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USE OF COMPUTER SIMULATION TECHNIQUE TO STUDY ATOMIC MIGRATION

IN SOLIDS*

by

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P. Vashishta
Materials Science and Technology Division
ARGONNE NATIONAL LABORATORY
Argonne, IL 60439

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ly the factor $\alpha_{AgI} z^2$ in the charge-dipole interaction term as well as W_{AgI} and W_{AgAg} in the van der Waal term vanish. Furthermore, a posteriori it is found that the van der Waal's interaction term W_{II} does not seem to play an important role; however, it was retained in all our calculations. We have used $\alpha_I = 6.52 \text{ \AA}^3$, $e_I = 3.13 \text{ eV}$. The number of unknowns is reduced by taking all $A_{ij} = A$ i.e. each "contact" is assumed to contribute the same repulsive energy A .

Since with the new MD technique^{3,5}, which allows for a dynamical variation of the shape and size of the cell, 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 change α_{Ag} from 0.63 to 0.53 $\text{\AA}$ and leaves $\sigma_I = 2.20 \text{ \AA}$ unchanged. It should be noted, however, that $\sigma_{Ag} = 0.53 \text{ \AA}$ and old exponents $n_{II} = n_{AgI} = n_{AgAg} = 7$ produced unsatisfactory results when used in conjunction with the new molecular dynamics technique.

The potential functions were refined by using different values of the exponents, n_{ij} . Using the experience with ionic solids we kept $n_{II} = 7$ but chose a higher value for the (Ag-Ag) repulsive exponent, $n_{AgAg} = 11$. A mean of the two values was taken for the (Ag-I) term, $n_{AgI} = 9$. The value of charge, $Z = 0.6$, was kept the same as before. We shall call the potential function with these constants as the "modified potential". We show below the modified potential in full detail in Eq(2)³.

$$\begin{aligned} V_{AgAg} &= H_{AgAg}/r^{11} + 0.36/r & (2) \\ V_{AgI} &= H_{AgI}/r^9 - 0.36/r - 1.1736/r^4 \\ V_{II} &= H_{II}/r^7 + 0.36/r - 2.3472/r^4 - 6.9331/r^6 \end{aligned}$$

where

$$\begin{aligned} H_{AgAg} &= A(\sigma_{Ag} + \sigma_{Ag})^{11} = 0.014804 \\ H_{AgI} &= A(\sigma_{Ag} + \sigma_I)^9 = 114.48 \\ H_{II} &= A(\sigma_I + \sigma_I)^7 = 446.64 \\ A &= 0.010248. \end{aligned}$$

The length is measured in $\text{\AA}$ units and energy in units of $e^2/\text{\AA}$ (-14.40 eV).

It is our hope that a single set of pair potentials of the form given above in Eq(2), where the constants are determined from a low temperature structure, will be adequate to describe not only the structural and dynamical properties of α -AgI with the "old" as well as with the "new" MD technique and the structural phase transition $\alpha \rightleftharpoons \beta$, but also the high pressure phases of AgI.

3. FREQUENCY DEPENDENT CONDUCTIVITY AND HAVEN'S RATIO IN α -AgI

For α -AgI, among the structural properties we have studied are: partial pair correlation functions for (Ag-Ag), (Ag-I) and (I-I), mean square displacement of iodines as a function of temperature, etc. The dynamical properties examined include cation self-diffusion and its temperature dependence, nature of cation jumps, bias in successive jumps, velocity auto-correlation functions and their fourier transforms which reflect the vibrational density of states for silver and iodine motion, current-current correlation function and its fourier transform which determines the frequency dependent ionic conductivity and Haven's ratio¹⁻³. Our calculated results are in good agreement with experiments^{3,7}.

We shall now briefly discuss the results for the frequency dependent conductivity and Haven's ratio. The results for other structural and dynamical properties mentioned can be found in reference 3.

For the calculation of ionic conductivity in α -AgI it is necessary to calculate the corre-

lation of the charge current fluctuations. We use the basic Kubo relation^{8,9}

$$\sigma(\omega) = \frac{1}{30k_B T} \int_0^\infty \langle \vec{J}(t) \cdot \vec{J}(0) \rangle e^{i\omega t} dt \quad (3)$$

where σ is the conductivity, Q the volume and

$$\vec{J}(t) = \sum_j q_j \vec{v}_j(t) \quad (4)$$

is the charge current where $q_j = Ze_j$ is the charge of the j^{th} particle with velocity $\vec{v}_j(t)$ at a time t . We will now transform the expression for $\sigma(\omega)$ in a more convenient form for the calculation of Haven's ratio¹⁰.

Let us define $\vec{N}(t) = \sum_j q_j \vec{r}_j(t)$, then $\vec{J}(t) = \dot{\vec{N}}(t)$ and

$$2\langle \vec{J}(t) \cdot \vec{J}(0) \rangle = \frac{d^2}{dt^2} \langle (\vec{N}(t) - \vec{N}(0))^2 \rangle. \quad (5)$$

Let $\gamma(t)$ denote the normalized current-current correlation function

$$\gamma(t) = \langle \vec{J}(t) \cdot \vec{J}(0) \rangle / \langle J(0)^2 \rangle \quad (6)$$

then

$$\sigma(\omega) = \frac{\langle J(0)^2 \rangle}{30k_B T} \int_0^\infty \gamma(t) e^{i\omega t} dt \quad (7)$$

where $\langle J(0)^2 \rangle$ is simply

$$\langle J(0)^2 \rangle = 3k_B T \sum_j (q_j^2 / m_j) \quad (8)$$

and in the case of $\alpha\text{-AgI}$

$$\langle J(0)^2 \rangle = 3k_B T q^2 / (\nu N_{\text{Ag}}) \quad (8')$$

where $\nu^{-1} = m_{\text{Ag}}^{-1} + m_{\text{I}}^{-1}$, and since all the silver ions are mobile in $\alpha\text{-AgI}$, $N_{\text{Ag}} = N_{\text{I}} = N$. Hence for $\alpha\text{-AgI}$ we get

$$\sigma(\omega) = \frac{q^2 N_{\text{Ag}}}{\nu Q} \int_0^\infty \gamma(t) e^{i\omega t} dt. \quad (9)$$

It is usual to express $\sigma(\omega=0)$ as a diffusion constant. This conversion (the Hernst-Einstein expression) at any ω can be written as

$$D_0(\omega) = \frac{Qk_B T}{q^2 N_{\text{Ag}}} \sigma(\omega) \quad (10)$$

$$D_0(\omega) = \frac{k_B T}{\mu} \int_0^\infty \gamma(t) e^{i\omega t} dt \quad (11)$$

in complete analogy with the equation for particle (i.e. tracer) diffusion

$$D_{\text{Ag}} = \frac{k_B T}{m_{\text{Ag}}} \int_0^\infty \phi_{\text{Ag}}(t) dt \quad (12)$$

where $\phi(t)$ is the normalized velocity autocorrelation function for Ag

$$\phi(t) = \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle / \langle v_i^2(0) \rangle. \quad (13)$$

The so called Haven's ratio¹⁰ is then

$$D_{\text{Ag}} / D_0(\omega=0) = 1.68 / 3.4 \sim 0.5.$$

A plot of $D_0(\omega)$ is shown in Fig.1

FIGURE 1. $D_0(\omega)$ in units of $10^{-5} \text{ cm}^2/\text{sec}$ from the Fourier transform of the normalized current-current correlation function, Eq.(11). Solid dots were obtained when the correlation function was truncated in time at 3 ps; when a smoothing function was used one obtained the continuous curve.

The fact that the experimental value¹¹ of the ratio is -0.6 again emphasizes the correctness of the model of α -AgI that we are dealing with. Our calculated value of -0.5 for the Haven's ratio is also in good agreement with the theoretical estimates¹².

4. STRUCTURAL TRANSITIONS IN AgI

As a function of temperature and pressure (or density), silver iodide undergoes a number of interesting structural transitions. It should be noted however that within the context of molecular dynamics and Monte Carlo techniques structural transitions are amongst the most difficult to study.

The results described in the previous section were obtained using "traditional MD" or "old MD" technique by which we mean that in the MD calculation the system was confined in a fixed volume of constant shape with periodic boundary conditions. The iodine lattice, confined in a cubic cell and given a bcc structure, can not undergo a structural transition and transform e.g. into an hcp or fcc structure when the "old MD" technique is used.

The most remarkable feature in the behaviour of AgI is the structural difference between γ - and β -AgI on the one hand and α -AgI on the other. The former have a close packed iodine structure and silver diffusion is absent while in α -AgI the iodines form a bcc lattice and silver ions show a large constant of self-diffusion.

It has now become possible to study structural change by computer simulation. Recent work of Parrinello and Rahman⁵ has shown that, by using appropriate Lagrangian one can set up a molecular dynamics calculation in which both the volume and the shape of the periodically repeating cell change with time. The direction of the change is dictated by the difference between the externally applied stresses and those generated internally because of the velocities

of the particles and the forces acting between them.

A brief comparison between the old and new MD techniques is given in the following table.

=====	
Old MD	New MD
Constant cell volume	Variable cell shape and cell volume
Number of particles constant	Number of particles constant
Density constant	Pressure constant
Pressure varies with time	Density varies with time
Energy $E = \text{constant}$	Enthalpy $H = E + pQ$ = constant
3N variables	3N + 9 variables

The additional 9 dynamical variables describe the time dependence of the shape of the MD cell. The change in shape of the MD cell is determined by the difference between internal (kinetic + potential) stress tensor and the externally applied stress

Parrinello, Rahman and Vashishta⁶ have used this new technique to study structural transformations in AgI. The aim of this calculation was to invent a simple potential function scheme for AgI which will make the iodines adopt a bcc structure at elevated temperatures with the silver ions jumping between tetrahedral sites in the manner discussed in the previous section. On cooling the system the interaction potentials all on their own should modify the bcc structure into a close packed one while at the same time the silver ions should settle down into a four coordinated non diffusive configuration with respect to the iodines.

It is important to understand the following geometrical facts when studying the bcc to fcc transformation of the iodine lattice in α to γ phase change of AgI using the "new MD" technique in which the shape and size of the MD cell

FIGURE 2

Schematic representation to show that a body centered tetragonal (marked shoe box in the figure) lattice with edges $1, 1, \sqrt{2}$ is an fcc structure

change with time. As shown in Fig 2, consider a bcc lattice in a cube whose side is of length a . The plane ABCD passing through the face diagonal, is a rectangle with sides $\sqrt{2}a$ and a . It has an atom at the center and four atoms at the corners. If the cube is stretched along the edge BC such that $A'B' = B'C'$, then $A'B'C'D'$ is indeed a square and the (100) face of an fcc lattice with lattice constant $\sqrt{2}b$. The main point of this illustration is to convey the fact that a body centered tetragonal lattice (shoe box in Fig 2) with edges $1, 1, \sqrt{2}$ is an fcc structure and inversely a tetragonal face centered structure with edges $\sqrt{2}, \sqrt{2}, 1$ is a bcc structure. Hcp and simple cubic structures can also be generated out of a body centered tetragonal structure by appropriate changes of lengths, angles and the position of the body center.

A well equilibrated 500 particle α -AgI system in a "cube" at 700K with an apparent n.n. (I-I) coordination of 14, (Ag-Ag) coordination of 4 and having a constant of self-diffusion $D_{Ag} = 4 \times 10^{-5} \text{ cm}^2/\text{sec}$ was cooled to 350K. Structural and dynamical behavior of iodines and silvers was monitored as a function of time.

Only after 1,000 time steps ($2 \times 10^{-11} \text{ sec}$) it

became clear that n.n. (I-I) coordination was changing from 14 toward 12 indicating a structural change of the iodine lattice from bcc toward fcc or hcp. The n.n. (Ag-Ag) coordination remained unchanged from the value 4. The system was well equilibrated for 2,500 time steps ($5 \times 10^{-11} \text{ sec}$) and no further changes in the n.n. (I-I) or (Ag-Ag) coordinations were observed as a function of time. The constant of self-diffusion for both silver and iodine was found to be zero showing that both types of ions oscillate around stable mean positions. The crystallographic B-factors were found to be $B_{Ag} = 6.3 \text{ \AA}^2$ and $B_I = 4.0 \text{ \AA}^2$. The partial pair correlation functions for (Ag-I) and (I-I) are shown in Fig 3. The nearest neighbor iodine and silver coordinations clearly indicate that the α -AgI system has transformed into a zincblende or Wurtzite structure. Upon examining the MD cell structure it was found that the cubic shape had transformed into a non-cubic cell. From the (I-I) pair correlation function in Fig 3 it cannot be determined conclusively whether the iodine lattice is fcc or hcp, though the structure around 10 $\text{\AA}$ indicates an hcp structure. To sharpen the peaks in the (I-I) pair correlation

FIGURE 3

Partial pair correlation functions for AgI after the system is cooled from 700K. On the left, the first peak of (Ag-I) pair correlation; the number of Ag under the peak is 4. The complete (I-I) pair correlation is also shown; the first peak contains 12 neighbours. Note the arrow at 9.75 $\text{\AA}$ indicating a total coordination of 55.6 iodines. For a perfect fcc and hcp lattice the number is 54 and 56, respectively.

function, the system was quenched. The results are shown in Fig 4.

Integrating the (I-I) pair correlation up to the minimum at 9.8 Å (Fig 4) the value obtained for the coordination number is 55.6. In an hcp structure this coordination is 56 and it is 54 in an fcc arrangement. The discrepancy between 55.6 and the ideal value 56 is probably due to stacking faults in the closed packed structure. Such defects have been found in similar calculations by Parrinello and Rahman⁵. Thus we conclude that the $\alpha \rightarrow \beta$ transition was successfully achieved upon cooling α -AgI.

The $\beta \rightarrow \alpha$ transition was studied by heating to 495K the β -AgI system obtained as explained above. After 1000 time steps the n.n. (I-I) coordination started to be more than 12. A well thermalized system at 495K, Fig 5, clearly shows a n.n. (I-I) coordination of 14: the characteristic value for a heated bcc lattice. Silver ions were found to be diffusing with $D_{Ag} = 2 \times 10^{-5} \text{ cm}^2/\text{sec}$ and n.n. (Ag-I) coordination was

FIGURE 4

Partial pair correlation functions for AgI at 343.8K on quenching to a very low temperature to eliminate thermal vibration. On the left, the (Ag-I) peak at 2.8 Å is sharpened. The (I-I) pair correlation shows much more structure upon quenching. The first peak at 4.6 Å shows a coordination of 12. The ratio between (I-I) and (Ag-I) n.n. distance is $\sqrt{3}/3$. Also the peaks containing 6, 2, 18, 12 and 6 particles are seen clearly. There are six peaks up to 9.75 Å containing a total of 56 particles; the two peaks marked hcp contain 2 and 12 particles. This shows that iodines form an hcp lattice and that the pair correlation are for β -AgI.

determined to be tetrahedral. To confirm the structure of the iodine lattice the system was quenched. This led to a clear identification of the first two shells of the bcc lattice each containing 8 and 6 particles, respectively.

Using several MD calculations we studied the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transition; these calculations indicated that the transition temperature lies between 470K and 490K. This is in satisfactory agreement with the experimental value of 420K¹³. The calculated transition temperature will decrease as the number of particles in the system is increased⁹, thus further improving the agreement between the calculation and the experiment.

The principal shortcoming of the potential scheme is that it does not produce the experimentally observed density increase in $\beta \rightarrow \alpha$ transition. All the structural and dynamical properties of AgI, however, are in semi-quantitative accord with experiments.

One important quantity which can be accura-

FIGURE 5

Partial pair correlation functions for AgI obtained by heating from β -AgI at 343.8K. On the left, first peak of (Ag-I) containing 4 particles. The peak in (I-I) correlation, continuous curve, shows an apparent coordination of 14. This is characteristic of a thermally agitated bcc lattice. Upon quenching the system, (I-I) correlation, dashed curve, shows two peaks containing 8 and 6 particles, respectively. This confirms that iodines form a bcc lattice and that the figure describes the pair correlation of α -AgI.

tely measured by EXAFS is the first peak of the (Ag-I) pair correlation function. In Fig 6 we compare our new MD results with the experimental results of Hayes and Boyce¹⁴. The agreement between the EXAFS and the new MD results is indeed very good. To account for the discrepancy of $\sim 0.05\text{\AA}$, it is probably necessary to make further MD and EXAFS investigations.

FIGURE 6
The first peak of the (Ag-I) pair correlation function in α -AgI. New MD results based on modified potential, Eq.(2), are in good agreement with EXAFS results of Hayes and Boyce.

5. CRYSTAL GROWTH FROM MOLTEN AgI

In the previous section we discussed the structural transformation in which a system of 500 particles interacting via a radially symmetric pair-wise potential transforms from the non-diffusing β -AgI to superionic α -AgI and vice versa.

We can now ask the following question: Would we get crystalline phases of α - and β -AgI if we were to cool a system of molten AgI to different temperatures and observe the crystal growth? The answer is indeed yes! We have successfully shown that within our model of AgI when particle interactions are described by the "modified potential" given in Eq.(2) and "new molecular dynamics" technique as outlined in sec.4 is used, the molten AgI crystallizes into the α - and

β -phases depending on the temperature to which the melt is cooled.

Preparation of the liquid: A 500 particle system of β -AgI, whose radial distribution functions are shown in Fig.3, was heated from 343.8K to 1025.7K. The equilibrated liquid showed constants of self-diffusion for Ag and I $D_{Ag} = 10 \times 10^{-5} \text{ cm}^2/\text{sec}$ and $D_I = 5 \times 10^{-5} \text{ cm}^2/\text{sec}$, respectively.

Homogeneous Nucleation: To cool the system of molten AgI, a certain amount of thermal energy was removed by reducing the kinetic energy of all the particles. This was done in 10 molecular dynamics steps ($2 \times 10^{-13} \text{ sec}$). After the removal of desired amount of thermal energy, the system was allowed to evolve uninterruptedly and the time evolution of the system was monitored, and the trajectories of the particles were analyzed. In brief, the system evolves so as to bring the potential energy of the particles in equilibrium with the reduced temperature of the system.

Nucleation occurs after about 5,000 steps (10^{-10} sec) and the Iodines begin to show a shell structure. Results for crystallization of the α -phase from the melt are summarized in Fig.7.

Homogeneous Nucleation

FIGURE 7
A schematic representation of the nucleation and crystal growth.

Several calculations were carried out where starting from the 1025.7K AgI system, different amount of thermal energy was removed from the melt. We successfully obtained the α and β phases whose properties were in agreement with those of our earlier calculations and with the experiments. From our nucleation studies the $\alpha \rightleftharpoons \beta$ transition temperature was estimated to be ~ 460 K in agreement with the studies on $\alpha \rightleftharpoons \beta$ structural transformation calculations discussed in sec.4. A summary of nucleation and crystal growth studies is given in Fig.8. A detailed discussion of these nucleation and crystal growth studies will be presented in the future.

FIGURE 8

A summary of the nucleation and crystal growth studies. When the same melt was cooled from 1025.7K to different temperatures, α and β phases of AgI were obtained depending upon the final temperature of the system.

6. MOLECULAR DYNAMICS STUDY OF Ag_2S

Structure and dynamics of superionic conductor Ag_2S : A model of the superionic conductor Ag_2S is proposed and studied by molecular dynamics technique using effective pair-potentials derived within the potential function scheme discussed in sec.2¹⁵. Interesting experimental results have been obtained by Cava and McWhan¹⁶ who have studied x-ray diffuse scattering in $\beta\text{-Ag}_2\text{S}$. They observe in the superionic phase anisotropic discs of intensity in the

vicinity of the point $Q = (1.6, 1, 0)$. In addition, Grier et al¹⁷ in their inelastic neutron scattering experiments observe anomalous intensities similar to those observed in diffuse x-ray scattering. A low energy ($\sim 2\text{meV}$) excitation is also observed in the non-superionic phase which disappears in the superionic phase.

We have calculated a number of structural and dynamical properties of Ag_2S ¹⁵. For a detailed discussion of our calculation and the comparison with the experimental results see the paper by Vashishta, Ebbsjö and Dejus in these proceedings.

Fractal Dimensions of Ionic Trails and Isosets in Superionic and Molten Ag_2S : Although the ions of superionic conductors obey well defined equations of motion, the rapidly changing environment of each diffusing ion results in its following a trajectory that, to a microscopic observer, appears as a random walk in space. The fractal behavior of Brownian motion has two aspects¹⁸, one of which is associated with ionic trajectories and the other with Brownian Isosets. The self-similarity in the ionic trajectories and Brownian isosets as a function of the length of ionic trajectories and temperature of the system (superionic and molten phases) are discussed by Vashishta, Ebbsjö, Kalia and de Leeuw in these proceedings.

7. CONCLUDING REMARKS

The modified potential function given in Eq.(2) with new molecular dynamics technique successfully describe structure and dynamics of $\alpha\text{-AgI}$, the $\alpha \rightleftharpoons \beta$ structural transitions and homogeneous nucleation and crystal growth of the α and β phases from molten AgI. We have also studied structural transitions to the rocksalt structure under external pressure.

Structure, Dynamics¹⁹ and fractal dimensionalities of ionic trajectories and isosets²⁰ are studied for Ag_2S . The origin of the anomalous diffuse scattering intensities are explained and

their origin elucidated.

We are working on the following problems:

Microscopic mechanisms of structural transitions and structure of defects and mixed phases; symmetries of critical nucleus in crystal growth studies when the same liquid crystallizes into α , β and rocksalt structures under different temperature and density conditions; structure and dynamics of glasses.

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