

Scientific Session of the Division of General Physics and Astronomy of the Russian Academy of Sciences (27 April 1993)

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A scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences was held on January 27, 1993 in the P. L. Kapitsa Institute of Physics Problems. The following reports were presented at the session:

1. *I. M. Khalatnikov*. From instantons to inflation of the universe.

2. *V. K. Malinovskii, V. N. Novikov, and A. P. Sokolov*. Nanometer-scale structure of disordered bodies.

The content of one report is presented below.

V. K. Malinovskii, V. N. Novikov, and A. P. Sokolov. *Nanometer-scale structure of disordered bodies.*

The low-energy vibrational spectra of disordered bodies have characteristic features which distinguish them from the spectra of crystals. In crystals the phonon density of states (PDS) at low energy is described well by Debye's law. The situation is different in glasses and amorphous bodies. First, at energies less than 1 K the PDS is constant. Second, in glasses there is an excess (compared with the Debye) PDS in the energy range 2–10 meV (3–15 K). The excess PDS looks like a peak, which in different materials is two-six times greater than the Debye PDS at this energy. The excess PDS is observed in all glasses; it is manifested in the low-energy inelastic neutron scattering spectra, low-frequency Raman scattering spectra ("boson peak"), far-IR absorption, as well as the low-temperature heat capacity and thermal conductivity. The very-low-energy features (<1 K) are explained well within the standard model of two-level systems. The nature of the second feature—the excess PDS at 2–10 meV—is not completely understood. The existing models agree, however, in the fact that the vibrational excitations responsible for the excess PDS in glasses are localized in a region containing from several tens to hundreds of atoms, and therefore they carry indirect information about the structure of the material on scales of medium-range order, i.e., 1–2 nm.^{1–4} Investigation of the low-energy features of the spectra of disordered materials in connection with their nanometer-scale structure is the main object of this work.

Low-energy quasilocal excitations in glasses were studied in this work by the methods of incoherent inelastic neutron scattering and Raman scattering of light. The first method gives the most direct information about the phonon density of states. Figure 1 displays the low-frequency PDS of three glassy materials of different chemical composition and their crystalline analogs As₂S₃, SiO₂, and Mg₇₀Zn₃₀. The excess PDS, defined as $\Delta g(\omega) = g(\omega) - g_D(\omega)$, where $g_D(\omega)$ is the Debye PDS, and found with the help of experimentally determined sound speeds, has in all three materials a universal spectral

shape (Fig. 2) in the reduced coordinates $\Delta g'$ and ω' , where $\Delta g' = \Delta g / \Delta g_{\max}$, $\omega' = \omega / \omega_{\max}$, ω_{\max} is the frequency of the maximum of $\Delta g(\omega)$, and $\Delta g' = \Delta g(\omega) / \Delta g(\omega_{\max})$. The universality of the spectral shape of $\Delta g'(\omega)$ in glasses with different chemical composition and different character of short-range order and type of chemical bond (planar structure in As₂S₃, covalent bonds in SiO₂, and close packing in the metallic glass Mg₇₀Zn₃₀) indicate that the structural features responsible for the appearance of low-frequency spectral anomalies in amorphous bodies are universal.

A more convenient method for studying the excess vibrational excitations is Raman scattering.

Figure 3 displays a typical Raman spectrum of glasses (for the example of As₂S₃). The stretching modes corresponding to vibrations of the structural units lie in the frequency range $\omega \gtrsim 200 \text{ cm}^{-1}$. A wide structureless peak with $\omega_{\max} \sim 20\text{--}100 \text{ cm}^{-1}$ and half-width $\Delta\omega \sim \omega_{\max}$ is observed at low frequencies ($\omega < 100 \text{ cm}^{-1}$). This peak is absent in the Raman spectra of the corresponding crystals. Analysis of the spectra showed that the low-frequency peak is associated with the first-order scattering of light by vibrational excitations satisfying Bose statistics. As a result, the low-frequency peak is referred to in the literature as the "boson" peak. The characteristic frequency of the maximum of the boson peak lies in the region of acoustic vibrations, and in different materials it constitutes 1/3–1/7 of the Debye frequency ω_D . This means that the characteristic localization length of the vibrational excitations, scattering by which gives the boson peak, is several interatomic distances. The boson peak is a reflection of the excess PDS in the Raman spectrum. In reduced coordinates, similar to those employed above for describing $\Delta g'(\omega)$, the spectral shape of the boson peak is found to be the same in the most diverse glasses. This assertion was checked for several tens of different glasses.⁵ It should be noted, however, that for amorphous materials, i.e., materials obtained not by cooling of melt, as in the case of standard three-dimensional glasses, but rather by sputtering on a substrate and by other methods, the shape of the boson peak is substantially different from the universal law characteristic for glasses. Typical examples are the tetrahedral semiconductors α -Si and α -Ge (Fig. 4).

The experimental spectra of the excess PDS and the boson peak in glasses can be described adequately by an entire series of adjustable functions. The log-normal distribution, which contains the least number of adjustable parameters, is the best one. In the reduced coordinates it is determined by only a single dimensionless parameter—the variance σ of the distribution, which is a universal param-

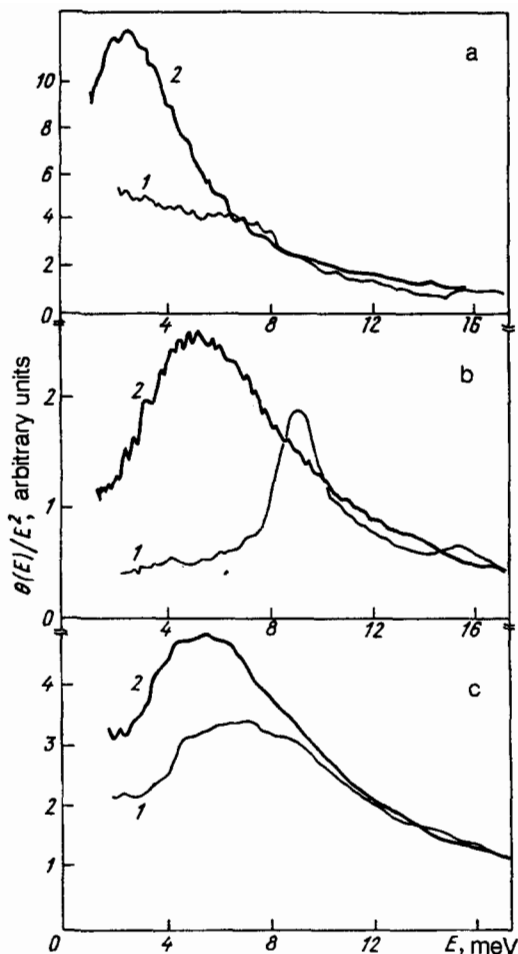


FIG. 1. Phonon density of states in crystalline (1) and glassy (2) samples. a— As_2S_3 , b— SiO_2 , c— $\text{Mg}_{70}\text{Zn}_{30}$.

eter, the same number for all low-molecular glasses:

$$\Delta g'(\omega) = \exp \left[-\frac{\ln^2(\omega/\omega_{\max})}{2\sigma^2} \right], \quad (1)$$

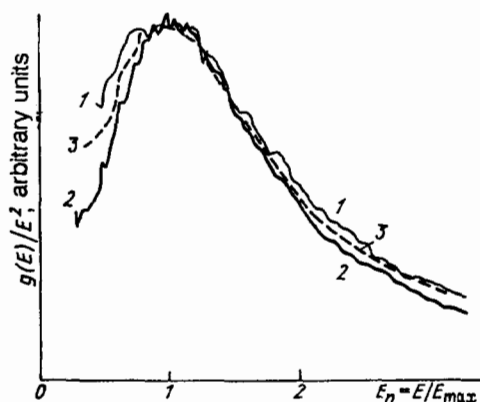


FIG. 2. Phonon density of states in glasses in Debye coordinates $g(E)/E^2$ on a unified energy scale $E_n = E/E_{\max}$. 1— As_2S_3 ($E_{\max} = 2.65$ meV), 2— SiO_2 ($E_{\max} = 5.1$ meV), 3— $\text{Mg}_{70}\text{Zn}_{30}$ ($E_{\max} = 5.5$ meV).

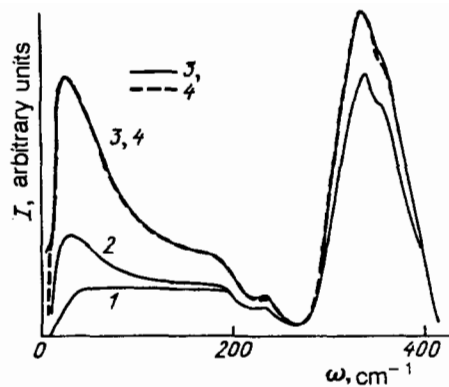


FIG. 3. Raman spectra in glassy As_2S_3 at different temperatures. 1—10 K, 2—100 K, 3—300 K, 4—spectrum measured at $T = 100$ K and referred, taking into account the temperature factor $n(\omega) + 1$, to $T = 300$ K.

where $\sigma = 0.48 \pm 0.05$.⁶ Thus there is a new universal parameter in the physics of glasses—the parameter σ , associated with the characteristics of the nanometer-scale structure.

We feel that there is every reason to associate the excess low-energy PDS in glasses to the existence of a characteristic length in them—the radius of medium-range order, which is of the order of a nanometer. The low-energy vibrational excitations responsible for the excess PDS are localized in our model on nanometer-size structural non-uniformities. A series of experiments confirming that such a mechanism of excess PDS is in principle possible have been performed on model objects. Thus Malinovsky *et al.*⁷ used low-frequency Raman scattering to study glasses whose matrix contained clusters having a different chemical composition and a size of several tens of angstroms. Specifically, they employed photochromic glasses with a $\text{SiO}_2\text{--B}_2\text{O}_3$ matrix, which contained clusters of silver halide. The size of the clusters depended on the annealing time of the samples and ranged from ~ 40 to 80 Å. When clusters are present in the glass matrix ($\sim 2\%$), an additional band appears in the inelastic light-scattering spectrum (Fig. 5). A boson peak, characteristic for the spectra of all glassy materials, is observed at frequencies $\omega \lesssim 60$ cm^{-1} . Annealing of the samples alters the spectrum only at

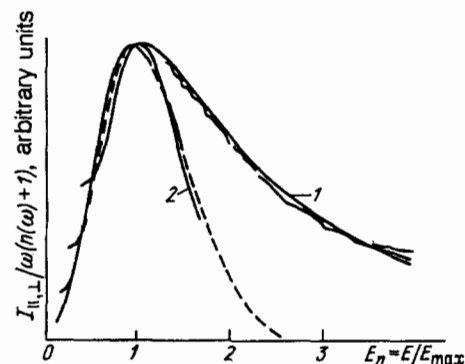


FIG. 4. Typical Raman spectra for different glasses (1) and for amorphous semiconductors (2).

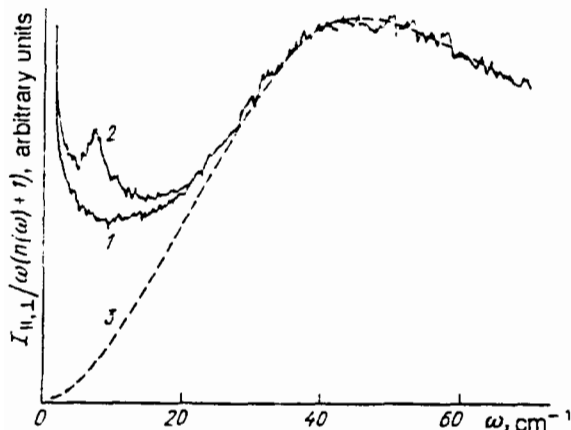


FIG. 5. Low-frequency Raman spectra in photochromic glasses. 1—control sample, 2—after annealing, 3—computed spectra for the contribution of acoustic phonons.

frequencies $\omega < 20 \text{ cm}^{-1}$: A peak appears at $\omega_{\text{max}} \sim 10 \text{ cm}^{-1}$. The difference of the spectra of the annealed and control samples (Fig. 6) corresponds to the spectrum of surface vibrational modes of the clusters, and only fundamental modes with the frequency

$$\omega^T \sim 0.8 v_t / D; \quad (2)$$

where v_t is the transverse sound velocity, D is the diameter of a spherical cluster, and ω^T is the frequency of the fundamental torsional mode, can be seen in the experimental Raman spectrum. In Ref. 8, where similar spectra were recorded in $\text{Al}_2\text{O}_3 \cdot \text{Mg}_2\text{O}$ glasses with MgCr_2O_3 – MgAl_2O_3 clusters, only spherical vibrational modes with the frequency

$$\omega^S = 0.8 v_l / D; \quad (3)$$

where v_l is the longitudinal sound velocity, appeared in the spectrum. The difference between the first and second cases is that their ratios of the elastic constants of the cluster and the matrix are different: The matrix (photochromic glasses) that is more rigid than a cluster suppresses spherical vibrations.

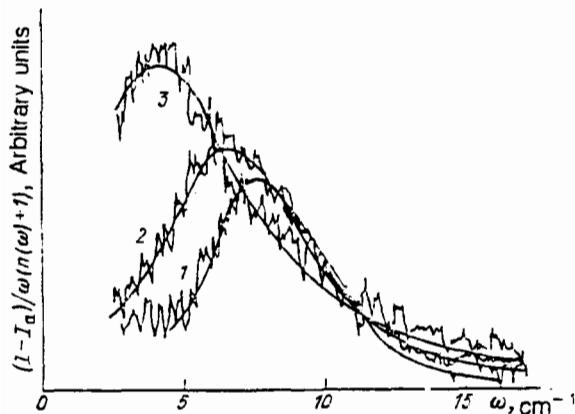


FIG. 6. Differences of the spectra of a control sample and samples with different degree of annealing.

Another example is the experimental work of Graebner and Golding,⁴ who modeled the localization of vibrations in glass on an aggregate system, consisting of clusters of small but macroscopic size ranging from 0.02 to 3 μm . It was shown that the thermal conductivity of these materials has a plateau, whose characteristic position is correlated with the size of the clusters in this sample. This linear relation between the wavelength of the vibrations, which corresponds to the characteristic temperature at which the plateau starts, and the cluster size is observed over a size range of two orders of magnitude. This is a strong argument in support of the fact that the localization of vibrations in these aggregated materials occurs on a scale determined by the characteristic cluster size. Clar and Freeman⁹ analyzed data on the low-temperature thermal conductivity of a wide range of glasses and they concluded that in the region of the plateau the Ioffe–Regel’ criterion for phonon localization is satisfied: $\lambda \sim l$, where l is the mean-free path, determined in the strong-scattering regime by the size of the structural nonuniformity, and λ is the phonon wavelength. Comparing these data with the measurements of the thermal conductivity in aggregates, where localization appears on a scale equal to the correlation length of the structure, they found that the correlation length for glasses is 10–30 \AA .

The different properties of the boson peak and the so-called first sharp diffraction peak (FSDP) in the structure factor $S(k)$ of glasses were compared in Ref. 10. The FSDP has a number of anomalous properties, which distinguish it from the main peaks of $S(k)$; the FSDP lies at $q \sim 1\text{--}1.5 \text{ \AA}^{-1}$ and, as shown in an entire series of works, it appears due to correlations in the arrangement of the atoms at distances up to the second and third coordination spheres. It was found that there exist correlations in the dependence of the positions and intensity of the FSDP and boson peak on the chemical composition, heat treatment, and pressure. These correlations are additional evidence supporting the existence of a relation between the low-energy excitations and the characteristic length scale in the structure of the glass—the radius of medium-range order. The connection between the FSDP and the boson peak was investigated further in Ref. 11. The values of the correlation length l_c estimated from the position of the boson peak and the width of the FSDP agree quite well and give the value $L_c \sim 10 \text{ \AA}$.

We performed a direct calculation of the excess low-energy PDS in a medium with fluctuating elastic constants on the basis of perturbation theory in small fluctuations.¹² The computational results show that the existence of fluctuations of the elastic constants with a definite correlation radius $R_c \sim 1\text{--}2 \text{ nm}$ results in the appearance of excess PDS in the low-energy region, $\omega \sim v/R_c$. It can be shown that for any reasonable correlation function for the elastic constants, which decays with increasing distance, some high-frequency vibrational modes are displaced into the low-frequency part of the spectrum, forming the excess PDS.

As already mentioned above, the excess PDS spectrum is approximated well by a log-normal function with a universal value of the variance of the logarithm of the fre-

quency $\sigma=0.48$. In a model where the excess PDS is due to vibrational excitations localized on nanometer-size structural nonuniformities the frequency ω of quasilocal vibrations is related to the size L of the nonuniformity by the relation $\omega=Kv/L$, where K is a constant of order unity. This means, in particular, that the size distribution of nanometer-size nonuniformities can also be described by a log-normal function, similar to Eq. (1) with the same variance σ :

$$F(L) \sim \exp \left[-\frac{\ln^2(L/L_0)}{4\sigma^2} \right]; \quad (4)$$

where L_0 is the most likely cluster size. There exists a geometric model of the partitioning of the glass volume into clusters that reproduces both the functional form of $F(L)$ (4) and the numerical value of σ in glasses.¹³ In this model the centers of the clusters are distributed randomly in space (Poisson distribution), and the partitioning into clusters is realized by a Voronoï construction for the system of these randomly distributed points. Computer modeling shows¹⁴ that the cluster-size distribution function in such a system is described well by the expression (4) with $\sigma=0.4-0.5$, depending on how the cluster size was determined. Gilbert¹⁵ has obtained the exact value of the variance of the distribution of the logarithm of the cluster volumes in this model: $\sigma=0.43$. The closeness of these values to the value found by fitting the experimental excess PDS spectra is not accidental and supports the cluster model of the structure of glasses.

The relaxational properties of glassy and amorphous materials are determined, to a significant degree, by their nanometer-size structural features. Investigation of the evolution of the low-frequency Raman spectra of glasses as a function of temperature in the interval from $T < T_g$ up to $T \sim T_m$ (T_g and T_m are the glass-formation temperature and the melting points, respectively) enabled us to obtain information about the relaxational properties of the material and the glass-liquid transition. In Ref. 16 we proposed a model that describes the low-frequency Raman spectrum at different temperatures. This model makes it possible to obtain from the experimental Raman spectra information about the magnitude and temperature dependence of the relaxation times and other parameters. The model is based on taking into account the influence of the structural relaxation of the material on the light scattering by the quasilocal vibrational excitations responsible for the boson peak. The model made it possible to determine, in a number of low-molecular organic materials, from the evolution of the wing of the Rayleigh line as a function of temperature the critical temperature T_c of the transition from α to β type relaxation. At this temperature, which exceeds by 30–40° the glass-formation temperature, the temperature dependence of the relaxational parameters exhibits a characteristic break. This agrees with the predictions of the coupled-mode model¹⁷ as well as with experimental data on nuclear magnetic and electron paramagnetic resonances.¹⁸

The boson peak discovered by Gochiyaev *et al.*¹⁶ in the spectra of the supercooled liquid indicates that clusters are also present in the liquid state right up to T_m , at least at

times of the order of the lifetime of the quasilocal vibrational excitations responsible for the boson peak, i.e., $10^{-11}-10^{-12}$ sec.

The low-energy features of the vibrational spectra of glasses can influence significantly the properties of glasses at both low and high temperatures T , right up to the glass-formation temperature. These properties include those for which the influence of the low-temperature PDS is stronger than in the region of the spectrum near the Debye frequency. Thus the contribution of low-energy phonons to the rms thermal vibrations of atoms is intensified by a factor equal to the inverse squared vibrational frequency. As a result, as shown in Ref. 19, due to the existence in glasses of low-energy excess PDS, making an integral contribution of $\sim 10\%$, the amplitude of the thermal vibrations is 30–40% higher in them than in the corresponding crystals at the same temperature. At the glass-formation temperature the amplitude of the thermal vibrations is very close to its value in the corresponding crystals at the melting point. The ratio, found in Ref. 19 taking into account Lindemann's criterion, between the glass-formation temperature and the melting temperature in a material with the same chemical composition is determined by the parameters of the excess low-energy PDS—its amplitude, the position of the maximum, and the universal value of the variance of the log-normal frequency distribution of the excess PDS. The ratio T_g/T_m was found to be very close to 2/3—the well-known empirical rule. In materials such as amorphous silicon and germanium there is no excess PDS in the low-energy region of the spectrum—the boson peak actually merges with the TA mode. Correspondingly, these materials do not form glasses. When cooled below the melting point, they crystallize rapidly in accordance with the fact that in them, in contrast to glasses, the amplitude of the thermal vibrations is close to the value in the crystalline state.

Interest in the vibrational properties of disordered fractal systems has increased in the last few years. Such systems include a wide range of materials, such as aerogels and other porous materials, polymers, colloidal aggregates, sols, and others. This wide range of materials, with its universal characteristics, is distinguished from low-molecular three-dimensional glasses by the shape of the low-energy vibrational spectra. Vibrational excitations of a fractal system—fractons—are localized, and they are manifested in real systems only in some frequency range. Zemlyanov *et al.*²⁰ made a detailed study of fractons in polymers and their relation to the structure of polymers on scales of 5–50 Å. Comparative study of samples of standard and deuterated polymethyl methacrylate (PMMA) by the methods of low-energy inelastic neutron scattering and low-frequency Raman scattering as well as the model, proposed in Ref. 20, of Raman scattering by fractons, enabled us to determine a number of fractal indices of the material and the size of a fractal cluster. The results enabled us to determine how the polymers studied differ from ideal linear polymers, to estimate the relative strength of the intermolecular interaction in different polymers, and to determine the effect of uniaxial elongation and variations

of chemical composition on the polymer structure.

In conclusion we note that the universality that we found in the spectral shape of the low-energy vibrational spectra of glassy and amorphous bodies indicates that the structure of these materials is based on some general structural principles. In this chaos, to which the structure of amorphous bodies and glasses was usually associated, there is a universal spatial scale—a unique order parameter, characteristic of glasses of different nature (dielectric, semiconductor, metallic). It can play just as important a role in the theory of the glassy or liquid state as does the unit cell in the theory of crystals.

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