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LETTER TO THE EDITOR

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Abstract. It is shown that the excess low-energy (2–10 meV) density of vibrational states (LEDOS) in glasses leads to an increase of the mean-square atomic displacements $\langle R^2 \rangle$ in comparison with the case of crystalline counterparts. The estimations show that due to the excess LEDOS $\langle R^2 \rangle$ at the glass temperature, T_g in glass is the same as in its crystalline counterpart at the melting point T_m. The relation between T_g and T_m is expressed through the parameters of the excess LEDOS and is shown to be in good agreement with the experimental rule $T_m/T_g \approx 3/2$. A criterion of glass-forming ability, based on the important role of the excess LEDOS, is formulated.

It is well known that the greatest difference between vibrational spectra of glassy and crystalline modifications of the same compound are in the low-energy part of the *spectrum* (Hunklinger and Raychaudhuri 1986, Buchenau 1989). In this case, at the energy 2–10 meV, there is an excess low-energy vibrational density of states (LEDOS) (in comparison with the Debye one, estimated with experimental values of sound velocities). At its maximum it exceeds the Debye density of states (DOS) by a factor of $\frac{2}{8}$ for different materials, and the integral of the excess LEDOS is equal to ≈ 0.1 of the total number of vibrational degrees of freedom. The excess LEDOS has the same shape in different glasses (Malinovsky *et al* 1990). The excess LEDOS can be seen in the spectra of inelastic neutron scattering (Hunklinger and Raychaudhuri 1986, Buchenau 1991), light scattering ('boson' peak (Jäckle 1981)), IR-absorption (Strom and Taylor 1977), and in the excess low-temperature specific heat at $T = 5/20$ K (Jäckle 1981).

Although the nature of the excess LEDOS is not clear, the information that we have makes it possible to obtain some consequences for the physics of glass. In this letter we draw attention to the fact that the transition of part of the vibrational degrees of freedom in glasses from the high-frequency region of the spectrum to the low-frequency one (if comparing respective crystals) which gives the excess LEDOS, leads to an increase of the mean-square displacement of atoms $\langle R^2 \rangle$. Indeed, it is easy to express $\langle R^2(T) \rangle$ through the DOS, $g(\omega)$. At high temperatures

$$\langle R^2(T) \rangle = \frac{3k_B^T}{m} \int \frac{g(\omega)\,\mathrm{d}\omega}{\omega^2}. \tag{1}$$

Here T/ω is the high-temperature boson occupation number, and the factor $(m\omega)^{-1}$ arises due to the squared matrix element of an oscillator (the vibrations are supposed

to be harmonic). From equation (1) one can see that the low-frequency part of the DOS spectrum is reinforced by the factor ω^{-2}. This is the reason for the increase of $\langle R^2(T) \rangle$ at fixed T in glasses as compared with that for crystals of the same composition. In what follows we shall estimate the value of $\langle R^2(T) \rangle$ for glasses using previously established (Malinovsky *et al* 1990) general properties of the excess LEDOS in glasses. In both crystals and glasses the LEDOS has a general spectral form. In crystals it is described by the Debye law, $g(\omega) \propto \omega^2$, and in glasses the excess LEDOS is well described by a log–normal fit with standard deviation $\sigma \approx 0.5$ (Malinovsky *et al* 1991). This universality allows us to find a general expression for $\langle R^2(T) \rangle$ in glasses, to a good approximation, as a function of parameters of the excess LEDOS, because high-frequency non-universal features of the density of vibrational states are unimportant for $\langle R^2(T) \rangle$, due to the above mentioned factor ω^{-2} in (1). Taking into account the excess LEDOS we find that the mean-square atomic displacements in glasses $\langle R_g^2(T) \rangle$ at $T = T_g$, where T_g is the glass temperature, are equal to the value $\langle R_c^2(T_m) \rangle$, which they have in their crystalline counterparts at the melting temperature T_m:

$$\langle R_g^2(T_g) \rangle \simeq \langle R_c^2(T_m) \rangle \tag{2}$$

(within the accuracy of the method).

This result can be easily understood if we take into account the Lindemann criterion for melting (Lindemann 1911). According to this criterion, at the melting point (T_m) the mean square displacements of atoms are equal to a fixed, small fraction of the interatomic distance. This fraction is a near-universal parameter for many materials. Equality (2) is in accordance with the Lindemann criterion if we consider melting and glass transitions from the point of view of their common feature—the sharp drop in viscosity. If temperature is increasing this drop takes place when $\langle R^2 \rangle$ reaches some critical value (which can be found from the Lindemann criterion) both for a glass and for a crystal. Similarity of short-range order in vitreous and crystal modifications of a solid means that this value of $\langle R^2 \rangle$ is nearly the same in these two forms. Structural fluctuations make the drop of viscosity at the glass transition smoother than at the melting point of a crystal. Some consequences of this for the nature of the glass transition will be considered below.

In order to estimate the mean-square atomic displacements for a glass $\langle R_g^2(T) \rangle$ it is necessary to know the DOS, $g(\omega)$. In glasses the low-frequency DOS, $\bar{g}(\omega)$, can be written as a sum of two parts:

$$\bar{g}(\omega) = \bar{g}_D(\omega) + \Delta g(\omega) \tag{3}$$

where

$$\bar{g}_D(\omega) = \gamma \omega^2 \tag{4}$$

is the Debye part of the glass DOS, and $\Delta g(\omega)$ is the excess LEDOS. A constant γ will be determined below. Recently it has been shown that in glasses of different chemical composition and short-range order the excess LEDOS has log–normal spectral form (Malinovsky *et al* 1991):

$$\Delta g(\omega) = A \exp\left(-(\log \omega/\omega_0)^2/2\sigma^2\right). \tag{5}$$

Here A and ω_0 are the amplitude and the position of the maximum of the excess LEDOS, which can be different for different glasses, and a standard deviation $\sigma^2 \approx 0.24$ is a universal parameter.

Using expression (1) for $\langle R^2(T) \rangle$ it is easy to obtain for glasses

$$\langle R_g^2(T) \rangle = (3k_BT/m)\left(\gamma\bar{\omega}_D^2 + (A/\omega_0)\exp(\sigma^2/2)\right) \tag{6}$$

where $\bar{\omega}_D$ is the Debye frequency for glass. For crystals in the Debye model with

$$g_D(\omega) = 3\omega^2/\omega_D^3 \tag{7}$$

one can find

$$\langle R_c^2(T) \rangle = 9k_BT/m\omega_D^2. \tag{8}$$

It is more convenient to introduce, instead of parameter A, another parameter β, which is equal to the amplitude of the ratio of the excess LEDOS to that of the Debye DOS:

$$\beta = \left(\Delta g(\omega)/\bar{g}_D(\omega)\right)_{\text{max}}. \tag{9}$$

This parameter can be easily determined from experimental data. Using (6) and (8) one can obtain for the ratio $\langle R_g^2(T) \rangle / \langle R_c^2(T) \rangle$, which we will denote by P,

$$P \equiv \langle R_g^2(T) \rangle / \langle R_c^2(T) \rangle = \left(1 + \beta(\omega_0/\bar{\omega}_D)\exp(-3\sigma^2/2)\sqrt{2\pi\sigma^2}\right)B \tag{10}$$

where B is a factor that is close to unity (to within 10%):

$$B = \gamma\bar{\omega}_D\omega_D^2/3. \tag{11}$$

The estimation of B can be made as follows. It is known that the contribution of the excess LEDOS to the total spectrum of DOS is small: $\alpha = 0.1$ (Buchenau 1991, Ahmad *et al* 1986). Integration of (3) allows one to express $\gamma\bar{\omega}_D^3$ through α:

$$\gamma\bar{\omega}_D^3 = 3(1 - \alpha). \tag{12}$$

From (11) and (12)

$$B = (1 - \alpha)\omega_D^2/\bar{\omega}_D^2. \tag{13}$$

Introducing in (10) the value of σ^2 we obtain an expression which will be used below for estimations:

$$P \equiv \langle R_g^2(T) \rangle / \langle R_c^2(T) \rangle = \left(1 + 0.85\beta\omega_0/\bar{\omega}_D\right)B. \tag{14}$$

Parameter β ranges in value from 1.5 to 7, and $\omega_0/\bar{\omega}_D$ from 1/3 to 1/5. Let us estimate P for two concrete materials—As$_2$S$_3$ and SiO$_2$. The experimental values of the parameters are the following: for As$_2$S$_3$, $\bar{\omega}_D = 120$ cm^{-1} (170 K), $\omega_0 = 37$ cm^{-1} (Malinovsky *et al* 1991) and $\beta = 1.5$ (Malinovsky *et al* 1990). For SiO$_2$, $\bar{\omega}_D = 342$ cm^{-1} (490 K), $\omega_0 = 69$ cm^{-1} (Malinovsky *et al* 1991), $\beta = 4$ (Malinovsky *et*

al 1990), $\omega_D = 328$ cm^{-1} (Shaskolsaya 1983). With these values of the parameters, (13) gives $P = 1.4$–1.5 both for As$_2$S$_3$ and SiO$_2$.

It is easy to see from (6) and (8) that equal values of $\langle R_g^2(T)\rangle$ and $\langle R_c^2(T)\rangle$ correspond to glass and crystal temperatures such that their ratio is equal to P. This means that if $\langle R_c^2(T_m)\rangle$ is the value of $\langle R^2(T)\rangle$ in a crystal at the melting point, than in a glass $\langle R^2(T)\rangle$ has the same value at $T = T_m/P$. It is known that there is an experimental 3/2 rule: the ratio T_m/T_g is approximately equal to 3/2 (Feltz 1983). As was mentioned above, $\langle R_g^2(T_g)\rangle \approx \langle R_c^2(T_m)\rangle$. It is easy to see from (6) and (8) that this gives a relation between T_g and T_m:

$$T_g/T_m = P. \tag{15}$$

The value $P = 1.4$–1.5 is in good agreement with the experimental 3/2 rule. So the excess low-frequency DOS in glasses maintain the high value of $\langle R^2(T)\rangle$, which became less than that determined by the Lindemann criterion only at $T \leqslant T_g$. This result can provide a criterion of glass-forming ability. Indeed, it has been shown previously (Gochiyaev *et al* 1991, Phillips *et al* 1989) that the excess LEDOS exists both in glassy and undercooled liquid states up to about T_m. The spectrum of LEDOS in an undercooled liquid is slightly modified when the temperature increases from T_g to T_m: the frequency of the maximum of the excess LEDOS decreases to a fixed non-zero value at $T = T_m$ and the amplitude of the excess LEDOS increases. These changes lead to an additional increase of $\langle R^2(T)\rangle$. Now let us consider from this point of view the behaviour of a liquid when the temperature decreases from $T > T_m$ to $T < T_m$. If in a disordered state this material has an excess LEDOS, than for decreasing temperature this excess LEDOS will prevent solidification, so the material will be in the form of undercooled liquid until the temperature reaches T_g, where $\langle R^2(T)\rangle$ is equal to the value given by Lindemann criterion.

If this material has no excess LEDOS, than at T_m there will be crystallization of the liquid, because the value of $\langle R^2(T)\rangle$ corresponds in this case to the Lindemann criterion at temperatures close to T_m. Thus there is a correlation between low-energy anomalies of the vibrational spectra of a material and its glass-forming ability. For example, amorphous materials of a-Si type have no excess LEDOS at frequencies far from the end of the acoustic spectrum. In these materials the low-frequency peak in the Raman spectrum is in fact a TA-mode of the acoustic spectrum. In glasses, the low-frequency ('boson') peak which arises due to light scattering on the excess quasilocalized vibrations is an additional feature of the spectrum and corresponds to the spectral region in which the Debye behaviour of the LEDOS has been observed in crystalline counterparts (Malinovsky *et al* 1990). In other words, contrary to glasses, the excess DOS in a-Si or a-Ge is close to the TA-mode of acoustic vibrations and thus cannot greatly change the integral (1) for $\langle R^2(T)\rangle$ in comparison with the case of the crystalline phase.

In conclusion, in this letter the glass temperature is expressed through parameters of the excess LEDOS, which is characteristic for the glassy state. The excess LEDOS also exists in undercooled liquids and prevents solidification at temperatures between T_g and T_m. Amorphous materials like a-Si and a-Ge cannot be obtained by cooling of the melt because the excess DOS in these materials is close to the TA-mode of vibration. A correlation between the glass-forming ability and the low-energy anomalies of the density of vibrational states is stressed.

References

Ahmad N, Hutt K V and Phillips W A 1986 *J. Phys. C: Solid State Phys.* **19** 3765

Buchenau U 1989 *Dynamics of Disordered Materials* ed D Richter, A J Dianoux and W Petry (Berlin: Springer)

Buchenau U 1991 *Physica* B **174** 131

Feltz A 1983 *Amorphe und Glasartige Anorganische Festcorper* (Berlin: Akademie)

Gochiyaev V Z, Malinovsky V K, Novikov V N and Sokolov A P 1991 *Philos. Mag.* B **63** 777

Hunklinger S and Raychaudhuri A K 1986 *Progr. Low Temp. Phys.* **9** 267

Jäckle J 1981 *Amorphous Solids: Low-Temperature Properties* ed W A Phillips (Berlin: Springer)

Lindemann F A 1911 *Phys. Z.* **11** 609

Malinovsky V K, Novikov V N, Parshin P P, Sokolov A P and Zemlyanov M G 1990 *Europhys. Lett.* **11** 43

Malinovsky V K, Novikov V N and Sokolov A P 1991 *Phys. Lett.* A **153** 63

Phillips W A, Buchenau U, Nücker N, Dianoux A-J and Petry W 1989 *Phys. Rev. Lett.* **63** 2381

Shaskolsaya M P (ed) 1983 *Acoustical Crystals* (Moscow: Nauka)

Strom U and Taylor P C 1977 *Phys. Rev.* B **16** 5512