbers for each nonequivalent group of sublattices; those occupation numbers are determined by the site energies, which depend upon  $\delta$ , and the interactions between  $\text{Ag}^+$  ions. At low temperatures, the symmetry of the disordered phase is broken to give five nonequivalent groups of sublattices ( $\{1,3'\}$ ,  $\{4,6'\}$ ,  $\{1',3\}$ ,  $\{4',6\}$ , and  $\{2,2',5,5'\}$ ). The two sublattices 1 and  $3'$  or 4 and  $6'$  (the sublattices 1,  $3'$ , 4, and  $6'$  are set to have the lowest site energy) are mostly occupied in the ordered phase, which corresponds to the  $M$  phase in a deformed  $\text{I}^-$  lattice. The change of occupation numbers with temperature is shown in Fig. 2. The order-disorder transition from the disordered state to the ordered state at fixed  $\delta$  is first order for small  $\delta$ , but it becomes weakly first order or second order with increasing  $\delta$ .

The dependence on temperature of the free energy  $\beta\Delta F$  for several deformations is shown in Fig. 3. The change in slope of  $\beta\Delta F$  at low temperature in the figure indicates a transition to the ordered phase at fixed  $\delta$ , and it is sharp for smaller  $\delta$  and smooth for larger  $\delta$  depending on whether the transition is first order or second order. No hysteresis was found for  $\delta \geq 0.14$  when heating follows cooling, implying that the transition is weakly first order or second order for that range of  $\delta$ . One can see from Fig. 3 that the stable

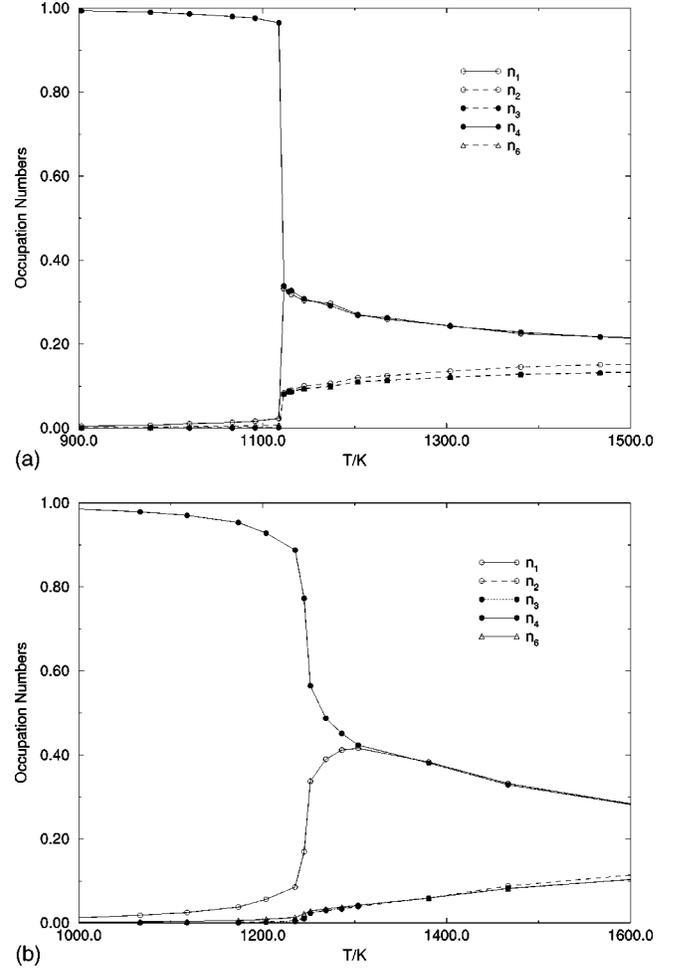


FIG. 2. Temperature dependence of occupation numbers for (a)  $\delta=0.1$  and (b)  $\delta=0.155$ . The occupation numbers  $n_1$ ,  $n_2$ ,  $n_3$ ,  $n_4$ , and  $n_6$  are averages over equivalent sublattices.

high-temperature phase is a disordered state in the undeformed lattice, and it undergoes a first-order transition to an ordered state with deformation  $\delta \approx 0.155a$  at around 1100 K. The free energies are plotted against  $\delta$  for several temperatures in Fig. 4, showing explicitly the occurrence of a second

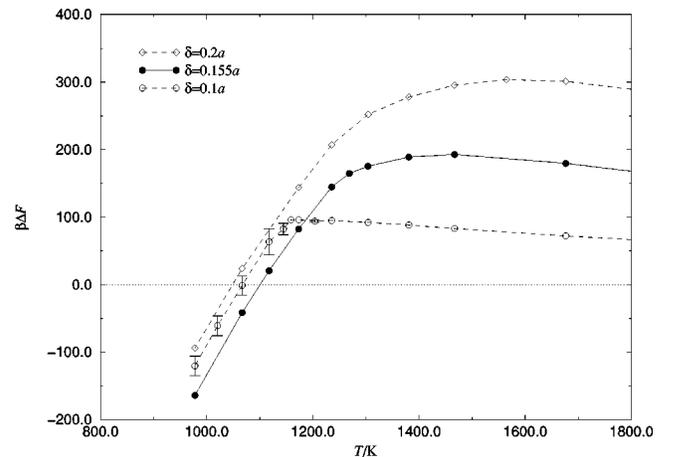


FIG. 3. Free energy vs temperature for three values of  $\delta$ .  $\beta\Delta F = \beta[F(\delta) - F(0)]$  is for 1024  $\text{Ag}^+$  ions. The error bars for  $\delta=0.1$  show the uncertainties arising from the hysteresis effect.

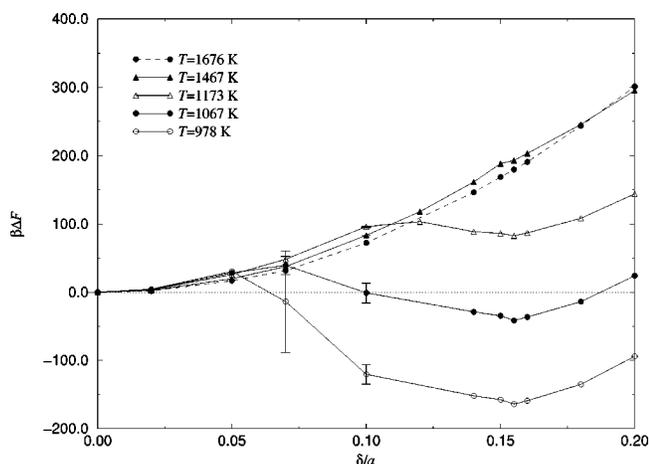


FIG. 4. Free energy vs  $\delta$  for several temperatures. No error bars are necessary for very small  $\delta$ 's since the transition temperature is lower than the region of interest here.

minimum near  $\delta=0.155a$  at low temperatures. The high transition temperature compared to Madden's result (400 K) must come from the simple lattice approximation in our simulations. Fluctuations in the positions of  $\text{Ag}^+$  ions as well as  $\text{I}^-$  ions around potential energy minima, or occupation of other than tetrahedral sites by  $\text{Ag}^+$  were not allowed.

In summary, we have shown that an ordering transition of the  $\text{Ag}^+$  ions like that observed in Madden's simulation may be accompanied by a deformation of the  $\text{I}^-$  lattice even within the constraint of a cubic unit cell, as suggested in Ref. 5. The two steps can occur together, rather than the ordering tendency of  $\text{Ag}^+$  being the initiator of the transition.<sup>3</sup> We found no order-disorder transition within the  $\alpha$  phase as proposed by Perrott and Fletcher.<sup>7</sup> Possible candidates for the anisotropic intermediate phase seen by Raman experiments<sup>8</sup> are the disordered state or the ordered state near the second-order transition (where  $\text{Ag}^+$  ions are not completely ordered) with a deformed  $\text{I}^-$  lattice seen in our simulation, but those

states are found to be unstable or only metastable within the lattice approximation. However, one cannot exclude this possibility for a more realistic system or for real AgI where the density and shape of the unit cell can also change.

In Madden's and our studies, the  $\alpha$  to  $\beta$  transition was not allowed for theoretical purposes, but Tatsumisago *et al.*<sup>10</sup> found that real  $\alpha$ -AgI can be stabilized in AgI-based glass matrices even below the transition temperature of pure AgI. The  $\alpha$  to  $\beta$  transition in those composites are probably prevented because a large strain energy would be produced due to the volume change and deformation of the lattice that accompany the transition. Heat-capacity and electrical conductivity measurements<sup>10</sup> also showed that  $\alpha$ -AgI in a glass matrix undergoes an order-disorder transition. Because the resulting ordered phase is not the  $\beta$  phase and has large lattice strain,<sup>10</sup> it might be related to an ordered phase involving deformation of the  $\text{I}^-$  lattice discussed above, although  $\alpha$ -AgI in the complex environment of a glass matrix may not give an ideal uniform deformation. It is also interesting to note that some of the close-packed polytypes found at intermediate pressures in a molecular-dynamics study by Rains *et al.*<sup>11</sup> have structures that can be formed by sliding of (110) planes in the bcc structure in different directions, just as in the case of the  $\beta$  phase.

We applied a density-functional formalism to the same problem, as outlined in Ref. 5, but it was not successful. The use of a homogeneous reference state gives a lower free energy for larger deformations even for very large deformations, which is contrary to the x-ray experiments.<sup>9</sup> When the ideal lattice gas was used as a reference state, we were not able to get convergent solutions for the direct correlation functions.

This work was supported by the National Science Foundation through Grant No. CHE 9800074 and through the Materials Research Science and Engineering Center at the University of Chicago.

<sup>1</sup>M. Parrinello, A. Rahman, and P. Vashishta, Phys. Rev. Lett. **50**, 1073 (1983).

<sup>2</sup>G. Szabó, J. Phys. C **19**, 3775 (1986).

<sup>3</sup>P. A. Madden, K. O'Sullivan, and G. Chiarotti, Phys. Rev. B **45**, 10 206 (1992).

<sup>4</sup>W. G. Burgers, Physica (Utrecht) **1**, 561 (1934).

<sup>5</sup>C. Seok and D. W. Oxtoby, Phys. Rev. B **56**, 11 485 (1997).

<sup>6</sup>J. P. Hansen, Phys. Rev. A **8**, 3096 (1973).

<sup>7</sup>C. M. Perrott and N. H. Fletcher, J. Chem. Phys. **50**, 2770 (1969).

<sup>8</sup>A. Fontana and G. Mariotto, Phys. Rev. B **21**, 1102 (1980); G. Mariotto, A. Fontana, E. Cazzanelli, F. Rocca, V. Mazzacurati, and G. Signorelli, *ibid.* **23**, 4782 (1981).

<sup>9</sup>L. W. Strock, Z. Phys. Chem. Abt. B **25**, 441 (1934).

<sup>10</sup>M. Tatsumisago, T. Saito, T. Minami, M. Hanaya, and M. Oguni, J. Phys. C **98**, 2005 (1995).

<sup>11</sup>C. A. Rains, J. R. Ray, and P. Vashishta, Phys. Rev. B **44**, 9228 (1991).