

Universal Form of the Low-Energy (2 to 10 meV) Vibrational Spectrum of Glasses.

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Abstract. – By means of inelastic cold neutron scattering the density of vibrational states (DVS) has been determined for a series of vitreous materials: SiO_2 , As_2S_3 and metallic glass $\text{Mg}_{70}\text{Zn}_{30}$. In the low-energy range of the spectrum ($E \sim (2 \div 10)$ meV) for these materials DVS reveals a universal, but non-Debye form. The data obtained are compared to different models. A comparison with the Raman scattering data provides the spectral dependence for the coupling of the light to the vibrational excitations.

The most important differences between elementary excitation spectra of crystalline and amorphous materials manifest themselves in the low-energy range. The low-temperature ($T \leq 1$ K) anomalies in specific heat and thermal conductivity of amorphous materials are well known. The phenomenology of these anomalies is available in the framework of the models which involve two-level systems [1, 2]. Less clear is the nature of excess density of vibrational states (DVS) in the energy range 2 to 10 meV. These vibrational states cause the excess specific heat of vitreous and amorphous materials in the temperature range of 10 to 30 K [2]. They are manifested in neutron scattering spectra [3, 4] and IR absorption spectra [5] as well as in Raman scattering spectra in the form of the so-called boson peak at low energies [2, 6].

In the present paper DVS is studied in a series of vitreous materials by means of neutron scattering. For the first time the low-energy (2 to 10 meV) DVS is found to have a universal form for glasses which are different in their chemical composition and character of short-range order. Additional data obtained by means of Raman scattering spectroscopy show that the universal form revealed is characteristic of a wide series of vitreous solids. On the basis of the results obtained a conclusion is drawn that the low-energy features in the vibrational mode spectra are caused by universal structural features of glasses.

The neutron scattering spectra were measured at scattering angles 30° , 45° , 60° , 75° and 90° by the time-of-flight technique presented in details in ref. [4]. The Raman scattering

spectra were measured by the standard technique [6] in a right angle scattering geometry with the scattered light polarization being normal to the scattering plane and initial light polarization being parallel to this plane. All measurements were performed at room temperature. The spectra were processed according to the routine procedure accounting for all necessary corrections.

The neutron experiment in noncoherent approximation provides for the so-called generalized vibrational spectrum $\theta(E)$ reconstruction with no biatomic models involved and its relation to the usual density of vibrational states $g(E)$ is given by the equation

$$\theta(E) = \sum_{i=1,2} \frac{\sigma_i c_i}{m_i} \exp[-2W_i] |e_i(E)|^2 g_i(E), \quad (1)$$

where σ_i , m_i , c_i and e_i are the cross-section of the scattering, mass, concentration and vibrational polarization vector and $2W_i$ is the Debye-Waller factor, respectively, of the i -th component. The momentum-transfer averaging of the spectra has been made in the range

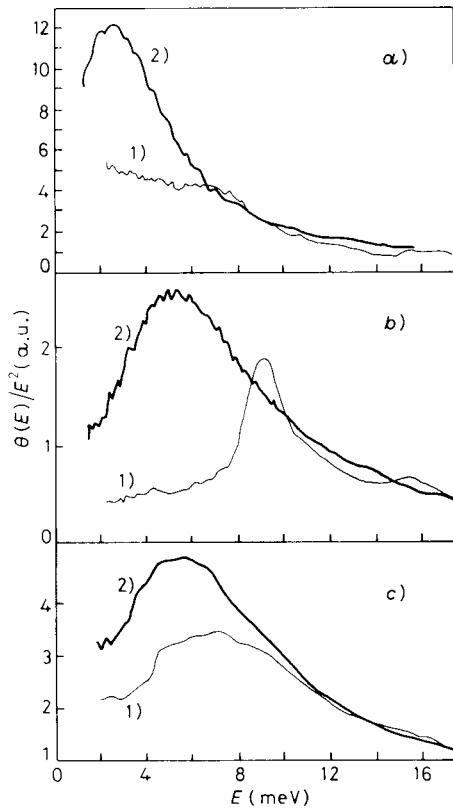


Fig. 1.

Fig. 1. - $\theta(E)/E^2$ dependence in crystalline (1) and vitreous (2) samples: a) As_2S_3 ; b) SiO_2 ; c) $\text{Mg}_{70}\text{Zn}_{30}$.

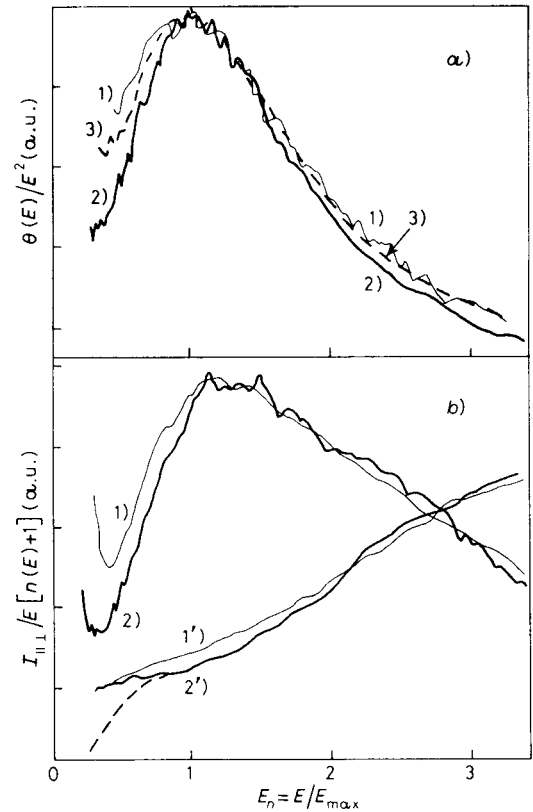


Fig. 2.

Fig. 2. - Low-energy spectra to the energy scale normalized by E_{\max} : a) $\theta(E)/E^2$ spectra, 1) As_2S_3 ($E_{\max} = 2.65$ meV), 2) SiO_2 (5.1 meV), 3) $\text{Mg}_{70}\text{Zn}_{30}$ (5.5 meV); b) Raman spectra (1) As_2S_3 , 2) SiO_2 , $C(E)$ dependence for As_2S_3 (1') and SiO_2 (2'), --- $C(E)$ with the contribution of quasi-elastic scattering taken into account.

from 1 to 3 Å⁻¹ for $E < 5.5$ meV. In more details the experiment and data analysis will be described in [7].

The measured data for $\theta(E)/E^2$ of As₂S₃, SiO₂ and Mg₇₀Zn₃₀ in crystalline and vitreous states are presented in fig. 1. In the density of states for crystalline samples at low E one can see an extensive region with Debye behaviour of $\theta(E) \sim E^2$. At the energy of 7 meV the spectra of the investigated crystals become markedly different. The spectra of the same substances in vitreous states are of distinct character. Debye behaviour here cannot be seen even at the lowest energies of (1 ÷ 2) meV attained. However, these spectra display an asymmetric peak as a common feature with maxima at $E = E_{\max} = 2.65, 5.1$ and 5.5 meV for As₂S₃, SiO₂ and Mg₇₀Zn₃₀, respectively. The DVS value in the maximum is considerably larger (by a factor 2 to 3) than that expected in Debye model.

To compare the spectra, we have reduced them to the same scale taking E_{\max} as a unit energy: $E_n = E/E_{\max}$ and renormalizing the whole spectrum over $\theta(E)/E^2$ value at the peak top (fig. 2a)). As one can see from the graph the peak shape is identical for all the three materials in spite of the marked difference in their structure: the silica glass is a three-dimensional network of covalent bonds, while the crystalline counterpart of the chalcogenide glass has a layered structure and the metallic glass consists of closely packed atoms and has basically different electronic properties.

Additional data are available from the Raman scattering (RS) spectra. The RS spectral intensity is related to the density of vibrational states by the equation [8]

$$I/E(n(E) + 1) = C(E)g(E)/E^2. \quad (2)$$

Here $C(E)$ describes the coupling between the light wave and vibrational mode, $n(E)$ is the Bose factor for the vibrational excitations. The RS spectra of the samples SiO₂ and As₂S₃ are plotted in fig. 2b) to the energy scale $E_n = E/E_{\max}$. In these spectra the peak position is shifted to larger energies, but its shape is identical for the investigated samples. Dividing Raman data for the l.h.s. of eq. (2) by the experimental values of $g(E)/E^2$, one can find spectral dependence of the coupling constant $C(E)$ (fig. 2b)). The universal form is observed in $C(E)$ dependence too. It is necessary to point out that $C(E)$ does not have any maximum close to $E \sim E_{\max}$ as followed from certain models [6, 9], but it grows steadily with growing E according to a linear law approximately. In the energy range $E < E_{\max}$ a considerable contribution to the RS spectrum comes from quasi-elastic scattering [2, 10] which distorts the true $C(E)$ dependence. If one takes the quasi-elastic scattering into account as suggested in ref. [10], then the $C(E)$ dependence in the range $E < E_{\max}$ will significantly change to become close to the limiting long-wavelength regime $C(E) \sim E^2$ [2, 9].

The universal form of the low-frequency peak in the Raman scattering spectra was found earlier in a wide series of oxide, chalcogenide and low-molecular organic glasses (fig. 3) [6, 11]. With all the above data taken into consideration (fig. 2) the assumption seems to be natural that to all these materials the universal form of DVS is also characteristic. Therefore, in spite of significant differences in chemical composition, short-range order structure and chemical-bond type (metallic or covalent) in the samples studied, the low-energy DVS has a universal form though it is a non-Debye form.

To describe the excess DVS in glasses a number of models has been suggested. Some authors relate it to vibrations of structural fragments which are characteristic for materials with a certain chemical composition. So in ref. [3] these vibrations in vitreous SiO₂ are assumed to be due to rotation of several SiO₄ tetrahedra. The author of ref. [12] does relate the low-energy modes in amorphous chalcogenides to vibrations of the layered structure, which is typical for chalcogenide crystals. But taking into account the discovered universal form of DVS, more general models are preferable. The needed generality is likely to be

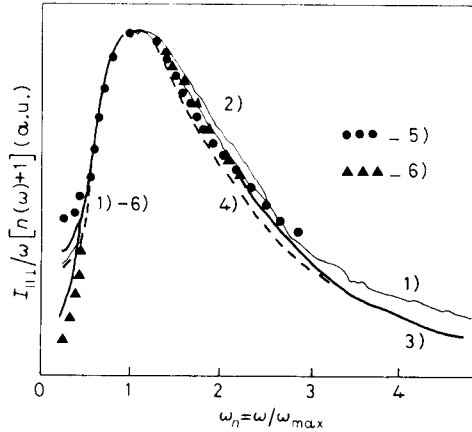


Fig. 3.

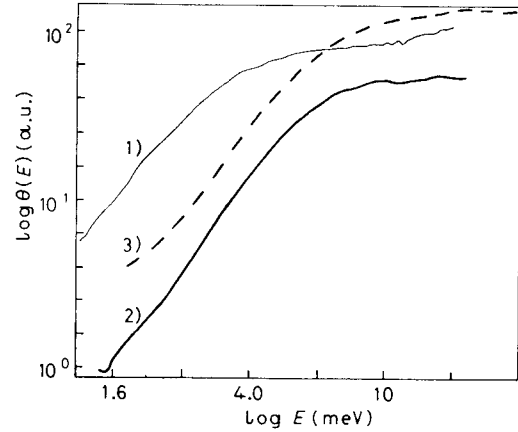


Fig. 4.

Fig. 3. – Low-energy Raman spectra to the scale $\omega_n = \omega/\omega_{\max}$; 1) As_2S_3 ($\omega_{\max} = 26 \text{ cm}^{-1}$); 2) $\text{Bi}_4\text{Si}_3\text{O}_{12}$ (34 cm^{-1}); 3) SiO_2 (52 cm^{-1}); 4) B_2O_3 (28 cm^{-1}); 5) $\text{C}_3\text{H}_5(\text{OH})_3$ (42 cm^{-1}); 6) GeS_2 (22 cm^{-1}).

Fig. 4. – $\theta(E)$ dependence plotted to log-log scale: 1) As_2S_3 ; 2) SiO_2 ; 3) $\text{Mg}_{70}\text{Zn}_{30}$.

inherent in the fractal models [13, 14], the soft potential model [15] and the models involving structural correlations over $(10 \div 20) \text{ \AA}$ scales [6, 10, 16]. Let us consider these in more details.

According to the fractal model [13, 14], vibrational modes with wavelength $\lambda < L$ (where L is a characteristic length) are localized because of geometry and have DVS corresponding to a reduced dimensionality: $g(E) \sim E^{\bar{d}-1}$, where $\bar{d} \leq 3$ stands for the spectral dimension. This model is known to be successfully applicable to a number of materials such as polymers [17, 18], aerogels [19] and others. To reveal the regions of power dependence in $\theta(E)$ we plotted it to a log-log scale (fig. 4). It is evident that for $E > E_{\max}$ the spectrum can be interpreted in terms of fractons with $\bar{d} = 1.2 \div 1.4$. The inflection point in this case determines the characteristic length where the fracton regime is replaced by the phonon one $L \sim V/E_{\max} \sim 1 \text{ nm}$, here V is the sound velocity. However, in contrast to polymers and aerogels the physical reasons are obscure for fracton behaviour of vibrational modes in the three-dimensional network of the glasses in question. Moreover, the value of \bar{d} obtained is close to the spectral dimension of a perfect linear polymer; it is less than that for a realistic polymer of PMMA [17] or DGEBA [18] type. This looks particularly strange with reference to metallic glasses which have the close packed disordered structure and nonoriented metallic bonds.

A noticeable progress in the recent years is gained by the soft potentials model [15]. This model assumes the excess DVS to be due to vibrations of atoms in the strongly anharmonic potentials resulting from disorder in glass structure. The maximum position and the form of the excess DVS in the vibrational modes spectrum will depend on parameters of the anharmonic potential in this case. Assuming a universal distribution of the potential parameters one can explain the discovered universal form of $\theta(E)$ in different vitreous materials. However, within the framework of this model a complete description of the excess DVS is not yet available hence its detailed comparison with the results presented here is not possible.

In a number of models the low-energy anomalies of DVS are related to the dimensional effect, namely to the presence of inhomogeneities in the structure with a size of

$R_c \sim (10 \div 20)$ Å, where R_c is the correlation radius of the structure. It is evident that such microinhomogeneties must result in appearance of anomalies in DVS in the range $E \sim V/R_c \sim (3 \div 10)$ meV. In particular the excess DVS was observed in the low-energy vibrational spectrum of glasses with microcrystalline inclusions of $L \sim (50 \div 100)$ Å size [20, 21]. It has been shown that the frequency of these vibrations is $\omega \sim 1/L$ [19, 20]. According to the model considered the spectrum of the excess DVS will be determined by the spatial distribution of fluctuations of the elastic constants in the amorphous structure [22], and the discovered universal form can be related to the universal profile of this distribution in glasses.

In conclusions, the presented results give an evidence that the vibrational spectrum in glasses differs significantly from the Debye law in the energy range 2 to 10 meV but its form is universal for the glasses with different chemical composition and short-range order structure in particular for the close packed metal and the covalent network. There is no agreed-upon model of vibrational excitations in the energy range 2 to 10 meV for glasses as yet. However, such a model should be based upon rather general principles to be capable of accounting for the universal form of vibrational spectrum which is revealed in the present paper.

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