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Subpeaks of structure factors for rapidly quenched metals

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From molecular-dynamics simulations, it is demonstrated that the structure factor has a second-peak splitting feature not only for glass states but also for supercooled-liquid states in some metallic cases. This appears to be due primarily to the presence of icosahedronlike clusters in these cases. This suggests that a laboratory or simulated metallic glass is generally a distorted metallic solid including a significant amount of icosahedra, each consisting of 13 atoms. This lends strong support to one of various existing structural models, namely, the Briant model.

It is well known experimentally that the structure factor $S(q)$ of a metallic glass has a subpeak (or shoulder) on the high-wave-vector side of its second peak.[1] This is often called the second-peak splitting of $S(q)$. Various structural models[2–6] have been proposed to clarify this splitting for both laboratory and simulated metallic glasses. Of these proposed models, the simplest structural model is that proposed by Briant.[3] According to his model, this splitting is largely due to the existence of many icosahedra, each consisting of 13 atoms. This model deserves further investigation because it comes simply from a study of quenched microclusters. The main purpose of this work is thus twofold: (a) to demonstrate that the second-peak splitting is also present in the structure factor of some supercooled-metallic liquid and (b) to examine the Briant model further as an extension of Ref. 7.

We start with a molecular-dynamics (MD) simulation of 500 aluminum atoms, subject to periodic boundary conditions, and interacting via the following pair potential:

$$V(r_{ij})=(Z_{\text{eff}}^2/r_{ij})\left[1-(2/\pi)\int_0^\infty dq\, F(q)\sin r_{ij}/q\right], \qquad (1)$$

Z_{eff} and $F(q)$ being, respectively, the effective ionic valence and the normalized energy wave number characteristic, defined in the energy-independent nonlocal model-pseudopotential theory[8] (see Ref. 7 for details of this simulation). The simulation is started at $T=943$ K (which is 10 K higher than the melting temperature T_m of pure Al metal). First, at this T, the system is run for 30 000 time steps to guarantee an equilibrium liquid state, for which the mean atomic volume, $\Omega=135.13$ a.u., used for the simulation is taken from the Ω-T curve in Ref. 9 for the supercooled-liquid states of Al. Next, taking the values of 500Ω, obtained using (i) the Ω-T curve in Ref. 9 for supercooled-liquid states and (ii) that in Ref. 10 for glass states, as the volumes of the 500 Al atoms, the damped force method[11] is employed to decrease the temperature of the system with the cooling rate of 4×10^{13} K/sec. The atomic configurations are recorded at particular temperatures during the cooling process. For each of the recorded configurations, another run of 4000 time steps at the corresponding temperature is performed in order to determine the structure-dependent part of energy E_p and the pair distribution function $g(r)$, i.e.,

$$E_p=(2N)^{-1}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N}{}' V(r_{ij})\right\rangle \qquad (2)$$

and

$$g(r)=(\Omega/N)\left\langle \sum_{i=1}^{N} n_i(r,r+\Delta r)/(4\pi r^2\Delta r)\right\rangle . \qquad (3)$$

Here, $V(r_{ij})$ is the pair potential between the ith and jth atoms separated by the distance r_{ij}, the prime on the summation means the exclusion of $j=i$ in the sum, N stands for the total number of atoms involved, n_i denotes the number of atoms in the radial distance between r and $r+\Delta r$ for the i atom and the brackets $\langle\ \rangle$ show the time average. The $g(r)$'s thus obtained are displayed in Fig. 1 for selected T's. The corresponding structure factors, $S(q)$'s, obtained using these $g(r)$'s through the formula

$$S(q)=1+\int d\mathbf{r}[g(r)-1]\exp(1\mathbf{q}\cdot\mathbf{r})/\Omega , \qquad (4)$$

are displayed in Fig. 2. These $S(q)$'s are similar to those

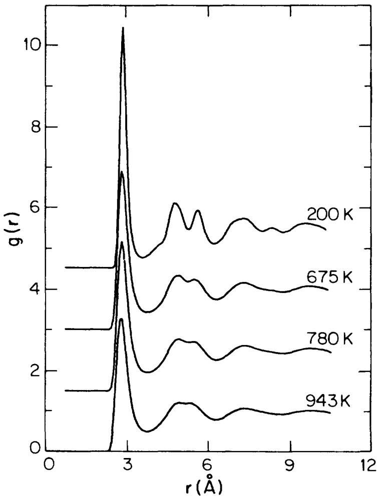

FIG. 1. Temperature-quench results for the $g(r)$'s of pure Al metal.

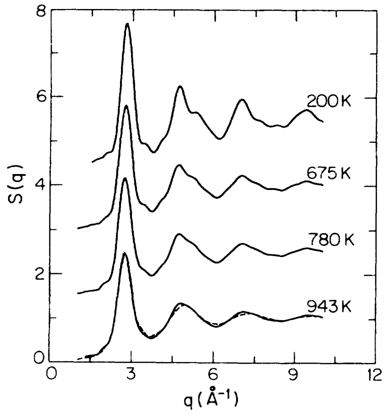

FIG. 2. Temperature-quench results for the $S(q)$'s of pure Al metal (for which $T_m = 933$ K and $T_g \simeq 500$ K in the present MD simulation, in which the quenching rate is 4×10^{13} K/sec). Also included is the experimental $S(q)$ at 943 K, dashed curve (Ref. 1).

obtained in Ref. 12 using a $V(r_{ij})$ different from that given by Eq. (1). Now, it appears from Fig. 2 that, for pure Al metal (which can form a glass in the laboratory through a vapor-quenching process), the second-peak splitting is present not only in the $S(q)$'s for the glass states but also in the $S(q)$'s for supercooled-liquid states at T's between T_m and T_g ($\simeq 500$ K, deduced from both (i) the $E_p - T$ curve and (ii) the temperature dependence of the Wendt-Abraham ratio,[13] R [$= g_{\min}/g_{\max}$, $g_{\min}$ and $g_{\max}$ being, respectively, the first minimum and the first maximum of $g(r)$] (Fig. 3)). The same can be expected for pure Cr metal because the corresponding $g(r)$ has a second-peak splitting feature as in Fig. 1 (Ref. 14) not only for glass states but also for supercooled-liquid states. However, this is not the case for most metallic systems, for which there is no second-peak splitting in the $g(r)$ for any supercooled-liquid state.

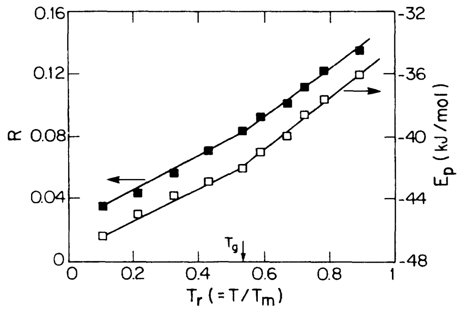

FIG. 3. Values of $E_p(T)$ and $R(T)$ from the present MD simulation for pure Al metal.

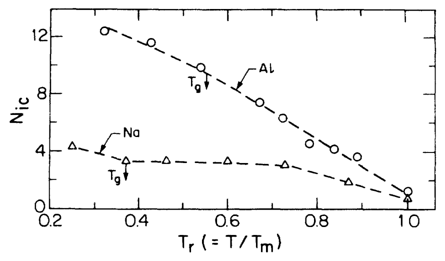

FIG. 4. Values of $N_{\rm ic}$ of the 500-atom system on cooling for pure Al metal and pure Na metal [for which $T_m = 373$ K and $T_g \simeq 140$ K from computer simulations (Ref. 16)].

In order to see if the Briant model[3] mentioned above can be used to clarify the presently calculated results, the pair analysis technique of Honeycutt and Andersen[15] is applied to the presently simulated atomic configurations to extract the number of icosahedra $N_{\rm ic}$ formed in the systems of interest and the coordinates of the 13 atoms in each icosahedron at each T. The results obtained (Fig. 4) indicate that $N_{\rm ic}$ for Al at $T \ll T_m$ is about two times larger than that for pure Na metal, for which $g(r)$ or $S(q)$ does not exhibit any peak splitting for supercooled-liquid states.[16] This occurs because the Al atoms in a liquid state have a large probability of forming a polyhedron,[17] as compared with the Na case. This, in turn, arises because the pair potential is more attractive for Al atoms than for alkali atoms.[9] The values obtained for the above-mentioned coordinates have been used to calculate the structure factor of an icosahedron, that is,[18]

$$[S(q)]_{\rm ic} = 1 + (2/13) \sum_{i=1}^{13} \sum_{j=1}^{13}{}' \sin(qr_{ij})/(qr_{ij}) \, . \qquad (5)$$

Of the results obtained for the different distorted icosahedra, those for the typical icosahedra in the supercooled Al and Na metals are displayed in Fig. 5. Apparently, there is a shoulder on the high-wave-vector side of the second peak in $[S(q)]_{\rm ic}$. Furthermore, the positions of the peaks in this $[S(q)]_{\rm ic}$ are consistent with those in Fig. 2 for Al. This is also found to be the case for Na. At this point, it is worth noting from the present MD simulation that the number of other types of polyhedra (or clusters), which differ from icosahedra in structure, in any presently considered supercooled liquid is small compared to $N_{\rm ic}$. Accordingly, a supercooled-metallic liquid can be regarded as a metallic liquid including $N_{\rm ic}$ icosahedron-like clusters. Hence, the total $S(q)$ of a supercooled liquid must include the contribution of the $[S(q)]_{\rm ic}$'s of these clusters. Since both $N_{\rm ic}$ and the second-peak splitting feature of $[S(q)]_{\rm ic}$ are more significant for Al metal than for Na metal at T considerably below T_m (Figs. 4 and 5), the effect of this contribution on the second peak of $S(q)$ is not negligible for the former metal. This would

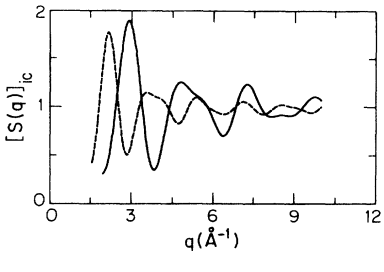

FIG. 5. Theoretical $[S(q)]_{\rm ic}$ as a function of q for Al, full curve, and that for Na, dashed curve.

lead to a shoulder in $S(q)$ for the supercooled-liquid states as shown in Fig. 2.

Having satisfactorily interpreted the splitting of the second-peak in $S(q)$ for supercooled Al liquid as above, this interpretation can be extended to clarify the second-peak splitting in $S(q)$ for glass states because the physical origin must be the same for both. Accordingly, it may be concluded that the splitting of the second peak of $S(q)$ of a metallic glass into two peaks is due to the contribution of the $[S(q)]_{\mathrm{ic}}$'s to $S(q)$. This, in turn, suggests that a metallic glass is generally a disordered metallic solid including N_{ic} icosahedra, this being consistent with the Briant model.[3] Finally, it should be noted that the value of N_{ic} involved here is small compared to the total number of polyhedra in the system under consideration, as indicated by Fig. 4 and Table I of Ref. 7 for the metallic glass $\mathrm{Ca_{0.7}Mg_{0.3}}$ (which can form a glass in the laboratory through the liquid-quenching process). This, in turn, prompts us to suspect the basic assumption of other models,[5,6,19] i.e., every atom in a metallic glass has 12 atoms in its first-neighbor shell to form an icosahedron, in general.

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