

Relation between the β and rapidly quenched liquid phases of gallium

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From molecular-dynamics simulations, it is demonstrated that (1) a rapidly quenched Ga liquid contains many 1201- and 1311-types atomic bonded pairs and (2) the 1311-type atomic bonded pairs decrease along with a corresponding increase in the 1201 atomic bonded pairs in the crystallization, so that the β -type crystal transition occurs from the supercooled Ga liquid on cooling, or from the pure Ga glass on heating.

I. INTRODUCTION

In general, a metal crystallizes to a simple and stable phase in the supercooled-liquid to crystal transition under standard conditions. However, this is not the case for pure Ga metal, because this metal is one of the few metals that does not crystallize to any of the simple crystal structures. Experimentally, the pure Ga liquid metal tends to crystallize to the metastable crystalline β phase at $T \approx 150$ K in any supercooled-liquid to crystal transition.¹ It is also known experimentally that the same β phase occurs in the crystal transition from a reheated Ga glass, prepared by vapor deposition onto a cold substrate.^{2,3} Extensive experimental and theoretical studies⁴⁻⁶ imply that there must be some close relation between the structures of the β phase and the rapidly quenched liquid phase.⁷

This relation deserves investigation. Hence, a molecular-dynamics (MD) calculation of 500 Ga atoms in the supercooled-liquid and glass states is carried out. The calculation is presented in Sec. II and is used to study the relation of interest. Some conclusions are drawn in Sec. III.

II. CALCULATION

The present calculation is based on an MD simulation of 500 Ga atoms, which adopts (i) the Verlet algorithm⁸ with a time step equal to 1.5×10^{-15} sec and (ii) standard periodic boundary conditions for the involved particles, interacting with one another through an interatomic pair potential⁹ (Fig. 1). Also, in the calculation the variation of metallic volume with temperature at constant pressure is introduced (see Ref. 10 for detail) so that the simulation can be performed in the manner as in the well-known constant-volume calculation¹¹ for given constant pressure ($p = 1.00 \pm 0.15$ bar in this work) at each temperature. This constant-pressure calculation is applicable, as indicated by the results in Table I and Fig. 1 of Ref. 10, for both the normal and quenched metallic liquids.

The present MD simulation is started at 323 K, which is about 20 K higher than the standard melting temperature T_m of pure Ga metal. First, at this temperature, a system of 500 Ga atoms, involved in the simulation, is run for 24 000 time steps to obtain a perfect equilibrium

liquid state of these atoms and, at the same time, the corresponding mean atomic volume Ω is determined from its relation with pressure, as was done in Ref. 9. Next, the damped force method¹² is employed to decrease the temperature of the system with a fast cooling rate R_c , and to determine (i) Ω again from its relation with constant pressure for $T_s < T_m$ and (ii) the other quantities involved as in Ref. 9. The results, obtained using various cooling rates (i.e., $R_{c1} = 5 \times 10^{13}$ K/s, $R_{c2} = 5 \times 10^{12}$ K/s, $R_{c3} = 5.5 \times 10^{11}$ K/s, $R_{c4} = 5 \times 10^{11}$ K/s, and $R_{c5} = 3 \times 10^{11}$ K/s), for the corresponding internal energy E are displayed in Fig. 2. The determined pair-distribution functions [PDF, denoted by $g(r)$] and corresponding structure factors, $S(q)$'s, for the solids produced from the presently considered rapidly quenched Ga liquids are noted, respectively, in Figs. 3 and 4. Of these structure factors, which obtained using R_{c1} , R_{c2} , and R_{c3} are glass-like, as indicated by the comparison of the calculated and experimentally¹³ $S(q)$'s in Fig. 4. The other calculated $S(q)$ in Fig. 4 and the related PDF in Fig. 3(b) have been compared with the corresponding experimental results in Refs. 4 and 5 for all the possible phases of Ga metal. It now turns out that the peaks of the $S(q)$ under considera-

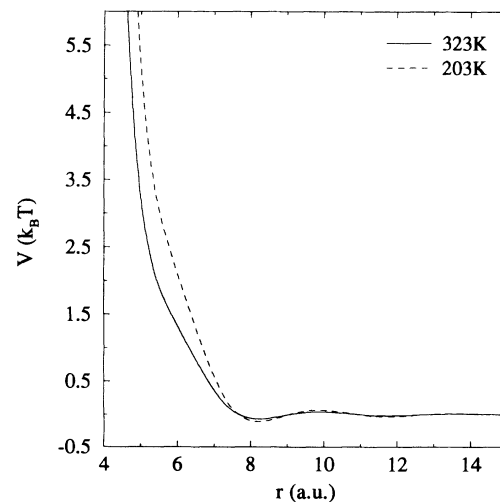


FIG. 1. The interatomic pair potential $V(r)$, obtained as described in Ref. 9, for pure Ga metal.

TABLE I. The relative numbers of the essential atomic bonded pairs, N_{ijkl} , appearing in the MD simulation on (i) the liquid to β -phase transition (denoted by $l \rightarrow \beta$) on cooling at -5×10^{11} K/s rate, (ii) the liquid to glass transition (denoted by $l \rightarrow g$) on cooling at -5×10^{13} K/s, and (iii) the glass to β phase, then to liquid transition (denoted by $g \rightarrow \beta \rightarrow l$) on heating at 5×10^{11} K/s. The relative numbers of the other atomic bonded pairs involved are negligible. Here, g , β , sl , and l are, respectively, the abbreviations of glass, β phase, supercooled liquid, and liquid.

Transition	T (K)	N_{1201}	N_{1211}	N_{1301}	N_{1311}
(a) $l \rightarrow \beta$ (-5×10^{11} K/s)	323(l)	0.215	0.049	0.137	0.246
	203(sl)	0.372	0.047	0.168	0.148
	100(β)	0.426	0.021	0.126	0.075
	4.8(β)	0.634	0.005	0.015	0.013
(b) $l \rightarrow g$ (-5×10^{13} K/s)	203(sl)	0.331	0.049	0.170	0.199
	153(sl)	0.385	0.045	0.165	0.147
	100(g)	0.425	0.033	0.171	0.119
	4.8(g)	0.436	0.021	0.127	0.042
(c) $g \rightarrow \beta \rightarrow l$ (5×10^{11} K/s)	4.8(g)	0.436	0.021	0.127	0.042
	104(g)	0.431	0.023	0.156	0.084
	204(β)	0.579	0.005	0.032	0.027
	274(sl)	0.303	0.060	0.138	0.209
	320(l)	0.206	0.051	0.135	0.246

tion compare favorably well with those of the β phase [Fig. 4(b)]. To be more precise, the theoretical PDF in Fig. 3(b) and structure factor in Fig. 4(b) are compared with those obtained by MD on an ideal β phase equilibrated at 100 K.¹⁴ The reasonably good agreement is found [Figs. 3(b) and Fig. 4(b)]. Accordingly, the structure of the crystals, presently produced using R_{c4} and R_{c5}

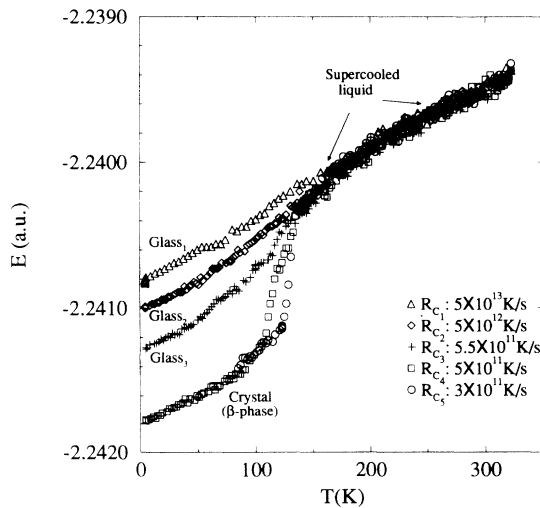


FIG. 2. The presently determined $E(T)$'s for the supercooled liquids and glasses of 500 Ga atoms, obtained using $R_{c1} = 5 \times 10^{13}$ K/s, $R_{c2} = 5 \times 10^{12}$ K/s, and $R_{c3} = 5.5 \times 10^{11}$ K/s. Also included are the values of $E(T)$ presently obtained for the crystal transition from the pure Ga liquid quenched from the melt with lower rates, i.e., $R_{c4} = 5 \times 10^{11}$ K/s, $R_{c5} = 3 \times 10^{11}$ K/s.

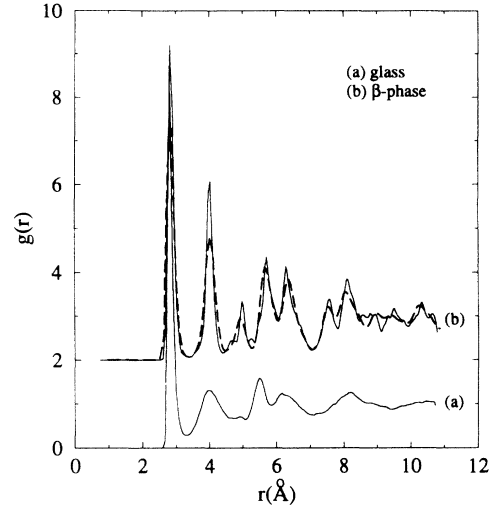


FIG. 3. The PDF's of the glasses and crystals at 4.8 K, noted in Fig. 2. This also includes the PDF of the presently considered ideal equilibrated β phase at 100 K, denoted by the dashed line.

and noted in Fig. 2 is β -type. To go further, we note that, when R_c used is between R_{c3} (which is about the critical cooling rate for preparing Ga glass on computer) and R_{c4} (required to produce the β phase), a solid, produced from the presently considered liquid-solid transition, is between the glass and β phase in structure. This means that the total energy is higher for the presently obtained β phase than for Ga's standard phase (α phase). Indeed, this is the case as can also be seen from the comparison of the internal energies of α -Ga (Refs. 5 and 6) and β -Ga (Ref. 3) at $T = 0$ K (Fig. 5), obtained alternatively from the variation of

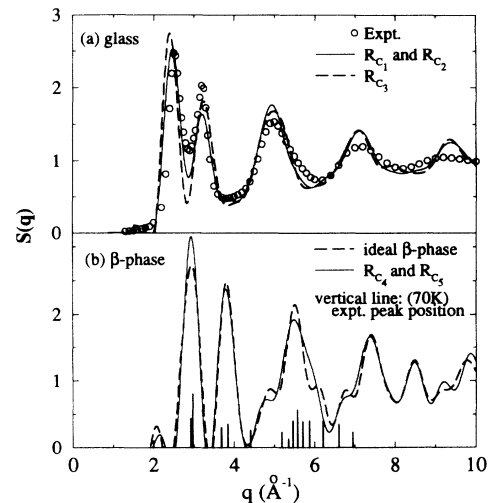


FIG. 4. The structure factors of the presently obtained Ga glasses and Ga crystal, compared with the available experimental results (from Ref. 13 for glass and from Ref. 5 for the β phase). Also included is the structure factor of the presently considered ideal equilibrated β phase at 100 K.

$$E = E_0 + (2N)^{-1} \sum_{i,j} V(r_{ij}), \quad (1)$$

with respect to Ω as usual, E_0 and $V(r_{ij})$ being, respectively, the structure-independent energy (see Ref. 15 for detail) and the interatomic pair potential between the i th and j th atoms for the involved N atoms. There are three points to be noted. First, the last term in Eq. (1) is evaluated in the same manner as in the usual calculation of Madelung energies. Second, in order to obtain a nearly convergent result, the value of N presently used is 2048 for α -Ga and 2000 for β -Ga. Third, the results displayed in Fig. 5 are consistent with those of Gong *et al.*,¹⁶ this showing that the β phase is metastable with respect to the α phase for the atomic potentials used.

Now, we may turn to study the supercooled-liquid to β -phase transition for Ga metal. To this end, the pair-analysis technique (see Ref. 17 for details) is applied to the atomic configurations obtained from the present MD simulation to determine the microstructures of Ga atoms in the supercooled-liquid to solid transitions. Of the obtained results, those that merit emphasis are summarized in Table I. In this table, N_{1201} , N_{1211} , N_{1301} , and N_{1311} represent, respectively, the relative numbers of 1201, 1211, 1301, and 1311 atomic bonded pairs in the system of 500 Ga atoms. It appears from Table I that the relative number of 1201 atomic bonded pairs continuously increases along with a corresponding decrease in the number of the 1301 and 1311 atomic bonded pairs in going down from T_m to a low T and also is the only significant number in the β phase. Accordingly, the 1201 atomic bonded pairs are characteristic of β crystalline structure. Indeed, this can also be seen from the crystal obtained from the present simulation and displayed in Fig. 6, this crystal being monoclinic with chains zigzagging around the c axis, as the experimentally determined β phase.^{1,4} This leads to the conclusion that many potential nuclei

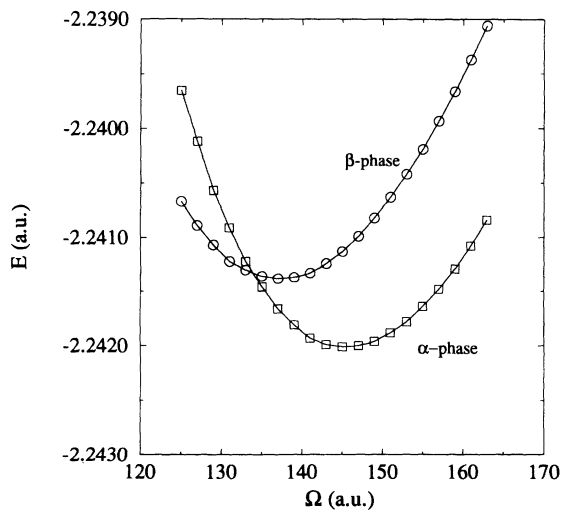


FIG. 5. Determination of the internal energy from its variation with respect to Ω for α -Ga and β -Ga at 0 K. The lattice constants of α phase and β phase are, respectively, $a = 4.47 \text{ \AA}$, $b = 4.553 \text{ \AA}$, $c = 8.4459 \text{ \AA}$ and $a = 2.766 \text{ \AA}$, $b = 8.053 \text{ \AA}$, $c = 3.332 \text{ \AA}$, corresponding to the minimum energy.

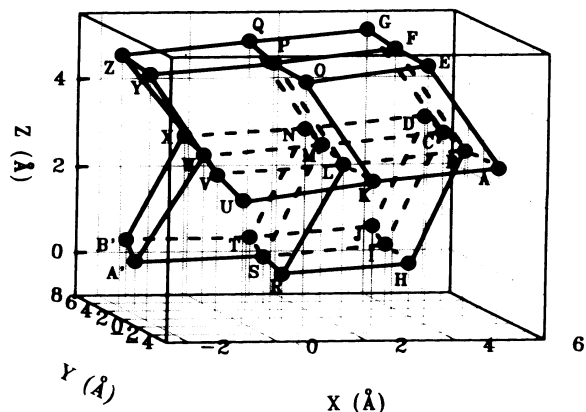


FIG. 6. The β -type crystal obtained from the present simulation at 4.8 K, in which the LB, LF, LH, LP, LR, LV, MC, MG, MI, MQ, MS, MW, NT, NJ, KE, TX, and SW bonded pairs are 1201-like.

for the start of β -type crystallization are present in the rapidly quenched Ga liquid, because the 1201 atomic bonded pairs are the most prevalent pairs in this liquid (Table I). Thereby, for Ga metal a phase rather than the standard phase (α phase) of this metal, i.e., β phase, occurs in the supercooled-liquid to crystal transition. This is not the case at all for the conventional metals, in which the repulsive part of the interatomic pair potential does not exhibit such ledges as those shown in Fig. 1. The reason for this is as follows. In a conventional rapidly quenched metallic liquid, such as Na liquid, the most prevalent atomic bonded pairs are the 1551-type rather than the 1201-type, which can hardly be formed in the atomic potential, which is hard-sphere-like for small ionic separation. Thereby, in the supercooled-liquid to crystal transition the 1551-type atomic bonded pairs convert to those atomic bonded pairs, which are characteristic of some stable crystalline structure (see Fig. 2 of Ref. 10 for Na), for the conventional metals, because the structure of the atoms involved in the 1551 pairs is noncrystalline. Hence, the pure Na metal crystallizes to its standard phase (bcc) in the supercooled-liquid to crystal transition as demonstrated by the present type MD calculation in Ref. 10.

In passing, it is worth noting that the relative number of the 1201 atomic bonded pairs, which appear in the potential nuclei for the start of β crystallization, is insensitive to the cooling rate, as can be seen from the comparison of the values of N_{1201} at $T = 203 \text{ K}$ for $l \rightarrow \beta$ and $l \rightarrow g$ cases (Table I). This is probably the reason why the crystal-transition temperature T_c in the present $l \rightarrow \beta$ transition (Fig. 2) is about the same as the corresponding experimental T_c ($\approx 150 \text{ K}$), for which the cooling rate is at least 100 times less than the presently used cooling rate ($-5 \times 10^{11} \text{ K/s}$).

To proceed further, the pure Ga glass, noted as Glass₁ in Fig. 2, is reheated in the same manner as in Ref. 10. The heating rate is $5 \times 10^{11} \text{ K/s}$ and is considerably slow compared to the cooling rate ($-5 \times 10^{13} \text{ K/s}$) used in preparing Glass₁ in this work. Of the simulated results,

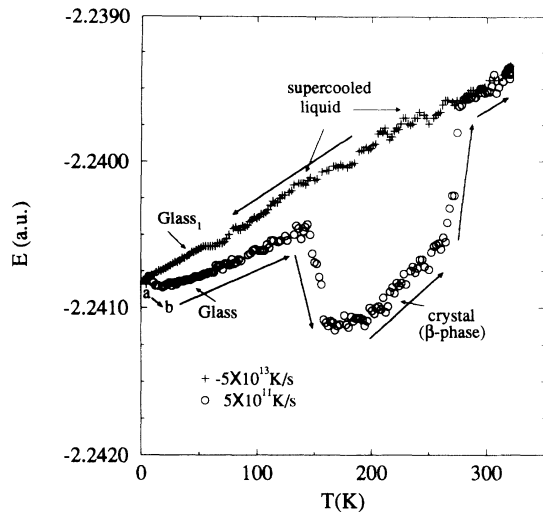


FIG. 7. The presently determined $E(T)$ for the reheated Ga glass along with the $E-T$ curve for Ga Glass₁ for comparison.

those for E and the atomic bonded pairs are, respectively, displayed in Fig. 7 and in part (c) of Table I. The corresponding calculated structure is (i) glasslike for $4 \text{ K} \leq T < 148 \text{ K}$, (ii) β -like for $148 \text{ K} < T < 274 \text{ K}$, and (iii) liquidlike⁹ for $T \geq 274 \text{ K}$. The aspects of the presented results that merit emphasis are as follows. (1) Initially, E decreases with increasing temperature as shown by the ab line in Fig. 7. This occurs because the rate of heating used here is slow enough (compared to the critical cooling rate for preparing Ga glass, which is about $-5.5 \times 10^{11} \text{ K/sec}$ for the present case) to allow E changes to take place in such a manner as shown by the ab line (corresponding to stabilization). (2) As T continuously increases, the reheated glass becomes a solid, that looks like another Ga glass, which can be produced through a cooling process with a cooling rate significantly less than the above-noted cooling rate ($-5 \times 10^{13} \text{ K/sec}$). (3) When further increasing temperature, the solid just noted above becomes a supercooled liquid and then tends to be a β -type crystal. (4) The corresponding crystal-transition temperature T_c is about 150 K (Fig. 7), this being consistent with the experimental T_c , which appears in the normal Ga liquid to β -phase transition. However, this T_c is considerably higher than $T_c \approx 15 \text{ K}$, appearing in the above-noted experimental Ga glass to β -phase transition.² This occurs probably because the Ga glass, prepared experimentally by vapor deposition onto a cold substrate, is unstable. (5) The melting temperature of the presently obtained β crystal is 274 K (Fig. 7), which is consistent with the corresponding experimental value [$=257 \text{ K}$ (Ref. 18)]. This melting temperature is lower than the corresponding standard T_m , which is 303 K (Ref. 18) for real Ga metal (being in the α phase in structure) in its crystal to normal-liquid transition. (6) From part (c) of Table I, the structure of

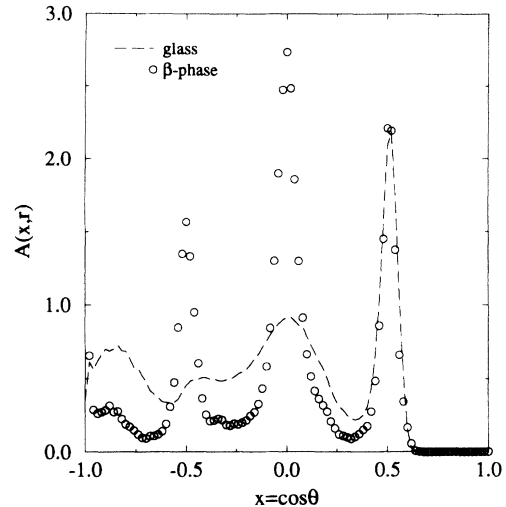


FIG. 8. Angular distribution functions, calculated in the same manner as in Ref. 19 for nearest neighbors in both the presently obtained β -type crystal and glass and denoted by the open circles for the former and the dashed curve for the latter.

the above-noted β phase is similar to that of the presently considered glass, because the most prevalent atomic bonded pairs are 1201-type in both the β -Ga and Ga glass. Indeed, this is the case as can be seen from (i) the comparison of the theoretical results shown in Figs. 3 and 8 for both the β -Ga and Ga glass and (ii) the previously reported experimental results.³ Accordingly, in the presently considered heating process the pure Ga glass can make a β -type phase transition, in which the 1201 atomic bonded pairs increase with increasing T along with a corresponding decrease in the 1301 and 1311 atomic bonded pairs [part (c) of Table I].

III. CONCLUSION

It appears that the 1201 atomic bonded pairs, being characteristic of β crystalline structures, are predominate in the supercooled Ga liquid (Table I) for a reason noted in the preceding section. Hence, the metastable crystalline β phase occurs in both (i) the supercooled-liquid to crystal and (ii) the glass to crystal transitions for Ga metal, as experimentally reported.

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