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Molecular-dynamics simulation of amorphous germanium

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We have developed a set of two-body and three-body potentials for modeling the structure of solid phases of germanium. The potential is of the same functional form as that of Stillinger and Weber for silicon, but it has different values of the parameters. The potential gives an excellent structural representation of amorphous solid Ge as well as crystalline Ge and gives good results for several thermodynamic properties of the crystalline phase and the phonon dispersion relations of the crystal.

I. INTRODUCTION

Germanium is of scientific interest because of the various electrical and structural characteristics of its condensed phases. Ge in its low-pressure crystalline and amorphous forms is a semiconductor and has a coordination number of 4, the crystal having the familiar diamond structure and the amorphous material forming a random tetrahedral network. Liquid Ge has a slightly larger average coordination number and is metallic. A high-pressure metallic form of crystalline Ge also exists.[1] Amorphous alloys of Ge with molybdenum exhibit various electrical properties (semiconducting, or metallic but not superconducting, or metallic and superconducting)[2] and have structures from that of a random tetrahedral network to that of dense random packing of spheres, depending on the composition.[3] While the structure of crystalline Ge is well understood, a better understanding of the amorphous as well as liquid-state structures is still a challenge.

There are several approaches to developing models for the structure and dynamics of amorphous materials. One makes use of interatomic potentials in conjunction with molecular dynamics or Monte Carlo simulations or energy-minimization techniques. Another generates structures (by hand or on a computer) according to some algorithm that builds certain features into the short-range structure. For simplicity, we will call these two approaches "potential models" and "structural models," respectively, although we note that structural-model approaches sometimes use potentials in adjusting or relaxing the structures.

Many structural models have been proposed to explain experimentally observed structure factors and radial distribution functions for tetrahedral amorphous materials as well as their melts. For example, there are the random-network model of Polk,[4] the distorted diamond-lattice model of Henderson and Herman,[5] and a model of a mixture of diamond tetrahedra and pentagonal dodecahedra by Grigorovici and Manaila.[6] Recently Wooten, Winer, and Weaire[7] proposed a new computer algorithm for generating structures for *a*-Ge. For liquid Ge, Gabathuler and Steeb[8] suggested a model consisting of random mixture of fourfold and sixfold coordinated structural units. Although the structural models have indeed helped to gain insights into the structures of amorphous materials, they cannot predict how structures will respond to changes in external conditions such as pressure and temperature, unless these changes are a simple rescaling of interatomic distances or a change in vibrational amplitudes. Of more importance, structural models for one-component materials can sometimes be difficult to generalize to mixtures or alloys.

There is a long history of using potential models to study semiconductor Ge and the closely related element silicon. The bond charge[9] model is very successful in calculating the phonon dispersion curves for diamond like crystals and the Keating potential[10] is suitable for describing the small amplitude vibrations. Recently Stillinger and Weber (SW)[11] modeled molten Si using a molecular dynamics simulation with two-body and three-body empirical potential-energy functions (discussed below). Subsequently, Abraham and Batra[12] carried out a study of surfaces of crystalline Si using the SW potential. Pearson *et al.*[13] proposed another kind of two- and three-body potential to study structural properties of crystalline Si. Biswas and Hamann[14] also proposed a potential that is in principle similar to the SW potential. Tersoff[15] formulated another potential for Si. All these potentials, except that of Tersoff, include the many-body interactions into effective two- and three-body potentials. Tersoff's potential includes many-body interactions explicitly, by allowing the bond order of a bond between two atoms to be dependent upon the neighbors of those atoms. No potentials mentioned above have been used to model the structure of amorphous solids.

Here we report use of the SW-type potential to model amorphous and crystalline Ge. Section II discusses how the potential function was determined. Section III describes the calculations used in developing the potential. Section IV presents the conclusions.

II. POTENTIAL FUNCTION

The Stillinger-Weber interatomic potential for Si is a combination of two-body and three-body potentials. The two-body potential describes the formation of a chemical bond between two atoms. The three-body potential favors structures in which the angles between two bonds made by the same atom are close to the tetrahedral angle. We refer the reader to the original reference[11] for the details of the functional form. Because of the structural similarities of germanium and silicon, it is reasonable to expect that the interactions among Ge atoms are similar to those of Si. Therefore, we adopted the SW potential form in this study of amorphous Ge.

In order to determine the parameter set of the potential, we used experimental data on crystalline Ge: e.g., the depth of the two-body potential was fitted to the cohesive energy of the crystal at 0 K and the location of the minimum was determined by the density of the crystal at a pressure of one atmosphere. The three elastic constants C_{11}, C_{12}, and C_{44} of the crystal were used in selecting other parameters. The fact that the diamond structure must be lower in energy than other structures, such as the fcc, bcc, and simple cubic structures, was used in limiting the choice of parameters. Simulations of the amorphous solid, of the type to be discussed below, and comparison with experimental radial distribution functions helped us to decide upon the values of the rest of the parameters, especially the strength of the three-body interaction. After the parameters were chosen, we calculated the phonon dispersion curves for crystalline germanium, and the agreement with experiment was found to be good.

We could find no parameters of the potentials that gave a good description of all three phases of germanium: liquid, diamond-lattice crystal, and amorphous solid. Our search of the parameter space was extensive enough to convince us that no such parameters exist for the SW potential. We were able to find parameters that gave a good description of the crystal and amorphous solid phases.

In summary the potential parameters we chose are: $A=7.049\,556\,277$, $B=0.602\,224\,558\,4$, $p=4$, $q=0$, $a=1.8$, $\lambda=31$, $\gamma=1.20$, $\epsilon=1.93$ eV$=3.085\times10^{-19}$ J, and $\sigma=2.181$Å. We note that except for the change in energy and length scale, the two-body potential we use for germanium has the same parameters as the two-body part of the SW potential for silicon. The reduced strength of the three-body interaction, represented by λ, is larger for this model of germanium than the value used for silicon by Stillinger and Weber.

III. CALCULATIONS

A. Molecular dynamics

Dynamical simulations on amorphous Ge were carried out with a fixed number of particles in a cubic box of a constant volume, subject to the conventional periodic boundary conditions. The velocity form of the Verlet algorithm[16] was used with a time step of 0.001 361 psec. The density of the sample was chosen as that of amorphous Ge, namely, 5.3 g/cm^3. The amorphous state was obtained by first equilibrating liquid Ge at a high temperature of 4500 K (for over 20 000 steps) and then quenching to room temperature. Kinetic energy was removed from the system by means of stochastic collisions; i.e., at random times, randomly selected particles were assigned new momenta chosen from a low-temperature Boltzmann distribution. The cooling process took about 20 000 time steps or about 27 psec. The quenched sample was then annealed for about 5000 steps before averaging was performed. Then data for calculation of the radial distribution function was collected for the next 3000 to 5000 steps and averaged to obtain the final results.

The structure obtained was not sensitive to annealing, i.e., the structure of amorphous state did not change if the annealing process was prolonged. A study of system size dependence was performed by using 216 and 512 particles at the same density. The structure was found to be insensitive to the change of the system size.

However, the structure found for the amorphous state is dependent on the quench rate used in the simulation. Faster quenching resulted in a radial distribution function with an unresolved third peak. For the quench reported here, the third peak developed. In this calculation, the material is cooled from liquid temperatures down to very low temperatures in about 27 psec. Thus the time spent at higher temperatures where it can change its structure from that of the liquid is of the order of 5–10 psec. The present calculations are a simulation of a very rapid quench of a homogeneous liquid. Amorphous germanium is prepared in the laboratory by vapor deposition rather than liquid quenching. In vapor deposition, a hot atom is deposited on a surface, leading to local heating of the area it hits. Various estimates of the time for the area to cool down[17] suggest that this cooling occurs on a time scale of about 1 psec. Each deposited atom is subsequently reheated and cooled again as other atoms are deposited on top of it, suggesting that each atom can spend several multiples of 1 psec at temperatures that are at or below the melting temperature but high enough for structural change to take place. Thus, we believe that the time scale for the present liquid-quench simulations corresponds approximately to that of the laboratory procedure used to prepare amorphous germanium.

The calculated radial distribution function of amorphous Ge is plotted in Fig. 1, together with the experimental results of Kortright. The two agree very well. The major discrepancy is in the sharpness of the third peak, which in the simulations is dependent upon the cooling rate. Table I gives the peak locations and heights as well as the coordination number of the first shell.

B. Phonon dispersion curves

The phonon dispersion curves for crystalline Ge were calculated by diagonalizing the dynamical matrix, the elements of which were expressed in terms of second derivatives of the potential function. The dispersion curves in the [110], [110], and [111] directions are plotted in Fig. 2, together with experimental results obtained from neutron inelastic scattering experiments by Nilsson and Nelin.[18] We note that (a) the low-q part of the acoustic phonon curves agree very well with experiment, corresponding to the fact that the model potential gives good values of the elastic constants of the crystal; (b) due to the intrinsic short-range behavior of the potential function, it is impossible for this type of potential to fit the transverse acoustic phonons at or near the zone boundaries;[19] (c) the calculated and experimental optical phonon curves differ by an al-

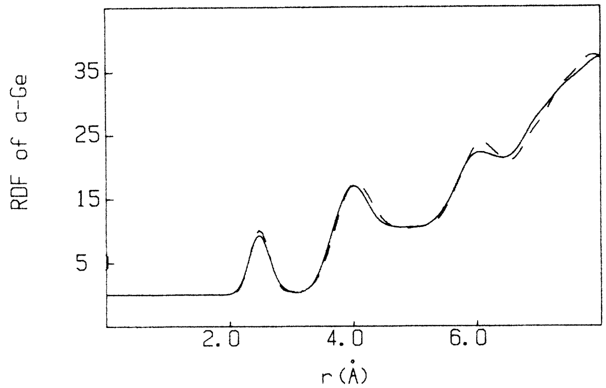

FIG. 1. Comparison of radial distribution functions from MD calculation (solid line) and experiment (dashed line) by Kortright (Ref. 3). The experimental data in **k** space was multiplied by a factor of exp($-ak^2$) with $a=0.01$ Å^2, truncated at $k_{\max}=18.5$Å^{-1}, and then transformed to **r** space to give the experimental (dashed) curve in the figure. The pair correlation function obtained from MD calculations was convoluted with an instrumental function, designed to have the same effect as the use of the window function and truncation, to give the theoretical (solid) curve in the figure.

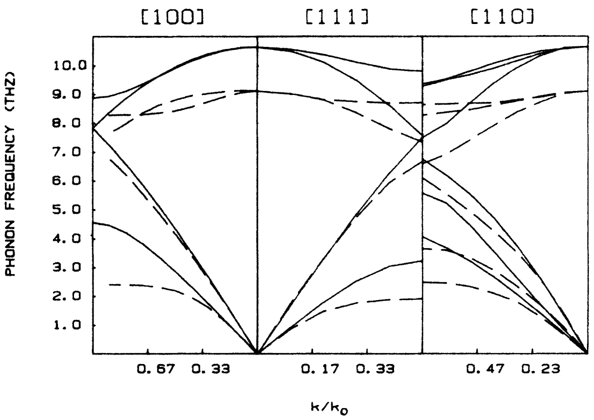

FIG. 2. Comparison of phonon dispersion curves, [100], [110], [111] of crystalline Ge from calculations using the model potential (solid curves) and from experiment by Nilsson and Nelin (Ref. 18) (dashed lines). $k_0=2\pi/L$ and L is the length of the unit cell.

most constant 10%. It is impossible to fit the frequencies of the optical branches and the slopes of the acoustic branches simultaneously with a potential of the SW type.

C. Liquid-state structure and additional results

As a further test of the potential, we performed molecular dynamics simulations on liquid germanium for comparison with experimental radial distribution functions of the liquid. The agreement was poor, namely, the calculated RDF has a spurious tetrahedral-like second peak which is absent from the experimental RDF of the liquid.[8,20] As mentioned above, we were able to find no potential of the SW type that reproduced the properties of all three condensed phases—the liquid, the crystalline solid, and the amorphous solid.

TABLE I. Comparison of the peak positions, minima positions, peak heights, and the coordination number of the first shell obtained from MD calculation and experiment.

	MD	Experiment[a]
$r1(A)$[b]	2.48	2.47
$r2(A)$[b]	4.00	4.02
$r3(A)$[b]	6.05	6.07
$r4(A)$[c]	3.09	3.02
$r5(A)$[c]	4.81	4.82
$r6(A)$[c]	6.42	6.52
RDF($r1$)	9.3	10.1
RDF($r2$)	17.0	17.4
RDF($r3$)	22.3	23.9
RDF($r4$)	0.30	0.41
RDF($r5$)	10.5	10.3
RDF($r6$)	21.4	21.0
CN[d]	4.01	4.00

[a] Reference 3.

[b] Positions of maxima in Å.

[c] Positions of minima in Å.

[d] The coordination number is equal to the area under the first peak up to 3.0 Å.

Stillinger and Weber parametrized their potential to fit the properties of two condensed phases of silicon—the liquid and the crystalline solid—and it gave an adequate description of the structures of these phases. As an additional test of their potential, we used their parameters for silicon in a simulation of the amorphous solid, using the method described above. We obtained a structure very different from the experimental result for amorphous solid silicon. The experimental radial distribution function (RDF) of a-Si prepared by vapor deposition[21] has well-defined, although broadened, peaks up to about 8 Å, whereas the RDF calculated using the SW potential gives an almost featureless third peak at about 5.5 Å. Of more importance, the calculated RDF curve shows a spurious shoulder at the small r side of the second peak. Although the position of the first peak (2.41 Å) differs from that of the corresponding experimental one (2.35 Å) by less than 3%, the difference between the coordination numbers of the calculation (4.6) and the experiment (4.0) amounts to 15%, which we think is unacceptably large. Thus the Stillinger-Weber parametrization of their potential for silicon does not give a good description of amorphous solid silicon.

The experimental radial distribution functions[3,21,22] for amorphous solid germanium and amorphous solid silicon are very similar to within the experimental uncertainties, except for a change in the length scale. The same holds for the RDF's of the two liquid phases. The crystal structures of the two materials are also the same, except for a change in length scale. It should not be surprising, therefore, that if only the length and energy scales are changed in the Stillinger-Weber parametrization of their potential for silicon, a good model for crystalline and liquid germanium is thereby obtained. Similarly, if only the length and energy scales of our parametrization of the SW potential are changed, a good model for crystalline and amorphous solid silicon can be obtained. In each of these cases, however, the potential does not give a good description of the remaining condensed phase. Thus for both silicon and germanium, a potential of the SW type can be found to fit the structure of two condensed phases, but the potential does not fit the third phase.

There are several possible explanations for the inability to fit all three phases. In our opinion, the most likely one is that the SW potential form may not be flexible enough to describe with equal accuracy the full variety of configurations seen in all three phases. Its functional form is ideal for stabilizing the diamond-lattice solid for a wide variety of parameters, and the parameters can then be adjusted to fit the properties of one other condensed phase. The structure of the third condensed phase simulated with such a potential would be dependent upon the behavior of the potential in rather different ranges of positions, and it should not be surprising if the potential function does not simultaneously fit all three phases.

Two other possible explanations should also be mentioned. (i) The potential-energy surface for the metallic liquid phase might be very different in character from that of the insulator solid phases. This might explain why our potential function does not work for liquid germanium, but this argument is weakened by the success of the SW potential for silicon in fitting the crystal and the liquid, and for its success in fitting crystal and liquid germanium after a simple change in energy and length scales. (ii) The computer-simulation method we used to prepare the amorphous solid, namely, the quenching of a liquid at constant volume, might lead to structures different from those obtained in laboratory preparation of amorphous materials by vapor deposition onto a cold surface. For reasons discussed above, we believe that the time scale of the simulation corresponds to the time scale in which vapor deposited materials cool to low temperatures. However, in the laboratory, additional structural relaxation may take place over long times at low temperatures, and it is not feasible to simulate this directly by molecular dynamics. Also, in the laboratory the material that cools is near a free surface, whereas the simulation is that of a homogeneous material. Whether or not this could influence the structure could be tested by direct simulation of the deposition of atoms on a free surface for comparison with liquid-quenching results for the same potential.

IV. DISCUSSION

This is, to our knowledge, the first molecular-dynamics simulation of a tetrahedral amorphous structure for a group-IV element on the basis of a set of potential functions. A structure very similar to that observed for real amorphous germanium was achieved by the rapid quenching of a liquid of atoms whose interatomic potentials have a strong tendency to promote tetrahedral coordination around each atom. The same potentials give good agreement with experiment for several of the properties of crystalline germanium in the diamond structure. They give poor predictions for the structure of the liquid, but it is not clear whether this is a result of the limitations of the potential model or of the impossibility of describing both insulating and conducting phases with the same potential function or of the unrealistic aspects of the dynamics method by which the amorphous structure was simulated. We suspect that the limitations of the potential model are the main reason.

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