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Ionic Motion in α-AgI

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A molecular-dynamics study of silver diffusion in superionic conductor α-AgI is performed. Interionic potentials are constructed using Pauling's ideas of ionic radii. The diffusion constant for silver and its temperature dependence are in good agreement with experiment. Good agreement is also obtained for the silver density map with the experiment of Cava, Reidinger, and Wuensch.

α-AgI has been extensively studied[1] because of its interest as a solid fast ion conductor (often called superionic conductor). In this Letter we present a molecular-dynamics (MD) study of this material. Our calculations show that in the computer model the diffusion constant of Ag^+ and their distribution in the interstices of the thermally agitated iodine lattice are faithfully reproduced. In addition, MD provides a detailed picture of the complete process of self-diffusion. The central issue in all such calculations is the construction of potential functions which, when used in the MD calculations, produce structural and dynamical correlations which compare favorably with those observed in the laboratory. The MD trajectories then porvide a wealth of microscopically detailed information which can be very hard to obtain by conventional experimental means. A study of CaF_2 along these lines has already been reported.[2]

For CaF_2 the ionic model given by Kim and Gordon[3] is sufficiently good.[2] In α-AgI this problem is not so straightforward. We have constructed effective pair potentials which provide a simple means of describing, with reasonable accuracy, the structural and dynamical properties of α-AgI. Schommers[4] had to use quite unphysical forces to keep the iodine lattice vibrating as a stable structure; in his model each iodine was attached to bcc lattice position by harmonic springs. In our model no such unphysical elements have been introduced. For AgI, we use

$$V_{ij}=\frac{A_{ij}(\sigma_i+\sigma_j)^n}{r^n}+\frac{Z_iZ_je^2}{r}-\frac{1}{2}(\alpha_iZ_i^{\,2}+\alpha_jZ_j^{\,2})\frac{e^2}{r^4}-\frac{W_{ij}}{r^6}, \qquad (1)$$

where i, j describe the type of ions; A_{ij} the repulsive strength; σ_i, σ_j the particle radii; α_i, α_j the electronic polarizabilities. If σ's, α's, and W's are known, we need to determine five parameters (namely A_{ij}'s, n, and $|Z_i|=|Z_j|$). By assuming $A_{ij}=A$, the situation is considerably simplified. The repulsive term then implies that each ionic "contact" contributes energy A, i.e., the coefficient of r^{-n} is scaled according to the sum of particle radii. Low-temperature crystal structure, cohesive energy, and compressibility may be used to determine these three parameters.

However, AgI, and α-AgI in particular, pose special problems in this respect. It is certainly not purely ionic and the estimate of the cohesive energy from the Born-Haber cycle can be in considerable error. The γ-AgI compressibility, however, is known[5] ($\simeq 1\times10^{-11}$ cm^3/erg) and from phonon dispersion measurement[6] there is evidence of $|Z|\simeq 0.6$.

As to the σ's, Pauling's[7] concept of ionic radii is a means of expressing the bond length. Using the concept literally, we write $\sigma_{Ag}+\sigma_I=$Ag-I distance and $2\sigma_I=$I-I distance. Because of the large size differences between Ag^+ and I^- both Ag-I and I-I interactions together determine the crystal structure. We get $\sigma_I = 2.2$ Å and $\sigma_{Ag} = 0.63$ Å; σ_{Ag} is less than the ionic radius of Ag^+, presumably because of the presence of covalent interaction. It should be realized that we are imposing a pairwise additive effective-interaction scheme for the purpose of doing molecular-dynamics simulations with relative facility.

Thus, using the compressibility as a guide, we choose $n = 7$; with $|Z| = 0.6$ and with the condition that crystal-energy minimum occur at the lattice distance = 5.06, (with $\alpha_{Ag} = W_{AgAg} = W_{AgI} = 0$, $\alpha_I = 6.52$, $W_{II} = 6.93$), we determine $H_{AgI} = 17.893$, $H_{AgAg} = 0.062$, $H_{II} = 394.934$, where $H_{ij} = A(\sigma_i + \sigma_j)^n$. Here Å is the unit of length, $e^2/\text{Å} = 14.39$ eV is the unit of energy. The potential functions are plotted in Fig. 1(a).

In the final analysis, MD results for α-AgI themselves serve as justification for the validity of the chosen potential functions.

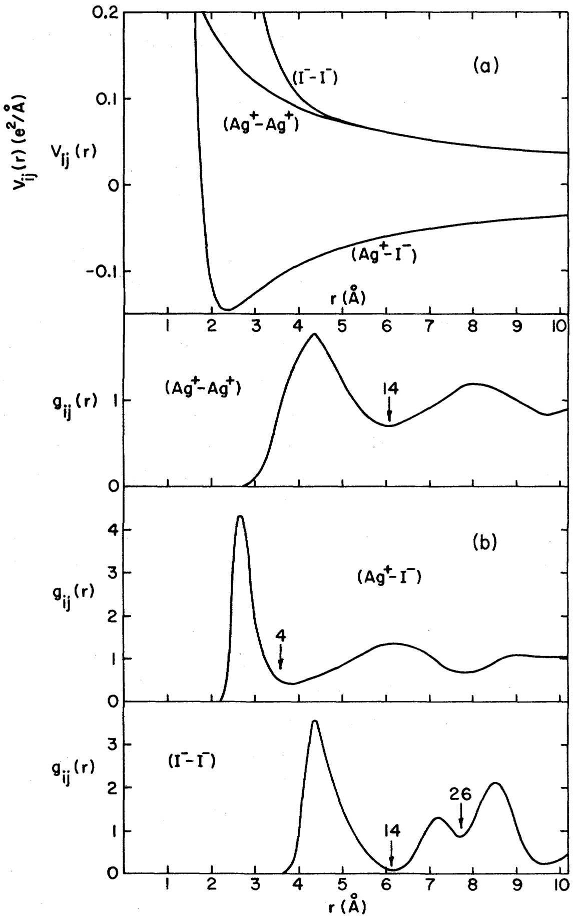

FIG. 1. (a) Interionic potentials in units of $e^2/\text{Å} = 14.39$ eV; (b) pair correlation functions.

The calculations were performed on a 256-particle system in a cubic cell of length 20.342 Å (mass density 5.928 g cm^{-3}) in which the iodines continue to form a thermally agitated bcc lattice with the lattice constant 5.0855 Å. Coulomb interactions were taken into account in the usual way.[8] The integration step was 2.5×10^{-14} sec and was quite satisfactory for energy conservation for several thousand steps. The calculation was initiated by placing the iodines in a bcc structure and the Ag ions in suitable tetrahedral sites.

After sufficiently long initial aging of the system (which was much longer than 10 psec), and because of large self-diffusion for Ag^+, the starting conditions have no effect on the results reported here. The calculations were performed at 430, 603, and 761 K, at the mass density mentioned above.

The correlation between the positions of the iodines clearly shows (as in all bcc structures at high temperatures) a coordination number of 14 (eight nn's + six nnn's) under the main peak of the radial distribution function. On the other hand, Ag^+-I^- correlation function gives a coordination of 4. The pair correlation functions are shown in Fig. 1(b). The main peaks in the I^--I^- and the Ag^+-Ag^+ pair correlation occur at about the same distance, but the former is much sharper. However, Ag^+-Ag^+ coordination number continues to be about 14, precisely the same as in I^--I^- structure. This structural information by itself cannot lead to any conclusion regarding the difference between the dynamical behavior of the two types of ions.

Since the iodines form a well-defined bcc structure, it is reasonable to use it as a reference frame to look at the presence of Ag ions in various positions. The most interesting region is a (100) face of the lattice and the presence of Ag ions in a plate of thickness 5.0855/16 Å was monitored. Using the density at the tetrahedral sites $[(\frac{1}{4}\,0\,\frac{1}{2})$ positions$]$ as a reference value, Fig. 2 shows the density along various paths on the cube face. The subsidiary maximum at (0.4 0 0.4) when going along *I*–*S*–*C* is unambiguous and was found by Cava, Reidinger, and Wuensch.[9] It will be most instructive to use the density distributions of Ag and I ions to calculate the diffracted intensity patterns for comparison with the experiment The local maximum just mentioned[9] will be discussed below.

The constant of self-diffusion *D* was determined by calculating the mean-square displacement

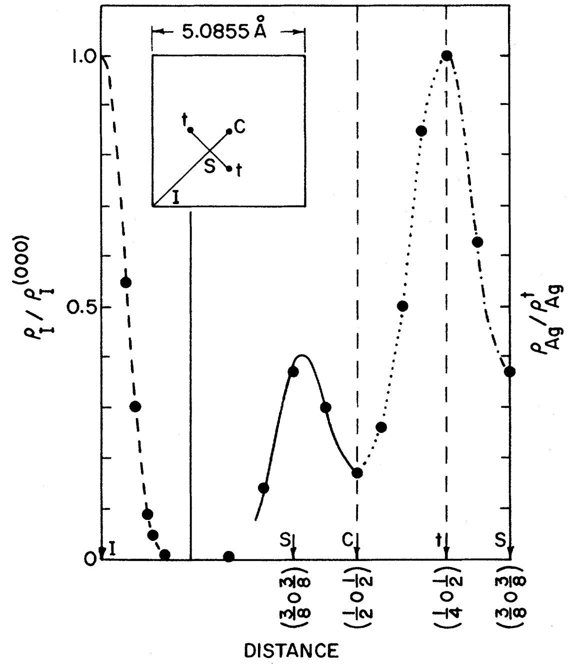

FIG. 2. Density distribution of I⁻ and Ag⁺ on the (100) face at 157°C. In the inset *I*, *C*, and *t* mark the corner (iodine), center, and tetrahedral positions, respectively. Solid line is the only experimental curve (from Ref. 9) in the figure. Solid circles are MD calculations. Dotted, dashed, and dash-dotted lines joining solid circles are for clarity: dashed line, $\rho_{I^-}/\rho_{I^-}^{(000)}$ along line *I*–*S*–*C*; solid line $\rho_{Ag^+}/\rho_{Ag^+}^{\,t}$ along line *I*–*S*–*C* compared with experiment; dotted line, $\rho_{Ag^+}/\rho_{Ag^+}^{\,t}$ along line *C*–*t*; dash-dotted line, $\rho_{Ag^+}/\rho_{Ag}^{\,t}$ along line *t*–*S*. Point *S* is a local minima along line *t*–*S*–*t*.

$\langle[\vec{r}(t+s)-\vec{r}(s)]^2\rangle$ for each ion type. As in the case of CaF_2,[2] the asymptotic time dependence of this quantity shows that Ag^+ has a large liquid-like D, whereas I^- has $D=0$. The asymptotic value of the function for I^- gives the extent of the Debye-Waller thermal cloud. In Figs. 3(a) and 3(b), calculated values of D and the mean-square displacement of iodine, B, are compared with the experiments.[9,10] For both quantities agreement is good, leading us to conclude that we are indeed dealing with a realistic model system for α-AgI.

Jacucci and Rahman[11] have analyzed the F^- diffusion in CaF_2 to show that the F^- motion is dominantly a jump in the [100] direction with a residence time of about 6 psec. It was already apparent from the behavior of the fourth moment of displacement, i.e., of $\langle[\vec{r}(t+s)-\vec{r}(s)]^4\rangle$, that the spreading of the probability distribution of the F^- ions [i.e., the Van Hove[12] function $G_s(\vec{r},t)$] was quite unlike its behavior in simple liquids.

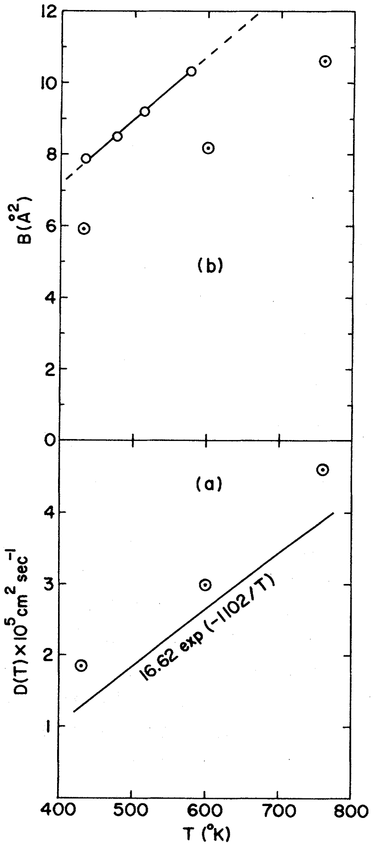

FIG. 3. (a) Constant of self-diffusion, $D(T)$, for Ag^+ in α-AgI. Circle with dot, MD calculation; continuous curve, experiment (Ref. 10). (b) Mean-square displacement, B, of iodine in α-AgI. Circles with dot, MD calculation; open circles connected by solid line, experiment (Ref. 9).

Using the method of Jacucci and Rahman, we find that the Ag ions diffuse by a jump process with jump frequency 0.34×10^{12} sec^{-1}; 82% of the jumps occur between nearest-neighbor tetrahedral sites (which can be characterized as [110] jumps), 9% in the [002] and 7% in the [112] directions from one *t* to the nearest *t* site in that direction. When successive [110] jumps occur, our analysis shows that there is no bias towards a rotation around the "*t*" sites which form a square on a (100) face of the bcc lattice. Each *t* site has four nearest-neighbor *t* sites (in [110] directions) and the analysis shows that when successive [110] jumps occur, there is a bias towards backward jumps in comparison with the other three possibilities which, so stated above, occur with equal probability. We find that among successive [110] jumps there are 40% in the backward direction and 20% each in the other three (in the unbiased case these would all be 25%).

Since the relative maximum in density at (0.4 0 0.4) in Fig. 2 is situated essentially along the line joining "*t*" sites, it is relevant to ask whether this site plays a role as a residence site. When the density is plotted from one "*t*" site to another, the location (0.4 0 0.4) is *a local minimum and not a maximum*; along this line the values of the density decrease from unity at ($\frac{1}{4}\,0\,\frac{1}{2}$) to 0.63 at (0.31 0 0.44) and then to 0.37 at (0.375 0 0.375), point *S*. A concise manner of describing the situation is that the Ag ions reside at the "*t*" sites for about 3 psec, developing a thermal cloud of half-width 0.6 Å in the (100) plane and move between the "*t*" sites along rather narrow channels.

The work reported here makes it quite clear that using classic notions regarding the interparticle potentials in ionic materials it is possible to construct model systems which reproduce with fair precision the observed structural and dynamical behavior of α-AgI. We are therefore proceeding further on an analysis of the structure and properties of other forms of AgI as well as other materials like CuI. The analysis of density fluctuations in α-AgI is now in progress.

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Elementary Excitations in the Fermi Glass

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We evaluate the lifetime of quasiparticles in the Fermi glass. An anomalous contribution to the lifetime is found. It is shown that this effect leads to a $T^{1/4}$ law for the dc conductivity of a disordered system.

The importance of understanding the effects of electronic correlations in disordered systems has attracted some attention[1] in recent years —most notably, in interpreting various observations in the inversion layer at the semiconductor surface. In particular, in these systems where the number of carriers may be varied, density-dependent effective masses are reported[2] as well as an anomalous frequency dependence of the cyclotron resonance.[3] It is a rigorous result of the translationally invariant case, however, that for stationary processes, many-electron effects will make no contributions to the measurements for high enough fields. Thus it must be argued that either the nature of the disorder in these systems is such as to disturb the homogeneity of the samples or that many-electron effects behave somewhat differently in non–translationally-invariant systems.

In addition, the difficulties of incorporating various other anomalies, such as a free-electron-like Hall effect[4] and the presence of Shubnikov–de Haas oscillations[5] for densities well into the localized regime (as inferred from dc conductivity measurements) within the framework of the mobility-edge model, has tempted some workers[6] to abandon the independent-electron picture altogether. Nevertheless, it should be noted that there still exists no theory which treats the effect of a magnetic field on the Anderson localized