

Ab initio molecular-dynamics simulation of liquid Ga-Ge alloys

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We report the results of *ab initio* molecular-dynamics simulations of liquid Ga-Ge alloys at four different concentrations. The physical quantities studied include the partial structure factors, bond-angle distributions, self-diffusion coefficients, electronic density of states, and the electrical conductivity. The introduction of Ga causes a distinct reduction of the shoulder in the structure factor of pure ℓ -Ge. Correspondingly, the partial structure factors, pair correlation functions, and bond angle distribution functions all show behavior characteristic of simple liquid metals except at 80% Ge. The electronic density of states shows a behavior consistent with the structure: it evolves from having a distinct pseudogap at low concentrations of Ga to being almost free-electron-like for high Ga concentrations. The calculated behavior of the electrical conductivity agrees qualitatively with previous calculations based on the Faber-Ziman theory of liquid alloys. The self-diffusion coefficients $D_{\text{Ge-Ge}}$ and $D_{\text{Ga-Ga}}$ are consistent with previous calculations and available experiments for the pure liquids. [S0163-1829(98)00517-7]

I. INTRODUCTION

The properties of liquid semiconductors are of both fundamental and practical interest. From a basic viewpoint, many such liquids, such as Si and Ge, are metallic, even though in the solid phase they are semiconductors; the metal-insulator transition on melting suggests a substantial structural change. From a more practical viewpoint, most useful semiconductors are grown from the melt. Thus, the properties of such melts, including the electrical conductivity and atomic transport coefficients, are important parameters which enter into the equations governing crystal growth. The behavior of liquid semiconductor alloys and compounds is of equal importance. There are many compounds, such as GaAs, which are of great commercial value. In addition, the pure semiconductors are strongly influenced by the presence of *n*- and *p*-type impurities such as As and Ga.

Until recently, most calculations of either the thermodynamic or transport properties of liquid metals and alloys employed a perturbation approach, based on the assumption that the electron-ion interaction was weak.^{1,2} However, since the pioneering work of Car and Parrinello,³ it has become possible to carry out *ab initio* molecular dynamics simulations for these systems. In this approach, the electronic structure is calculated quantum mechanically, by effectively solving the Kohn-Sham equations,⁴ in order to determine the forces acting on the ions; the ionic motion itself is handled using classical dynamics. For many liquids such as ℓ -Si and ℓ -Ge, the persistence of covalent bonding above the melting temperature necessitates a fully quantum-mechanical calculation of the electronic structure. However, the price one has to pay is that we can only study relatively small systems using this approach. Nonetheless, a number of groups have used *ab initio* approaches to obtain useful and accurate information about liquid metals and alloys.⁵⁻⁷

In this paper, we present the results of a simulation study of liquid $\text{Ge}_{1-x}\text{Ga}_x$ at four concentrations just above the melting temperature of pure Ge. This alloy system is of interest because Ga is a common impurity in ℓ -Ge, whose

transport properties are of interest in order to model crystal growth. In addition, of course, Ga is a common *p*-type dopant in solid semiconductors. Our calculations are carried out using *ab initio* molecular dynamics; in the version we employ, as opposed to the Car-Parrinello scheme, the electronic degrees of freedom are converged to the Born-Oppenheimer surface before each ionic move. In a previous work,⁸ we used this approach to calculate a number of properties of pure liquid Ge (ℓ -Ge), including the ionic structure factor, electronic density of states, bond-angle distribution, frequency-dependent conductivity $\sigma(\omega)$, and atomic self-diffusion coefficient at several temperatures. The present work extends the same approach to ℓ - $\text{Ga}_x\text{Ge}_{1-x}$.

The remainder of this paper is organized as follows. In Sec. II, we briefly review our method of calculation. Section III describes our results, and a discussion follows in Sec. IV.

II. METHOD AND COMPUTATIONAL DETAILS

To carry out our *ab initio* calculations, we use the standard plane-wave pseudopotential method. The details of the code used can be found in the literature.^{9,10} The exchange-correlation potential is calculated within local-density approximation (LDA), using the Ceperley-Alder form as parametrized by Perdew and Zunger.¹¹ We use generalized norm conserving pseudopotentials¹² in the Kleinman-Bylander¹³ form with the *d*-wave part treated as the local component.

In order to test the pseudopotentials we have calculated some of the structural properties for both Ga and Ge in the crystalline phase. The results for Ge were obtained with a plane-wave energy cutoff of 25 Ry and using ten special *k* points in the irreducible wedge of the Brillouin zone. To determine the lattice constants and bulk moduli, we fitted the calculated energies to the functional form¹⁴

$$E = A + BV^{-1/3} + CV^{-2/3} + DV^{-1}, \quad (1)$$

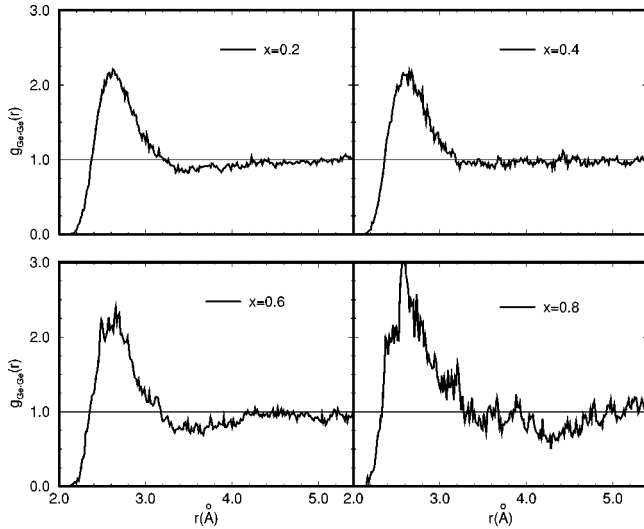


FIG. 1. Partial pair correlation function $g_{\text{Ge-Ge}}(r)$ for liquid $\text{Ge}_{1-x}\text{Ga}_x$ at the four concentrations $x=0.2, 0.4, 0.6$, and 0.8 .

where E and V are the energy and volume per atom, respectively. The resulting calculated values of the lattice constant and the bulk modulus were 5.59 \AA and 72.3 GPa , in good agreement with the experimental values of 5.65 \AA and 76.5 GPa . For Ga, we carried out these tests on the α phase. This crystal structure has a base-centered orthorhombic Bravais lattice specified by the experimentally determined¹⁵ lattice parameters $a=4.52 \text{ \AA}$, $b=4.53 \text{ \AA}$, $c=7.66 \text{ \AA}$. In our tests, we have fixed the ratios of these three lengths at their experimental values and varied the single parameter a . Using a plane-wave cutoff of 20 Ry and 39 special k points, we obtained the calculated values $a=4.38 \text{ \AA}$, $b=4.37 \text{ \AA}$, $c=7.40 \text{ \AA}$. These are nearly identical to the values obtained in previous *ab initio* simulations.^{16,17}

We carry out the liquid-state molecular dynamics simulations at 1273 K at four concentrations of Ga in Ge ranging from ~ 20 to $\sim 80 \%$ and a 64 -atom supercell with periodic boundary conditions. These concentrations correspond to 13 , 26 , 38 , and 51 Ga atoms. For each concentration, the initial configurations are generated from the results of a previously reported molecular dynamics simulation of liquid Ge (Ref. 8) at 1250 K , but with the appropriate number of Ge atoms randomly replaced by Ga. The densities for the four concentrations are determined from the experimental densities¹⁸ of pure liquid Ge and Ga, using Vegard's law (linear interpolation of atomic volumes) to obtain the densities for the alloys. We use a plane-wave energy cutoff of 10 Ry and Γ -point sampling for the supercell Brillouin zone. Since we expect the liquid system to be metallic, we use standard Fermi-surface broadening, taking the temperature of the electronic subsystem as $k_B T^{\text{el}} = 0.1 \text{ eV}$. In calculating the electronic wave functions we include eight empty bands for each concentration. The ionic temperature is controlled by means of a Nosé-Hoover thermostat^{19,20} and the equations of motion are integrated using the Verlet algorithm with an ionic time-step of 125 a.u. ($\sim 3 \text{ fs}$). After an initial equilibration period of about 0.2 ps , simulations were carried out for more than 3 ps at each concentration.

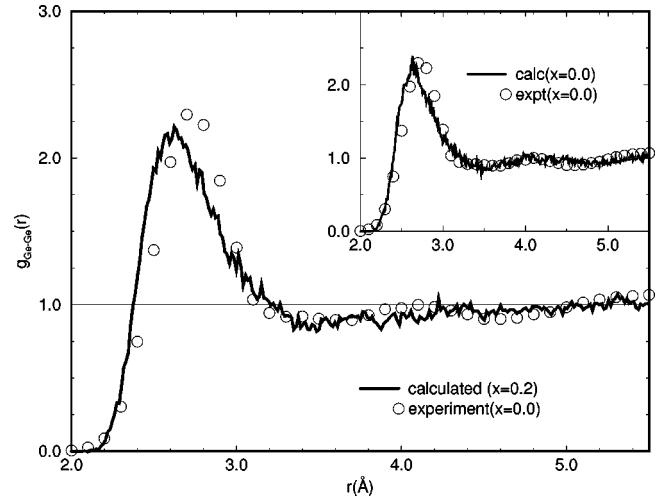


FIG. 2. Partial pair correlation function $g_{\text{Ge-Ge}}(r)$ for liquid $\text{Ge}_{1-x}\text{Ga}_x$ with $x=0.2$ at $T=1273 \text{ K}$ compared to experimental pair-correlation function for pure l -Ge at $T=1253 \text{ K}$. Dashed lines: present calculations. Circles: experiment (Ref. 1). The inset shows the results of previous calculations (Ref. 14) for pure liquid Ge as compared to experiment (Ref. 1).

III. RESULTS

Figure 1 shows the partial pair-correlation function $g_{\text{Ge-Ge}}(r)$ for the four alloys $\text{Ge}_{1-x}\text{Ga}_x$ with $x=0.2, 0.4, 0.6$, and 0.8 . For comparison, we have shown in Fig. 2 the pair-correlation function $g_{\text{Ge-Ge}}(r)$ with $x=0.2$ contrasted with the experimental results¹⁸ for pure l -Ge at a similar temperature. A number of features deserve mention. First, the position of the principal peak, which occurs at $r=2.61 \text{ \AA}$, is virtually unchanged from the value calculated for pure l -Ge ($r=2.63 \text{ \AA}$).⁸ However, the height of that peak is reduced, from ~ 2.4 to ~ 2.2 . In pure l -Ge, $g_{\text{Ge-Ge}}(r)$ also shows a weak intermediate peak between the two principal peaks. This intermediate peak reflects the characteristic feature of the structure factor in pure l -Ge, namely, the presence of a shoulder occurring at $k=2k_F$ distinct from the primary peak in the structure factor $S(k)$ (see below). However, as can be seen from Fig. 2, this intermediate peak has already flattened out at $x=0.2$. One would expect that this flattening would correspond to a weakening of the shoulder in the structure factor at nonzero x . This is indeed the case, as will be discussed below. A final point is that $g_{\text{Ge-Ge}}(r)$ is becoming noisier as the concentration of Ge is reduced. This is simply a consequence of the smaller number of Ge atoms which are included at these lower concentrations.

Figure 3 shows the partial correlation functions $g_{\text{Ga-Ga}}(r)$ at the same concentrations. The principal peak seems to show a slight shift to smaller r as the concentration of Ga diminishes; in general, this peak occurs at about the same r as that of $g_{\text{Ge-Ge}}(r)$, suggesting that the ‘‘atomic sizes’’ are similar in the liquid. The data is, as expected, noisier at the lowest concentrations of Ga. We can compare the results obtained by us for $g_{\text{Ga-Ga}}(r)$ with $x=0.8$ with the experimental results²¹ and simulations¹⁶ for pure l -Ga obtained at $T=982 \text{ K}$. Since our simulations are at a higher temperature than the experimental results, it is instructive to note the temperature dependence seen in previous simulations¹⁶ for

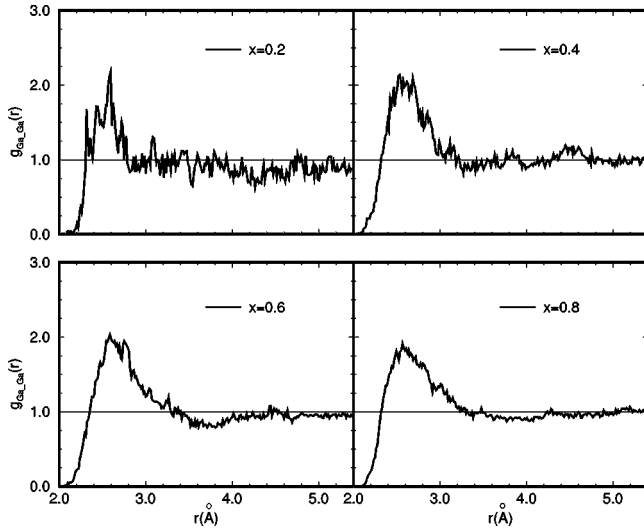


FIG. 3. Partial pair correlation function $g_{\text{Ga-Ga}}(r)$ for liquid $\text{Ge}_{1-x}\text{Ga}_x$ at the four concentrations $x=0.2, 0.4, 0.6$, and 0.8 .

pure ℓ -Ga. With increasing temperature, the height of the principal peak in $g_{\text{Ga-Ga}}(r)$ shows a marked reduction (from ~ 2.6 at $T = 702$ K to ~ 2.2 for $T = 982$ K) and shows a slight shift to smaller r . Our results for $g_{\text{Ga-Ga}}(r)$ with $x = 0.8$ show a principal peak at $r = 2.55$ Å with a peak height of ~ 1.9 as compared to $r = 2.67$ Å and ~ 2.2 for the simulations for the pure liquid at $T = 982$ K. These values seem to be consistent with the trend noted above.

We turn next to the partial structure factors $S_{\text{Ge-Ge}}(k)$ and $S_{\text{Ga-Ga}}(k)$, shown in Figs. 4 and 5 for the four alloy concentrations. The most striking feature in the calculated $S_{\text{Ge-Ge}}(k)$ is the shoulder on the large- q side of the principal peak. This shoulder is quite pronounced in pure ℓ -Ge, in agreement with experiment, but it disappears rapidly with increasing Ga concentration x . In fact, it has almost disappeared by $x = 0.2$ as indicated in Fig. 6, a fact that is also reflected in the flattening of the intermediate peak in $g_{\text{Ge-Ge}}(r)$ as mentioned earlier. Also, there is a distinct increase in the low- k values

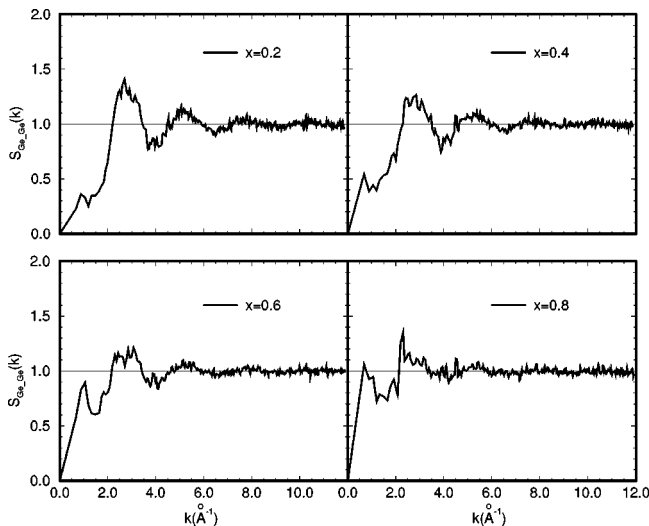


FIG. 4. Partial structure factor $S_{\text{Ge-Ge}}(k)$ as a function of wave vector k (in Å^{-1}) for liquid $\text{Ge}_{1-x}\text{Ga}_x$ at the four concentrations. $x = 0.2, 0.4, 0.6$, and 0.8 .

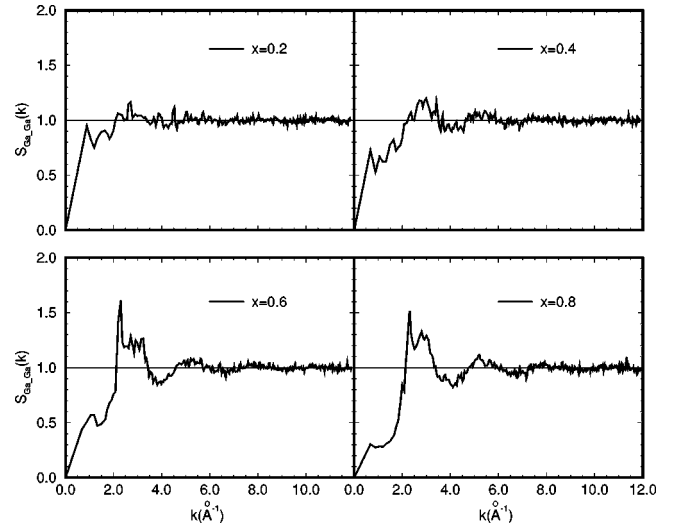


FIG. 5. Partial structure factor $S_{\text{Ge-Ge}}(k)$ for liquid $\text{Ge}_{1-x}\text{Ga}_x$ at the concentration $x = 0.2$ compared to the experimental structure factor for pure ℓ -Ga at $T = 1253$ K (Ref. 1). The inset shows the results of previous calculations (Ref. 14) for pure liquid Ge as compared to experiment (Ref. 1).

of $S_{\text{Ge-Ge}}(k)$ in comparison to the structure factor for the pure liquid. By $x = 0.8$, in spite of the poor statistics, Fig. 4 shows that $S_{\text{Ge-Ge}}(k)$ is similar to that of a dilute gas, being close to unity except at very small k . The partial structure factor $S_{\text{Ga-Ga}}(k)$ behaves similarly to that of a conventional (hard-sphere-like) liquid metal at $x = 0.8$, crossing over to nearly ideal-gas-like behavior at $x = 0.2$. Comparing our results for $x = 0.8$ with the published experimental results for pure liquid Ga at $T = 982$ K (Ref. 21) we see that the positions of the principal and secondary peaks are basically unchanged; however, the height of the principal peak is reduced and there is a distinct increase in the low- k values of the structure factor.

In Figs. 7 and 8, we show the *bond angle distribution*—that is, the distribution of angles formed by triplets of Ge atoms for $x = 0.2$ and of Ga atoms at $x = 0.8$, such that all three atoms lie within a suitable cutoff radius r_c . For com-

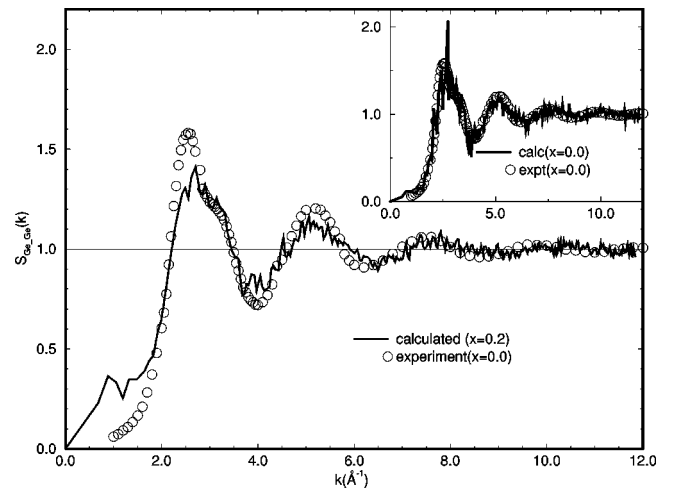


FIG. 6. Partial structure factor $S_{\text{Ga-Ga}}(k)$ as a function of wave vector k (in Å^{-1}) for liquid $\text{Ge}_{1-x}\text{Ga}_x$ at the four concentrations. $x = 0.2, 0.4, 0.6$, and 0.8 .

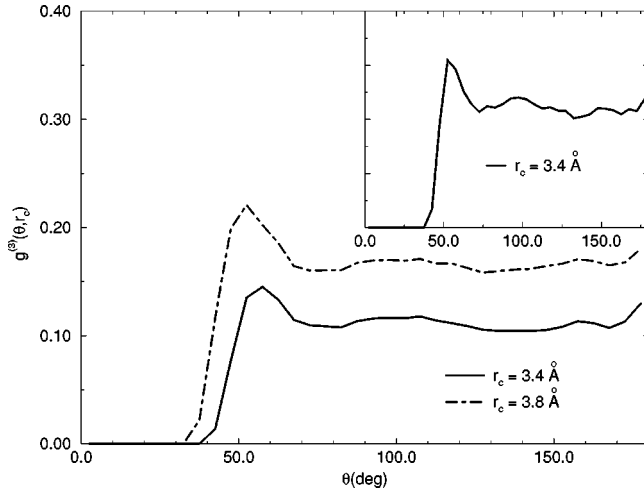


FIG. 7. Calculated bond angle distribution function for Ge atoms in liquid $\text{Ge}_{1-x}\text{Ga}_x$ with $x=0.2$ and different choices for the cutoff radius r_c . The inset shows the calculated bond angle distribution for pure liquid Ge (Ref. 8).

parison, we also show the corresponding distribution for pure ℓ -Ge in the inset for Fig. 7. For $x=0.2$, the bond angle distribution, such as that of pure Ge, shows a slight peak at $\sim 60^\circ$, corresponding to a close-packing arrangement. However, the peak observed in our pure Ge simulations at $\sim 100^\circ$ has been reduced to a barely detectable and rather broad plateau at $x=0.2$. This indicates that the addition of only $\sim 20\%$ of Ga already reduces the degree of covalent bonding present in pure ℓ -Ge, in agreement with the disappearance of the shoulder in $S_{\text{Ge-Ge}}(k)$ at that concentration. The bond-angle distribution for Ga clusters at $x=0.8$ is quite uniform except for a weak peak near $\sim 60^\circ$. This indicates close-packed bonding characteristic of simple liquid metals.

We have also calculated the values of the self-diffusion coefficients for Ge atoms $D_{\text{Ge-Ge}}$ (at 20% Ga) and $D_{\text{Ga-Ga}}$ (at 20% Ge), obtained in both cases by examining the mean square displacements of the respective atoms as a function of time as in our previous work for pure Ge (see Fig. 9). The self-diffusion coefficients can be extracted from the equation

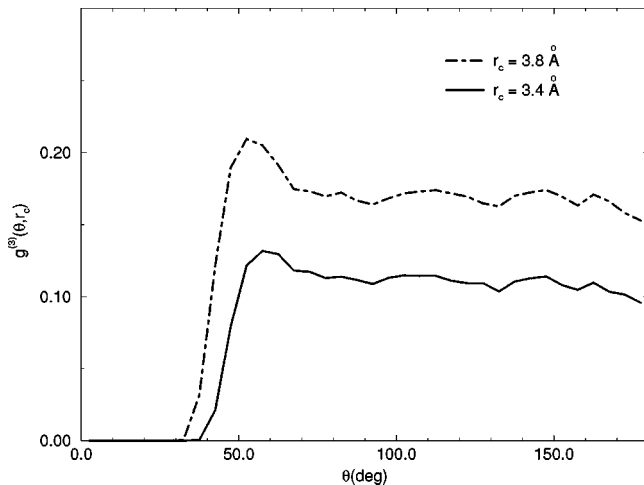


FIG. 8. Same as Fig. 7, but for Ga atoms and $x=0.8$.

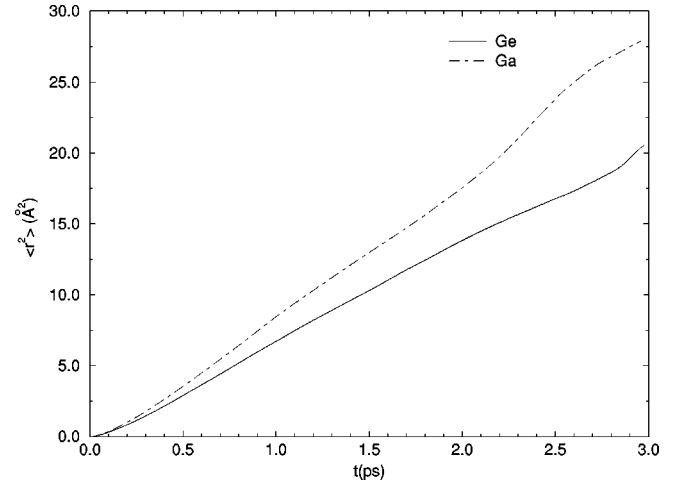


FIG. 9. Mean-square atomic displacements $\langle r^2 \rangle \equiv \langle |\mathbf{R}_I(t) - \mathbf{R}_I(0)|^2 \rangle$ (in \AA^2) versus time t (in ps) for Ge atoms in liquid $\text{Ge}_{1-x}\text{Ga}_x$ at $x=0.2$ and for Ga atoms at $x=0.8$.

$$D = \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{R}_I(t) - \mathbf{R}_I(0)|^2 \rangle}{6t}, \quad (2)$$

where $\mathbf{R}_I(t)$ denotes an ionic position at time t . The angular brackets denote an average over all the ions of the same species, and also over all time origins. In our calculations we have computed the average taking the beginning of each time step as a different time origin. For Ge self-diffusion, we obtain $D_{\text{Ge-Ge}} \sim 1.1 \times 10^{-4} \text{ cm}^2/\text{s}$, very close to the previously calculated values for pure ℓ -Ge of $1.2 \times 10^{-4} \text{ cm}^2/\text{sec}$ (our work⁸) and $1.0 \times 10^{-4} \text{ cm}^2/\text{sec}$ (Kresse and Hafner⁷). It is mildly surprising that the reduction in covalent bonding at $x=0.2$ does not translate into a more significant change in $D_{\text{Ge-Ge}}$. For Ga, we obtain $D_{\text{Ga-Ga}} \sim 1.7 \times 10^{-4} \text{ cm}^2/\text{s}$ for 80% Ga at $T=1273 \text{ K}$. This value seems to be in rough agreement with some old experimental values of 0.9×10^{-4} (702 K) and 1.3×10^{-4} (982 K) in pure ℓ -Ga.²²

We now turn to the electronic properties of ℓ - $\text{Ge}_{1-x}\text{Ga}_x$, which show a striking concentration-dependence. We calculate the electronic density of states $N(E)$ from the standard expression

$$N(E) = \sum_{\mathbf{k}, E_{\mathbf{k}}} w_{\mathbf{k}} g(E - E_{\mathbf{k}}). \quad (3)$$

Here $E_{\mathbf{k}}$ denotes the energy eigenvalues for the single-particle wave functions at a particular k point of the supercell Brillouin zone, and $w_{\mathbf{k}}$ is the weight of that k point (as defined below). $g(E)$ is a Gaussian function of width $\sigma = 0.2 \text{ eV}$, used in order to give a smooth variation to the calculated density of states. To carry out the calculation we sampled the supercell Brillouin zone using the same set of eight special k points, with equal weights $w_{\mathbf{k}}$, as used by Holender *et al.*¹⁶ in their simulation of pure ℓ -Ga, and we have included 40 conduction band states for each \mathbf{k} . For each concentration, the final results were then obtained by averaging over twelve representative configurations in the liquid state.

Figure 10 shows the resulting calculated $N(E)$ for $x=0.2, 0.4, 0.6$, and 0.8 as well as for pure ℓ -Ge for comparison. For pure ℓ -Ge, $N(E)$ shows a pseudogap at -4.6

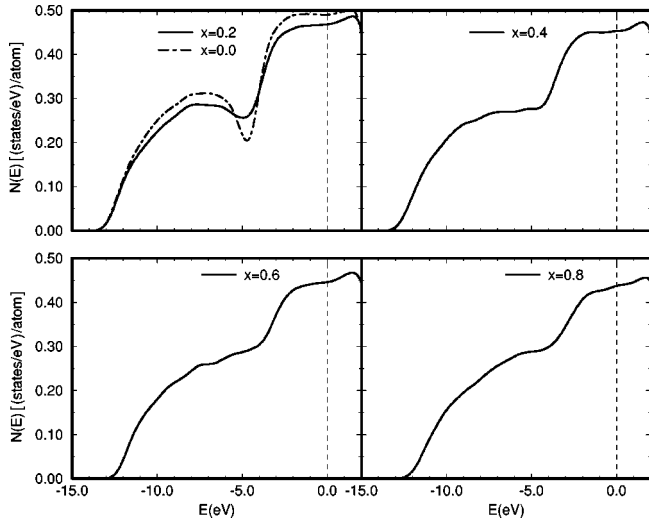


FIG. 10. Calculated electronic density of states $N(E)$ (in states/eV atom) for liquid $\text{Ge}_{1-x}\text{Ga}_x$ at the four concentrations $x = 0.2, 0.4, 0.6$, and 0.8 . Each curve is obtained by averaging over twelve characteristic atomic configurations; the supercell Brillouin zone is sampled using eight special k points.

eV separating the s -like and p -like bands.²³ On the other hand the density of states for ℓ -Ga at elevated temperatures is known to be almost free-electron-like.¹⁶ Thus we would expect a gradual progression towards free-electron-like behavior in $N(E)$ as x increases. This behavior is precisely what is seen in Fig. 10. The pseudogap is already substantially reduced below its value for pure ℓ -Ge, even at $x = 0.2$. With increasing concentration of Ga, $N(E)$ loses even more of its structure and approaches the free-electron-like behavior seen in pure ℓ -Ga at these temperatures. Of course, at all concentrations, $N(E)$ shows clear metallic behavior—that is, it is finite, with no dips, at the Fermi energy.

Finally, we have calculated the frequency dependent electrical conductivity $\sigma(\omega)$, and its low-frequency limit, the dc conductivity, as a function of concentration. As in our previous work, we obtain $\sigma(\omega)$ from the standard Kubo-Greenwood formula²⁴

$$\sigma(\omega) = \frac{2\pi e^2}{3m^2\omega\Omega} \sum_i \sum_j \sum_\alpha (f_j - f_i) |\langle \psi_i | \hat{p}_\alpha | \psi_j \rangle|^2 \times \delta(E_j - E_i - \hbar\omega). \quad (4)$$

Here m is the electron mass, and ψ_i and ψ_j are the single particle Kohn-Sham wave functions with Fermi occupancies f_i and f_j and energy eigenvalues E_i and E_j . \hat{p}_α is the component of the momentum operator in the direction α . We have calculated the conductivity using the same set of eight special k points employed for $N(E)$, and again averaged over twelve representative ionic configurations for each concentration. As in the density of states calculation, we have included 40 conduction band states at each \mathbf{k} .

By extrapolating $\sigma(\omega)$ to $\omega=0$, we can estimate the dc conductivity. The calculated values of $\sigma(0)$ for the four con-

TABLE I. Calculated dc conductivity of $\text{Ge}_{1-x}\text{Ga}_x$ at the four concentrations, obtained by extrapolating low frequency ac conductivity results.

Concentration (x)	0.2	0.4	0.6	0.8
σ_{dc} ($10^4 \Omega^{-1} \text{ cm}^{-1}$)	1.5	1.45	1.55	1.62

centrations are shown in Table I. We note that $\sigma(0)$ shows a weak minimum at 40% and then increases for higher concentrations of Ga. This behavior is in qualitative agreement with that predicted by calculations based on the weak-scattering Faber-Ziman theory of liquid alloys,¹ and presumably arises for the same reason: stronger scattering near $x = 0.5$ due to differences between the Ge and Ga scattering potentials. However, there is no clear evidence in the experimental data reported¹ of the weak minimum in conductivity seen in our calculations.

IV. CONCLUSIONS

In conclusion we have carried out *ab initio* molecular dynamics simulations for liquid Ga-Ge alloys at four different concentrations. The basic picture emerging from these calculations is that, as the concentration of Ga is increased at the temperatures considered, the alloy rapidly becomes more free-electron-like. This transformation manifests itself in a variety of ways. The atomic structure, which shows some residue of tetrahedral local arrangement in pure ℓ -Ge in both $g(r)$ and the distribution of bond angles, quickly becomes more close-packed and is almost entirely so for 40% or more atomic concentration of Ga. The structure factor $S_{\text{Ge-Ge}}(k)$, which has a noticeable shoulder in pure ℓ -Ge in both our calculations and experiment, becomes more hard-sphere-like with increasing Ga concentration, as does $S_{\text{Ga-Ga}}(k)$. Most noticeably, the deep pseudogap between p -like and s -like states in pure ℓ -Ge quickly fills in as the Ga concentration x increases, leading to a nearly free-electron-like density of states for $x = 0.8$. The electrical conductivity looks similar to what might have been obtained from a Faber-Ziman calculation: a weak minimum near $x = 0.4$ coming from enhanced alloy scattering. At all concentrations, the alloy is a reasonably good metal, with resistivities in the range of $70 \mu\Omega \text{ cm}$.

The present work can be extended in a number of ways. Of probably greatest interest would be to study such liquid alloy systems as CdTe or GaAs, both on and off stoichiometry. These materials may have quasi-metal-insulator transitions in the liquid state as a function of temperature or concentration. We hope to carry out calculations on such systems in the near future.

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- ¹N. Koubaa and J-G. Gasser, *J. Phys.: Condens. Matter* **2**, 2297 (1990).
- ²A. Arnold, N. Mauser, and J. Hafner, *J. Phys.: Condens. Matter* **1**, 965 (1989).
- ³R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- ⁴W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ⁵F. Kirchhoff, J. M. Holender, and M. J. Gillan, *Europhys. Lett.* **33**, 605 (1996).
- ⁶V. Godlevsky, J. R. Chelikowsky, and N. Troullier, *Phys. Rev. B* **52**, 13 281 (1995).
- ⁷G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14 251 (1994).
- ⁸R. V. Kulkarni, W. G. Aulbur, and D. Stroud, *Phys. Rev. B* **55**, 6896 (1997).
- ⁹M. Bockstedte, A. Kley, and M. Scheffler, *Comput. Phys. Commun.* **107**, 187 (1997).
- ¹⁰R. Stumpf and M. Scheffler, *Comput. Phys. Commun.* **79**, 447 (1994).
- ¹¹J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ¹²D. R. Hamann, *Phys. Rev. B* **40**, 2980 (1989); X. Gonze, R. Stumpf, and M. Scheffler, *ibid.* **44**, 8503 (1991).
- ¹³L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).
- ¹⁴D. M. Teter, G. V. Gibbs, M. B. Boisen, Jr., D. C. Allan, and M. P. Teter, *Phys. Rev. B* **52**, 8064 (1995).
- ¹⁵*Numerical Data and Functional Relationships in Science and Technology*, edited by K.-H. Hellwege, Landolt-Börnstein, New Series, Group III, Vol. 6. (Springer, Berlin, 1982).
- ¹⁶J. M. Holender, M. J. Gillan, M. C. Payne, and A. Simpson, *Phys. Rev. B* **52**, 967 (1995).
- ¹⁷X. G. Gong, G. L. Chiarotti, M. Parrinello, and E. Tosatti, *Phys. Rev. B* **43**, 14 277 (1991).
- ¹⁸Y. Waseda, *The Structure of Non-Crystalline Materials, Liquids, and Amorphous Solids* (McGraw-Hill, New York, 1980).
- ¹⁹S. Nosé, *J. Chem. Phys.* **81**, 511 (1984).
- ²⁰W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).
- ²¹M. C. Bellissent-Funel, P. Chieux, D. Levesque, and J. J. Weis, *Phys. Rev. A* **39**, 6310 (1989).
- ²²E. F. Broome and H. A. Walls, *Trans. Metall. Soc. AIME* **245**, 739 (1969).
- ²³W. Jank and J. Hafner, *Europhys. Lett.* **7**, 623 (1988).
- ²⁴D. J. Thouless, *Phys. Rep.* **13**, 93 (1974).