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Structure of rapidly quenched Ga metal

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A molecular-dynamics calculation of thermodynamic and structural properties is carried out for rapidly quenched Ga liquid metal. It is demonstrated that the experimentally observed splitting of the principal peak in the structure factor into two peaks for both supercooled Ga liquid and amorphous Ga (prepared by vapor deposition onto a cold substrate) is primarily due to the occurrence of those clusters containing 1210 atomic bonded pairs, which are formed in the metastable Ga metal.

I. INTRODUCTION

Gallium is in many respects a peculiar metal. Under appropriate conditions[1,2] pure Ga liquid can be supercooled in a laboratory to one-half of its melting temperature, T_m. It is also well known that the structure factor $S(q)$ of this liquid has a shoulder on the high-q side of its principal peak[3] for temperatures not significantly higher than its T_m. Further, it is known experimentally[4] that this shoulder develops into a peak on going from the normal liquid to a supercooled liquid. That is, in this case the principal peak of $S(q)$ of the Ga liquid splits into two peaks. Further, the other peaks of $S(q)$ are left unsplit. This is quite different from the behavior of $S(q)$ for conventional rapidly quenched metallic liquids. Hence, these observations have led to the speculation that the atoms in Ga liquid are highly ordered compared to the usual metallic liquids. In addition, the pure Ga metal can be prepared in amorphous form by vapor deposition onto a cold substrate.[5] The corresponding $S(q)$ has a splitting of its principal peak into two sharp peaks. This also differs from the structure factor of a conventional amorphous metal, in which it is the second peak of $S(q)$ that splits into two peaks. The latter effect has been recently demonstrated to be due to the presence of icosahedron-type clusters (or, local ordering units) in conventional amorphous metals.[6]

Hence, we carry out a molecular-dynamics (MD) calculation of rapidly quenched Ga liquid. This is presented in Sec. II and is used (i) to examine the thermodynamic and structural properties of rapidly quenched Ga liquid in relation to conventional rapidly quenched metallic liquids and (ii) to investigate both the above-noted speculation that liquid Ga might be more ordered than other liquid metals and the noted structure-factor differences.

II. CALCULATIONS

The present calculations are based on the well-known MD simulations applied to a model system composed of 500 Ga atoms, subject to periodic boundary conditions and interacting with one another via the interatomic pair potential

$$V(r;\Omega)=\frac{Z_{\text{eff}}^2}{r}\left[1-\frac{2}{\pi}\int_0^\infty dq\, F(q;\Omega)\sin(rq)/q\right], \tag{1}$$

with Z_{eff} and $F(q;\Omega)$ standing, respectively, for the effective ionic valence and the normalized energy wave-number characteristic, obtained from Eqs. (2.6) and (2.21) of Ref. 7 using first-principles generalized energy-independent nonlocal model-pseudopotential (GEINMP) theory.[8] This $F(q;\Omega)$ depends on the atomic volume Ω because of the contribution of the electron gas to $V(r;\Omega)$. At this point, it should be noticed that the exchange-correlation factor of the electron gas, present in the above $F(q;\Omega)$ and to which $V(r;\Omega)$ is very sensitive, is that derived by Ichimaru and Utsumi[9] and has been used widely in recent years by other authors. Also, it is worth noting that the potential given by Eq. (1) behaves unusually for Ga, as shown in Fig. 1, and does not change very significantly in the liquid-solid transition under constant pressure, provided the parameters β and δ, which account for the high-order corrections in the GEINMP theory, remain unchanged. The values of β and δ used here for pure Ga metal are $\beta=0.85$ and $\delta=0.03$, which are determined in the same way as in Ref. 8.

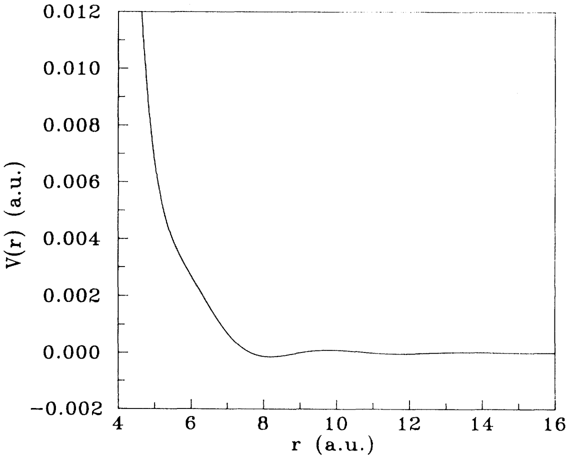

FIG. 1. The interatomic pair potential, obtained from Eq. (1), for pure Ga metal at T_m.

Having the interatomic pair potential for the system of interest, the usual MD procedure is applied first to prepare an equilibrium liquid state configuration of the 500 Ga atoms at $T=323$ K and, at the same time, to determine the corresponding mean atomic volume Ω from the relation between the pressure p and Ω, i.e.,

$$p=\frac{k_B T}{\Omega}-\frac{\partial F_0}{\partial \Omega} . \tag{2}$$

Here F_0 is the internal energy E minus $3k_B T/2$, where E is given by the sum of the first five terms in Eq. (1) of Ref. 10 in the GEINMP theory. In fact, F_0 can be written as

$$F_0=a_0+a_1 r^{-1}+a_2 r^{-2} , \tag{3}$$

where $r=(3\Omega/4\pi)^{1/3}$ and the a's can be determined by fitting F_0 to the calculated $E-(3k_B T/2)$ for different Ω's. Hence, the second term of Eq. (2) may be evaluated as

$$\frac{\partial F_0}{\partial \Omega}=-(4\pi r^{-4})^{-1}(a_1+2a_2 r^{-1}) . \tag{4}$$

Second, the damped-force method[11] is employed to reduce the temperature of the system under consideration with a rapid cooling rate (5×10^{13} K/sec in the present work) and to determine Ω as a function of T, subject to the condition that p involved in the simulation be constant at $p\pm\Delta p$. In fact, the Ω at 3 bars does not differ significantly from the Ω at 1 bar, because p is very sensitive to Ω. In view of this and of the computer time, $p\pm\Delta p$ is set to be 3 ± 1 bars in this work.

A. Thermodynamic properties

The values of $\Omega(T)$, obtained as described above, and the corresponding $E(T)$, calculated as in Ref. 10, are displayed in Fig. 2. As in the In case,[12] these values differ only slightly (by about 3% for Ω, as shown in Fig. 2) from those obtained from a variational thermodynamic calculation[13] for the supercooled-liquid states. Also included in Fig. 2 are the smoothed Ω-T and E-T curves, obtained from $\Omega=b_0+b_1T+b_2T^2$ and $E=c_0+c_1T+c_2T^2$ using the standard least-squares regression method. Compared to these curves, the fluctuation (or say, statistical noise) of the presently simulated results is overall small (less than 0.3%). Accordingly, the results displayed in Fig. 2 should not contain significant errors.

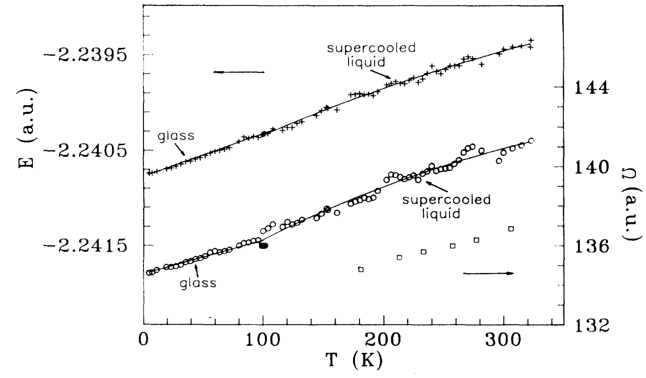

FIG. 2. The values of $\Omega(T)$ and of $E(T)$, determined as described in the text, for the presently considered rapidly quenched Ga metal. The squares denote the Ω's obtained from a variational thermodynamic calculation (Ref. 13).

Having determined $\Omega(T)$ and $E(T)$, involved in the liquid-to-glass transition, the time dependence of the atomic mean-square displacement [MSD(t)] can be calculated immediately[14] by performing another run of 20 000 time steps from the atomic configurations recorded at each particular temperature in the present MD simulation on both $\Omega(T)$ and $E(T)$. The results thus obtained for the MSD(t) are displayed in Fig. 3. There are two aspects of the displayed results that merit emphasis. (1) For temperature between T_m and 112 K, the MSD always increases with time, this being consistent with the generalized Einstein model in which the atom in a cage, formed by its surrounding atoms, oscillates about a center which itself is undergoing Brownian motion.[15] (2) In going down from $T=112$ K to a low T, the slope of the MSD(t) curve tends to vanish. This occurs because at low T the cages become localized so that the involved atoms tend to cease their diffusive motion, as clearly indicated by the self-diffusion coefficients D calculated from the standard formula[14] using the presently obtained MSD(T)'s (Fig. 4). This lends support to the regions given in Fig. 2 for the glass and supercooled-liquid states for the presently considered rapidly quenched Ga metal. To proceed further, aspect (1), applicable for the normal- and supercooled-Ga liquids, has been compared with the MSD's results for pure Al and Rb metals.[16] It is found that the behavior of MSD(t) is the same for both supercooled-Ga and Al liquids. Accordingly, the normal- and supercooled-Ga liquid are both entirely liquid like and thereby the speculation noted in Sec. I is in doubt. To proceed further, we now turn to examine the corresponding structural properties.

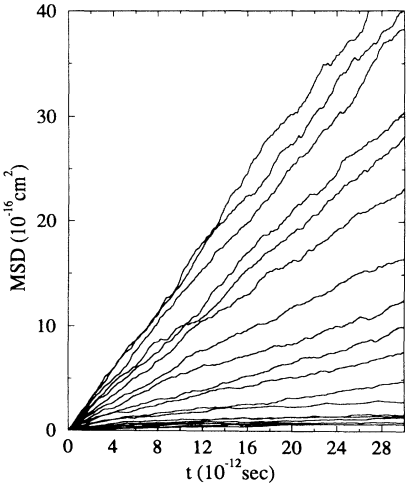

FIG. 3. The MSD-time curves, obtained from the present MD simulation for pure Ga metals. Curves from top to bottom correspond to the temperature T (K) = 322, 302, 282, 262, 242, 222, 202, 182, 162, 152, 132, 112, 92, 72, 53, 33, 13, and 4.8, respectively.

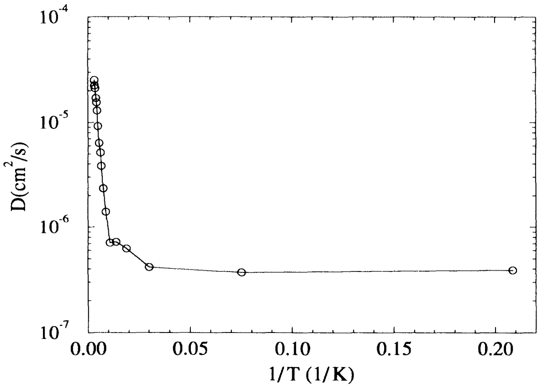

FIG. 4. The temperature dependence of diffusion coefficient D obtained from the standard formula (Ref. 14) using the MSD(t)'s as shown in Fig. 3 for pure Ga metal.

B. Structural properties

In order to examine the structural properties, the atomic configurations are recorded at particular temperatures in the present MD simulation on $\Omega(T)$ and $E(T)$. For each of the recorded atomic configurations, another run of 4000 time steps at a fixed temperature is performed and pair distribution function determined, i.e.,

$$g(r)=\Omega N^{-1}\left\langle \sum_{i=1}^{N} n_i(r,r+\Delta r)/(4\pi r^2\Delta r)\right\rangle . \tag{5}$$

Herein, N stands for the number of atoms involved in the system under consideration, n_i denotes the number of the atoms in the distance between r and $r+\Delta r$ from the ith atom and the notation $\langle A \rangle$ means the time average of A. The essential features of $g(r)$'s thus obtained are displayed in Fig. 5 for $T=323$, 153, and 4.8 K and are significantly different, in character, from those for conventional rapidly quenched metallic liquids. The corresponding structure factors $S(q)$ obtained in the usual manner from the formula[17]

$$S(q)=1+\int d\mathbf{r}[g(r)-1]\exp(i\mathbf{q}\cdot\mathbf{r})/\Omega , \tag{6}$$

are shown in Fig. 6. There are three aspects of these $S(q)$'s that merit emphasis. (i) There is no shoulder (or peak) on the high-q side of the second peak in $S(q)$, even for Ga glass at low T. This is contrary to the results of conventional rapidly quenched metals, in which the repulsive part of $V(r)$ does not exhibit a shoulder as shown in Fig. 1. (ii) A shoulder, however, is present on the high-q side of the principal peak of the presently obtained $S(q)$ at T near T_m (i.e., 323 K) and develops into a peak in going from the normal-liquid state to a supercooled-liquid state as experimentally reported[4] (Fig. 6). (iii) When the rapidly quenched Ga liquid is in a glass state, the $S(q)$ is similar to that of amorphous Ga prepared experimentally by vapor deposition onto a cold substrate (Fig. 6).

We now turn to clarify aspects (i) and (ii) just mentioned. In order to do this, we need to recall that the splitting of the second peak in the $S(q)$ for conventional rapidly quenched metals into two subpeaks is due to the presence of icosahedron-type clusters (each consisting of 1551 atomic bonded pairs) in those metals.[6] In view of this and the conclusion made above, i.e., the normal- and supercooled-Ga liquids are entirely liquidlike, the above aspects (i) and (ii) may be associated with the presence of other types of clusters in the Ga liquid under consideration. To be more precise, the pair-analysis technique (see Ref. 18 for details) is applied to the atomic configurations obtained in the present MD simulations and is used to determine the microstructure of the system in question. The points of the results that merit emphasis are as follows. (a) The relative number of 1551 atomic bonded

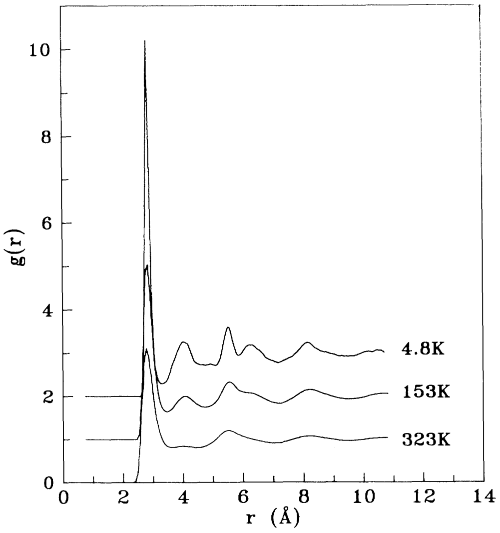

FIG 5. The pair distribution functions, obtained as described in the text, for the presently considered rapidly quenched Ga metal.

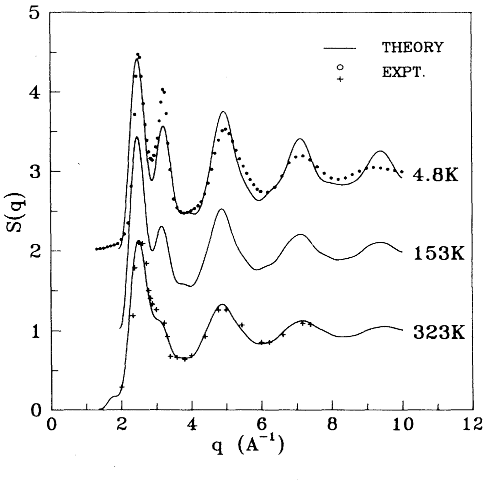

FIG. 6. The structure factors, obtained as described in the text, for (i) the normal-Ga liquid at 323 K and (ii) the presently considered rapidly quenched Ga metal at 153 and 4.8 K along with the experimental results, denoted by the crosses for case (i) and by the dots for the amorphous Ga noted in the text.

TABLE I. The number of icosahedra N_{ic} and the relative numbers of the essential atomic bonded pairs, N_{ijkl}, appearing in the present MD simulation on the liquid-to-glass transition of 500 Ga atoms.

T (K)	N_{ic}	N_{1201}	N_{1301}	N_{1311}
323	0	0.250	0.134	0.233
153	0	0.385	0.165	0.147
4.8	0	0.427	0.128	0.067

pairs is nearly zero so that no icosahedra occur in the present MD simulation. This occurs because the $V(r;\Omega)$'s used (Fig. 1) are not the type of pair potentials in which icosahedra can be easily formed, contrary to those used in Ref. 6 in which the repulsive part of $V(r;\Omega)$ does not exhibit a shoulder as shown in Fig. 1. As a result, the second peak of $S(q)$ remains unsplit in the present case. (b) Further, of the various atomic bonded pairs, the number of 1201 type is very significant in the present MD simulations, particularly at 4.8 K (Table I), even compared to the 1311 and 1301 types, all of which may have some effect on the high-q side of the principal peak of $S(q)$ considered here.[12] Accordingly, the shoulder and subsequent sharp peak on the high-q side of the principal peak in $S(q)$ in going from the normal-liquid state to a supercooled-liquid or glass state (Fig. 6) is probably due primarily to the presence of the those clusters, each containing 1201 atomic bonded pairs.

III. CONCLUSION

It appears from Sec. II A that the normal- and supercooled-Ga liquids are entirely liquidlike. Thereby, the speculation, as noted in Sec. I is questionable. With the use of an interatomic pair potential, as displayed in Fig. 1, the essential features in the experimentally reported $S(q)$ (Ref. 4) for rapidly quenched Ga liquid can be reproduced by the present MD calculation. The presently reported $S(q)$ at 4.8 K is very similar to the experimentally reported $S(q)$ for an amorphous Ga prepared by vapor deposition onto a cold substrate (Fig. 6). The agreement between the sharp peak on the high-q side of the principal peak in the presently reported $S(q)$ and that in the experimentally reported $S(q)$ can be improved by slightly changing the repulsive part of the interatomic potential through the values used for the above-noted β and δ. It is found that, when the agreement becomes better, the $S(q)$ of pure Ga glass becomes more like that of metastable crystalline β phase.[19] Also, the corresponding relative number of 1201 atomic bonded pairs are found to increase considerably, along with a corresponding decrease in the number of the 1311 atomic bonded pairs. This means that the above-mentioned 1201 atomic bonded pairs are characteristic of β crystalline structure. Hence, the shoulder and the splitting of the principal peak mentioned above appear to be due largely to the presence of the clusters of β type in the rapidly quenched Ga liquid.

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