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Abstract. A molecular dynamics simulation on the phase transitions of a reheated $Al_{0.86}V_{0.14}$ glass is presented. The results obtained demonstrate a number of aspects of the transitions involved, leading to the suggestion that such solids as the experimentally reported amorphized icosahedral quasicrystals in the literature may be considered as highly perturbed quasicrystals, in which the orientational order is lost through the random orientation of icosahedra.

Mayer *et al* [1] have demonstrated the similarity between the structure of an amorphized quasicrystal of $Al_{0.84}V_{0.16}$ alloy (produced by electron irradiation of the quasicrystalline phase of this alloy) and the structure of a typical liquid-quenched metallic glass. This was examined further (see, e.g., [2, 3]) and we are left with the following dilemma: either the amorphized quasicrystal is not really amorphous but rather microquasicrystalline or it may be thought of as highly defective quasicrystal.

The main purpose of the present work is to obtain some information that would advance our understanding of such states as that of the above-noted amorphized quasicrystal. For this, we considered a molecular dynamics (MD) simulation [4] on the liquid-to-glass and glass-to-other-solids transitions of binary $Al_{0.86}V_{0.14}$ alloy, which consists of 430 Al atoms and 70 V atoms, subject to the usual periodic boundary conditions, and interacting via an interatomic pair potential, i.e.

$$V_{ij}(r) = (Z_i Z_j - \rho_{i,d}\rho_{j,d})\, r^{-1}\left(1 - \frac{1}{\pi}\int_0^{\infty} [F_{ij}(q) + F_{ji}(q)]\,\frac{\sin(rq)}{q}\,\mathrm{d}q\right) \qquad (1)$$

Z_i, $\rho_{i,d}$ and $F_{ij}(q)$ being, respectively, the ionic valence, the depletion charge of the i-type atom and the normalized energy wavenumber characteristic, defined in the energy-independent non-local model-pseudo-potential (EINMP) theory [5]. This pair potential is reliable for both Al and V atoms in their metallic states, as indicated by the results obtained using the EINMP theory for pure Al and V metals in [5]. Also, the valence electron charge-transfer effects should not be large in the binary alloy of interest, because the electronegativity difference between Al and V is not significant. Accordingly, the above $V_{ij}(r)$ can be used immediately as an interatomic pair potential between any two atoms in the binary alloy under consideration. Having

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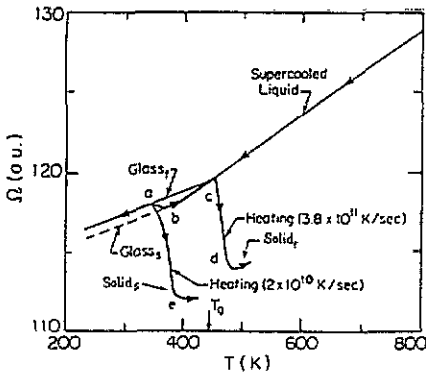
Figure 1. The $\Omega(T)$-values (in arbitrary units) determined for the liquid-to-glass and the glass-to-solid transitions in binary $Al_{0.86}V_{0.14}$ alloy.
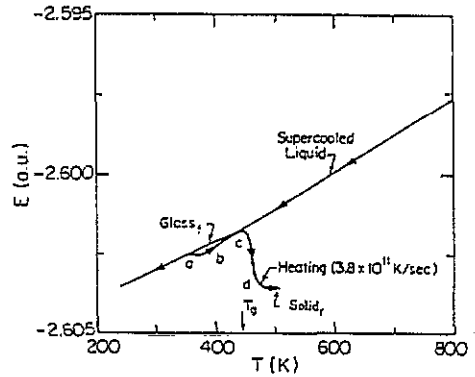
Figure 2. The internal energies determined, corresponding to the $\Omega(T)$-values (in arbitrary units) in figure 1 for $Al_{0.86}V_{0.14}$.

determined the potential for use, the MD procedure is first applied to arrange the atoms involved to be in a liquid-state configuration at a T somewhat above the corresponding melting temperature T_m and to determine the mean atomic volume Ω from its relation with the pressure p, i.e.

$$p = k_B T/\Omega - \partial E_0/\partial\Omega \qquad (2)$$

with E_0 being the internal energy E minus one-ion kinetic energy, i.e.

$$E_0 = E_e + E_1 + E_p + \Delta E + (2\Omega)^{-1}\int V(r)\,dr \qquad (3)$$

in the EINMP theory at present used [6]. Herein E_e and E_1 are, respectively, the electron-gas energy and the first-order energy in the EINMP theory (see, for details, [5]). E_p is the structure-dependent part of the energy, which can be obtained from the MD simulation using the formula

$$E_p = (2N)^{-1}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} V_{ij}(r) \right\rangle \qquad (4)$$

where N and $\langle A \rangle$ stand, respectively, for the number of atoms involved and the time average of A. ΔE is of the form

$$\Delta E = (Z_i Z_j - \rho_{i,d}\rho_{j,d}) \Big/ \left(2\pi\int_0^\infty [F_{ij}(q) + F_{ji}(q)]\,dq\right). \qquad (5)$$

Now, the second term in equation (2) may be evaluated numerically as

$$\partial E_0/\partial\Omega = -(4\pi r_0^4)^{-1}(a_1 + 2a_2/r_0) \qquad (6)$$

with a_1 and a_2 satisfying the relation

$$E_0 = a_0 + a_1 r^{-1} + a_2 r^{-2} \qquad (7)$$

for a given volume and $r_0 = (3\Omega/4\pi)^{1/3}$.

Next, the damped-force method [7] is employed to decrease the temperature of the system under consideration with a fast cooling rate, i.e. 2×10^{13} K s^{-1}, and to determine Ω as a function of T from the condition that p involved in the simulation be about 10 bar (p is so sensitive to Ω that Ω at 10 bar does not differ significantly from Ω at 1 bar). The results thus obtained for $\Omega(T)$ and the corresponding internal energy $E(T)$ are, respectively, denoted in figures 1 and 2 by the lines with arrows pointing to the left. The corresponding pair distribution function (PDF) at 400 K, obtained using its partial PDFs (figures 3–5) as usual, is shown in figure 6 by curve A, this being similar to those of the usual liquid-quenched metallic glasses. This means that the rapidly quenched $Al_{0.86}V_{0.14}$ liquid becomes a glass at $T < T_g$ shown in figures 1 and 2 as the glass transition temperature.

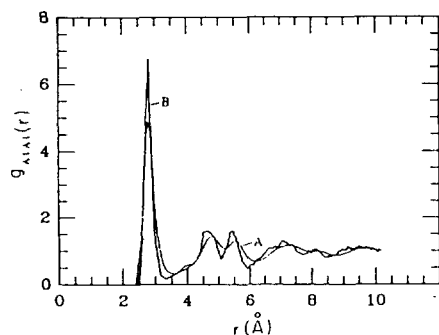**Figure 3.** The partial PDF $g_{AlAl}(r)$ between Al atoms for binary $Al_{0.86}V_{0.14}$ glass at 400 K (curve A) and for solid$_f$ at 470 K (curve B).

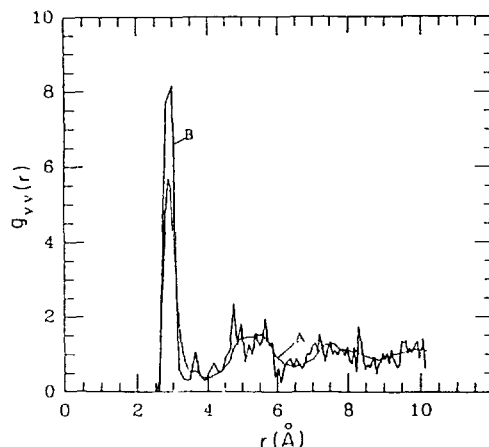**Figure 4.** The partial PDF $g_{VV}(r)$ between V atoms for binary $Al_{0.86}V_{0.14}$ glass at 400 K (curve A) and for solid$_f$ at 470 K (curve B).

Subsequently, we proceed to reheat the glass obtained (denoted as glass$_f$ in figures 1 and 2) at two heating rates: 2×10^{10} K s^{-1} and 3.8×10^{11} K s^{-1}. The corresponding Ω-values, determined as described above, are also displayed in figure 1 by the curves ae and abcd. The aspects of the displayed results that merit emphasis are as follows.

(i) In the slow-heating case, the volume of the glass decreases with increasing T before it makes a phase transition to another type of solid (solid$_s$ say) as indicated by the curve ae. This occurs because the corresponding heating rate is slow enough (compared with the cooling rate used here) to allow volume changes to take place in such a manner as shown by the curve ae (corresponding to stabilization).

(ii) When the heating rate is significantly faster than the slow-heating rate, the reheated glass first reduces its volume and then becomes another type of glass, glass$_s$ say (which can be produced from the binary $Al_{0.86}V_{0.14}$ liquid quenched with a slow cooling rate). On further increasing T, the glass$_s$ becomes a supercooled liquid (characterized by the curve bc in figure 1), because the atoms involved are being reheated too rapidly to attain equilibrium. Finally a phase transition to a solid (solid$_f$ say), as indicated by the curve cd, occurs. This is consistent with the temperature

dependence of the corresponding $E(T)$ (figure 2). In addition, in order to find the structures of the above-noted solid$_s$ and solid$_f$, the pair-analysis technique (see, for details, [8]) is applied to the atomic configurations resulting from the present MD simulation to determine the microstructure of the glass$_f$ at 400 K and those of the currently obtained solid$_s$ and solid$_f$. The important results obtained are summarized in table 1. In this table, N_{1551} denotes the relative number of 1551 atomic bonded pairs [8,9] in the system under consideration. These pairs are characteristic of the icosahedral structure, which may appear in a non-crystalline system. N_{1421} and N_{1422} stand, respectively, for the relative numbers of 1421 and 1422 atomic bonded pairs, being, respectively, characteristics of FCC and HCP structures [9]. N_{1441} denotes the relative number of 1441 atomic bonded pairs, which is characteristic of the BCC crystalline structure. N_{1541} and N_{1431} stand, respectively, for the relative numbers of 1541 and 1431 atomic bonded pairs, which are present in some non-crystalline systems. Also summarized in this table are the number $N_{a,ic}$ of atoms involved in the formed icosahedra, the number N_{ic} of icosahedra formed and the number N_{FCC} of FCC-type polyhedra. It now appears from this table that the above-noted solid$_s$ is an FCC-like crystal, this being consistent with the corresponding PDF (figure 7, obtained using its partial PDFs shown in figure 8), which is similar to that of an FCC crystal at an intermediate T.

Table 1. Relative numbers of the essential atomic bonded pairs at present obtained and the values of $N_{a,ic}$, N_{ic} and N_{FCC} determined for the defined glass$_f$ at 400 K, solid$_s$ at 410 K and solid$_f$ at 470 K, each consisting of 430 Al atoms and 70 V atoms.

System	N_{1551}	N_{1541}	N_{1421}	N_{1422}	N_{1431}	N_{1441}	$N_{a,ic}$	N_{ic}	N_{FCC}
Glass$_f$	0.305	0.081	0.004	0.009	0.082	0.073	98	9	0
Solid$_s$	0.001	0.014	0.661	0.086	0.023	0.001	0	0	216
Solid$_f$	0.344	0.168	0.017	0.034	0.175	0.055	186	17	0

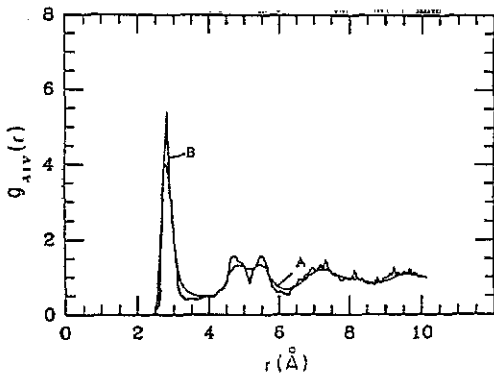

Figure 5. The partial PDF $g_{AlV}(r)$ between Al and V atoms for binary Al$_{0.86}$V$_{0.14}$ glass at 400 K (curve A) and for solid$_f$ at 470 K (curve B).
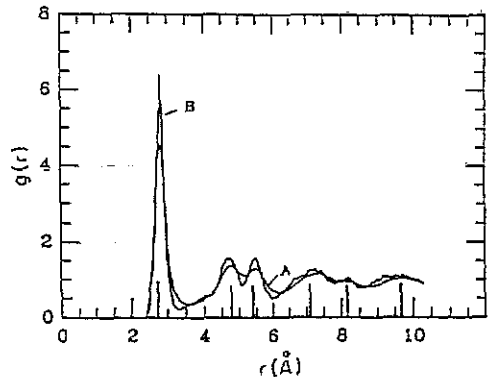
Figure 6. The PDF of binary Al$_{0.86}$V$_{0.14}$ glass at 400 K (curve A) together with that of solid$_f$ at 470 K (curve B). The vertical lines denote the peak positions of the experimental PDF for the amorphized quasicrystal of Al$_{0.84}$V$_{0.16}$ alloy [1].

We now try to clarify the solid$_f$ mentioned above. For this, we first note that the PDF of this solid is similar to that of the present liquid-quenched metallic glass

(denoted glass$_f$ in figure 1) as shown in figure 6 rather than to that of a quasicrystal [10]. Also, the theoretical bond-angle correlation function of the same solid is found to be not significantly different from that of the glass$_f$. Nevertheless, the solid$_f$ is clearly not a conventional metallic glass, as indicated by the significant differences obtained here (table 1 and figures 3–5) between the structures of the solid$_f$ and glass$_f$. At this point, there are two points to be emphasized.

(i) The number of icosahedra (which are responsible for the main characteristics of the PDFs of non-crystalline systems [11]) is so much greater in the solid$_f$ than in a glass (table 1) that the former looks like a perturbed icosahedral quasicrystal.

(ii) The peak positions of the PDF of the solid$_f$ are all in excellent agreement with those of the previously noted amorphized icosahedral quasicrystal [1–3].

Accordingly, the solid$_f$ appears to be similar in structure to an amorphized quasi-crystal rather than to a conventional metallic glass.
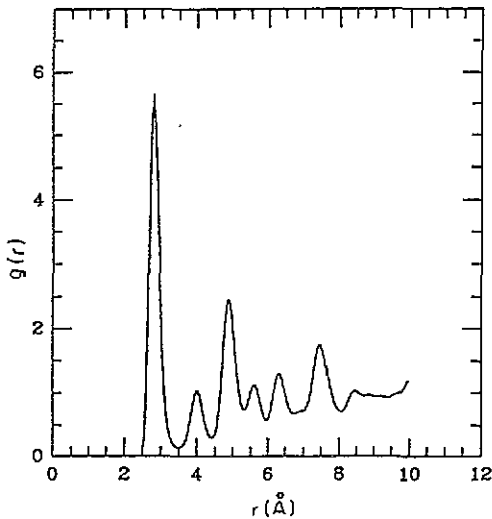

Figure 7. The PDF of solid$_s$ at 410 K, obtained from the slowly reheated Al$_{0.86}$V$_{0.14}$ glass (for which the heating rate is 2×10^{10} K s^{-1}).
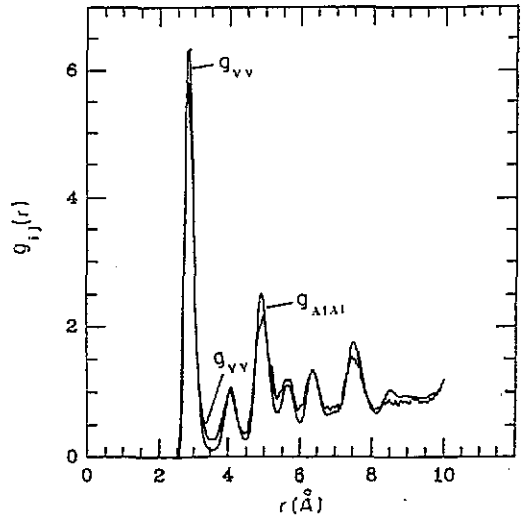
Figure 8. The partial PDF $g_{AlAl}(r)$ between Al atoms and the partial PDF $g_{VV}(r)$ between V atoms for solid$_s$ at 410 K. The corresponding $g_{AlV}(r)$ is not shown here but lies between $g_{AlAl}(r)$ and $g_{VV}(r)$.

We are thus left with the suggestion that the solid$_f$ produced as described above and the experimentally reported amorphized quasicrystals [1–3] may be considered as highly perturbed icosahedral quasicrystals, in which the orientational order is lost through the random orientation of icosahedra.

Finally, it is worth noting that we have also reheated the currently produced glass$_f$ at heating rates of 1.5×10^{11} and 2.8×10^{11} K s^{-1}, which lie between the two heating rates in figure 1. However, the solids obtained are all FCC-like. This seems to imply that the above-noted solid$_f$ and the quasicrystalline state of the binary Al$_{0.86}$V$_{0.14}$ system are thermodynamically unstable with respect to its FCC-like phase, at least in the model at present used.

Acknowledgments

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