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Phonon dispersion in a metallic glass

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Analytical expressions for the dispersion of the longitudinal and transverse phonons are obtained for a two-component metallic glass employing a self-consistent phonon theory for amorphous solids as developed by Takeno *et al.* The effective pair potential used for the computation of the eigenfrequencies of the longitudinal and transverse phonons in $Ca_{70}Mg_{30}$ glass is obtained by making use of the Ashcroft pseudopotential for the pure components. Eigenfrequency expressions reproduce the main characteristic features of the dispersion curves obtained by neutron scattering and computer simulation techniques, both for the longitudinal and the transverse phonons. The results of the present computations are in good agreement with the available experimental data.

I. INTRODUCTION

In recent years there has been considerable interest in the physics of the glass-forming alloys to investigate the properties of elementary excitations such as electrons, phonons and magnons. Phonons are of particular interest in the study of polycrystalline and amorphous solids and liquids because their dynamical structure factors can be measured by neutron inelastic scattering. These investigations involve the measurement of the collective density waves at larger momenta, and for a few metallic glasses it has been possible to follow the dynamical structure factors up to very large wave vectors.[1] Characteristically the dispersion relations derived from the dynamical structure factors show a minimum at a certain value of the wave vector, where the static structure factor of the glass forming alloy has its first maximum. Computer simulations[2,3] and analytic calculations[4] have demonstrated that this minimum arises from a process analogous to the Umklapp-scattering in the crystalline solids; the sharp first maximum in the static structure factor acts like a smeared out reciprocal-lattice vector. The experimental probe provides an evidence to the longitudinal density waves, contrary to that for the transverse excitations, which is monotonic and shows no minimum. However, at low momentum transfer the dispersion relations of both types of excitations are strictly linear.

Although we have sufficient understanding of the properties of collective density waves in amorphous solids, still these studies have paid relatively little attention to the multicomponent nature of the metallic glasses. Partial wave-number dependent spectral functions have been computed[5] for the simple metal Ca-Mg and Mg-Zn alloys, but there are very few systematic investigations[6,7] of dynamical concentration fluctuations in metallic glasses or glass-forming alloys. Although experimental studies are as yet scarce, computations and molecular dynamics have been done in a few metallic glasses[5,8] from the point of view of investigating the phonon dispersion.

In the present paper a detailed theoretical investigation of the dispersion relations of collective excitations in a glass-forming alloy, taking $Ca_{70}Mg_{30}$ as an example, have been presented. The theory[9] of phonons for amorphous solids and its application for the study of phonon dispersion in simple liquids and liquid metals is well tested[10] and well established. However, no efforts have been made to use the theory to study the phonon dispersion in metallic glasses. The expressions for the phonon eigenfrequencies for the binary metallic glasses are developed, treating them as amorphous materials.

II. THEORY

The proposed method for the calculation of the longitudinal and the transverse phonon modes is based on the theory of phonons for amorphous solids. Consider a glass-forming alloy of $A_{(1-x)}B_x$ type, which has $1-x$ concentration fraction of A component and x concentration fraction of B component.

The usual form of effective ion-ion pair potential in a single component fluid (metal) A or B is given as

$$V(r)=\frac{Z^2e^2}{r}+\frac{2}{\pi}\int d\mathbf{q}\,F(q)\exp(-i\mathbf{q}\cdot\mathbf{r}) \ . \qquad (1)$$

Z is the valence and $\mathbf{q}$ represents wave-vector transfer. The first term in the above relation gives the Coulomb repulsion between the ions and the second term is an indirect interaction through the conduction electrons, which adds an attractive contribution. The function $F(q)$ is known as the energy wave-number characteristic and is given as[11]

$$F(q)=\frac{\Omega q^2}{8\pi}\left[\frac{1}{\epsilon(q)}-1\right]|\omega_b(q)|^2 \qquad (2a)$$

when the pseudopotential is supposed to be local. The form factor of the ion, $\omega_b(q)$, is that of Ashcroft[12] and is given by

$$\omega_b(q)=-\frac{4\pi Ze^2}{q^2\Omega}\cos(qr_c) \ , \qquad (2b)$$

where r_c is an adjustable parameter and is known as the core radius, and Ω is the volume per electron. The dielectric response function, $\epsilon(q)$, is given by

$$\epsilon(q)=1-\frac{(4\pi e^2/q^2)X(q)}{1+(4\pi e^2/q^2)X(q)G(q)} . \tag{2c}$$

Here, $X(q)$ takes into account the Coulomb interaction between the electrons and is expressed as

$$X(q)=\frac{-mk_F}{\pi^2\hbar^2}\left[\frac{1}{2}+\frac{4k_F^2-q^2}{8k_F q}\ln\left|\frac{2k_F+q}{2k_F-q}\right|\right] , \tag{2d}$$

where m is the mass of the electron, e is the charge on the electron, h is Planck's constant, and k_F is the Fermi wave number.

The function $G(q)$, called the local field function, accounts for the exchange and correlation energies among the electrons, and is that of Hubbard and Sham:[13]

$$G(q)=\frac{q^2}{2(q^2+\nu k_F^2)} \tag{2e}$$

with

$$\nu=\frac{2}{1+0.153/\pi k_F} .$$

Once the pair potentials for the single components of the liquid metals are known, a mean effective density-dependent interatomic potential in the case of a glass-forming alloy of the type $A_{1-x}B_x$ can be written as

$$V_{\text{eff}}(r)=C_A^2V_{AA}(r)+2C_AC_BV_{AB}(r)+C_B^2V_{BB}(r) . \tag{3}$$

Here, $V_{AA}(r)$ is the pair potential for the A-A component, $V_{AB}(r)$ for A-B component and $V_{BB}(r)$ for the B-B component in the $A_{1-x}B_x$ alloy, having concentration C_A of A type and C_B of B type. These concentrations are obtained in terms of concentration fractions and molar volumes as

$$C_A=\frac{(1-x)V_A}{(1-x)V_A+xV_B}$$

and

$$C_B=\frac{xV_B}{(1-x)V_A+xV_B} ,$$

where V_A and V_B are the molar volumes of A and B components, respectively. Now, using Eq. (1), $V_{AA}(r)$, $V_{AB}(r)$, and $V_{BB}(r)$ can be written as

$$V_{AA}(r)=\frac{(Z_Ae)^2}{r}+\frac{2(Z_Ae)^2}{\pi}\int dq\frac{\sin(qr)}{(qr)}\cos^2(qr_c^A)\times\left[\frac{1}{\epsilon_{AA}(q)}-1\right] , \tag{4a}$$

$$V_{AB}(r)=\frac{(Z_{AB}e)^2}{r}+\frac{2(Z_{AB}e)^2}{\pi}\int dq\frac{\sin(qr)}{(qr)}\cos^2(qr_c^{AB})\times\left[\frac{1}{\epsilon_{AB}(q)}-1\right] , \tag{4b}$$

and

$$V_{BB}(r)=\frac{(Z_Be)^2}{r}+\frac{2(Z_Be)^2}{\pi}\int dq\frac{\sin(qr)}{(qr)}\cos(qr_c^B)\times\left[\frac{1}{\epsilon_{BB}(q)}-1\right] . \tag{4c}$$

$\epsilon(q)$'s used in Eq. (4) can be obtained using Eqs. (2c)–(2e). The value of r_c^{AB} can be obtained in terms of r_c^A and r_c^B from the expression

$$r_c^{AB}=\frac{Z_Ar_c^A+Z_Br_c^B}{\bar{Z}} ,$$

where $\bar{Z}$ is the mean valence of the glass-forming alloy.

The effective pair-potential obtained above has been used to study the structure and stability of binary metal glasses. The phonon eigenfrequencies are physically more meaningful quantities with which we study the anharmonicity of the glass-forming alloy under consideration. Besides the spherically symmetric effective potential $V_{\text{eff}}(r)$, the expressions of the longitudinal and the transverse phonon eigenfrequencies contain many-body correlation functions and are given by[9]

$$\omega_l^2(k)=\frac{(4\pi\rho^{AB})}{M^{AB}}\int dr\, g_{\text{eff}}(r)\left[rV'_{\text{eff}}(r)\left[1-\frac{\sin(kr)}{(kr)}\right]+[r^2V''_{\text{eff}}(r)-rV'_{\text{eff}}(r)]\times\left[\frac{1}{3}-\frac{\sin(kr)}{(kr)}-\frac{2\cos(kr)}{(kr)^2}+\frac{2\sin(kr)}{(kr)^3}\right]\right] \tag{5a}$$

and

$$\omega_t^2(k)=\frac{(4\pi\rho^{AB})}{M^{AB}}\int dr\, g_{\text{eff}}(r)\left[rV'_{\text{eff}}(r)\left[1-\frac{\sin(kr)}{(kr)}\right]+[r^2V''_{\text{eff}}(r)-rV'_{\text{eff}}(r)]\times\left[\frac{1}{3}+\frac{\cos(kr)}{(kr)^2}-\frac{\sin(kr)}{(kr)^3}\right]\right] , \tag{5b}$$

where, ρ^{AB} is the mean number density and M^{AB} is the mean atomic mass of the glass-forming alloy.

III. RESULTS AND DISCUSSION

The homovalent $Ca_{70}Mg_{30}$ glass alloy is investigated in the present studies. Equation (4) is used to obtain the pair potentials $V_{\text{Ca-Ca}}(r)$, $V_{\text{Ca-Mg}}(r)$, and $V_{\text{Mg-Mg}}(r)$ employing the local empty-core model potential approach of Ashcroft[12] and screening function of Hubbard and Sham.[13] The value of r_c^A and r_c^B in Eq. (4) are taken from Ref. 12 and the values of Fermi wave number of A-A and and B-B components in the alloy are taken from Harrison[14] whereas k_F for the A-B component is determined using the expression

$$k_F^{AB} = (3\pi^2 \bar{Z} \rho^{AB})^{1/3} .$$

These pair potentials are shown in Fig. 1. It could be noted from the figure that the $V_{\text{Ca-Mg}}(r)$ curve falls in between the $V_{\text{Ca-Ca}}(r)$ and the $V_{\text{Mg-Mg}}(r)$. Moreover, its minimum is shifted towards a lower r value and is deeper than the corresponding value for the average of $V_{\text{Ca-Ca}}(r)$ and $V_{\text{Mg-Mg}}(r)$. In Fig. 1 the potential that has been calculated for the Ca-Mg alloy provides an evidence in favor of the "additive hard-sphere" model. A change in the hard-sphere diameters of the pure component occurs due to charge transfer from one to the other on alloying. This is suggestive of the fact even if the same pseudopotential is used for a given ion, the screening varies from medium to medium resulting in a change in diameter. The effective pair potential for the glass-forming alloys is thus computed using Eq. (3) and is also shown in the same figure. It is observed that $V_{\text{eff}}(r)$ lies in between the $V_{\text{Ca-Ca}}(r)$ and $V_{\text{Mg-Mg}}(r)$ and shows long-range oscillations. Calculations of these potentials indicate that in general, if one sphere grows upon alloying the other decreases in such a way that the total hard-sphere volume remains practically constant.

The phonon eigenfrequencies are given using Eq. (5), which is analogous to the eigenfrequency relation obtained earlier for amorphous solids using the theory of phonons. The effective pair-correlation function $g_{\text{eff}}(r)$ is taken from the x-ray diffraction results of Nassif *et al.*[15] The computed phonon dispersion is shown in Fig. 2 for the longitudinal and the transverse phonon modes. The neutron scattering results of Suck *et al.*[7] at 273 K and the theoretical results of phonon dispersion in $Ca_{70}Mg_{30}$ glass by Hafner[5] and Bhatia *et al.*[8] are also shown in the same figure. It can be noted from Fig. 2 that the oscillations are prominent in the longitudinal phonon modes as compared to the transverse phonons and this provides evidence for the existence of the collective excitation at larger momentum transfer due to the longitudinal phonons only. Moreover, it is seen that the transverse phonons undergo larger thermal modulation than do the longitudinal phonons, due to the anharmonicity of atomic vibrations in the alloy. This effect may be closely connected with the instability of the transverse phonons in the alloy. It is also observed that the first minimum in the longitudinal phonon branch of the dispersion curve is at a value $k \simeq 2$ Å^{-1}, close to the value of k where the static structure factor $S(k)$ shows its first peak. Further, there is close agreement between the experimental results of Suck *et al.*, obtained from the neutron scattering data on the dynamic structure factor $S(k,\omega)$, and the present computations. But it should be noted that the $S(k,\omega)$

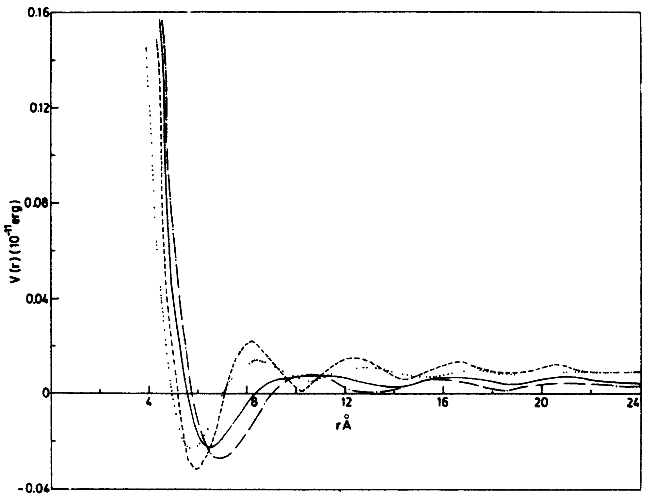

FIG. 1. Pair potential for $Ca_{70}Mg_{30}$: —·—·—·, $V_{\text{Ca-Ca}}(r)$; — — —, $V_{\text{Ca-Mg}}(r)$; · · · ·, $V_{\text{Mg-Mg}}(r)$; ——, $V_{\text{eff}}(r)$.

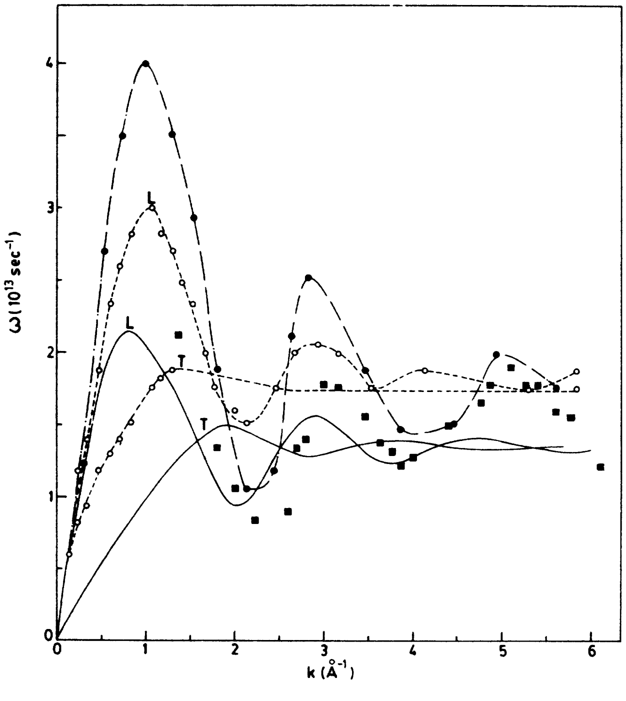

FIG. 2. The longitudinal (L) and the transverse phonon (T) dispersion relations for $Ca_{70}Mg_{30}$: ——, our results; – –○–○, those due to Bhatia *et al.* (Ref. 8); —●—●—, those due to Hafner (Ref. 5); ■, experimental points from neutron scattering obtained from Suck *et al.* (Ref. 7).

here, is an average of three dynamical correlations between the different (two) types of atoms, and an exact comparison between these ω values and those derived in Eq. (5) is not significant. It may also be noted from the same figure that the theories developed in Refs. 5 and 8 overestimate the frequencies as compared to the scattering experiments, and the minimum of the longitudinal mode does not fall at the k value of maximum static structure factor $S(k)$ precisely. Moreover, the calculations and computer simulations of these authors involve extensive parametrization and the phonon dispersions reproduced are in quantitative agreement with the experimental results. Thus, we conclude that the theory of phonons for amorphous solids is consistent in describing the collective excitations in glasses and glass-forming alloys quantitatively as well as qualitatively.

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