
The Nature of Central Peak of Light Scattering in Glass-Like Media

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Abstract

A theory describing frequency and temperature dependences of the quasielastic peak (QEP) of low-frequency Raman scattering in glass-like materials is suggested. It is based on the ideas about dynamical fluctuations of defects concentration at the internal surface of the glass consisting of nanometer-size clusters. The fluctuations lead to variations of the Laplace pressure in the clusters and, as a consequence, the appearance of QEP. The theory results in a good quantitative description of the experimental low-frequency Raman spectra, which could not be achieved in framework of the known double-level system model.

Key words: glass-like materials, Raman scattering, quasielastic peak, nanoclusters, adatoms.

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1. Introduction

Low-frequency Raman spectra (RS) of glass-like media have a series of peculiarities distinguishing such materials from their crystalline analogues. Following the work [1], presence of the so-called “boson” peak (BP) in the mentioned spectra is usually interpreted with the ideas of spatial correlation of fluctuations for elasto-optic constants caused by structural inhomogeneities of the glass at a nanometer scale. One can suppose (see, e.g., [2, 3] and references in [4]) that these inhomogeneities result in existence of so-called medium-range order (MRO) in the glass. MRO can be characterized by a set of ordered regions, whose sizes exceed the short-range order length close to the molecular one and typical for fluids. As a limiting case of the idea, the hypothesis about a crystallite structure of glass-like systems has been proposed long ago (see, e.g., [5]). Within the ideas of MRO, which can be interpreted in terms of nanometer-size clusters (or simply

nanoclusters, NC) in glass, the appearance of the BP can be easily understood qualitatively. Really, considering the simplest case of NC as an elastic sphere of radius R and solving the equations of the elasticity theory, one can show that the eigen frequencies of oscillations of the sphere are determined by the ratio $\sim c/R$, where c is a characteristic sound velocity in the material of NC. Then the BP shape can be obtained through averaging local RS intensities over the random distribution of spheres' radii R , while the temperature dependence of the BP intensity is described with a good accuracy by the Bose-Einstein factor. In this situation, as shown in [6], the phenomena at the boundary NC/glass-forming matrix would be essential for the interpretation of the experimental RS in the BP region.

According to the experimental results [7], beside of the BP, RS in many glass-like compounds contains also a quasielastic peak (QEP), whose intensity increases with

increasing temperature much faster than the Bose-Einstein function predicts. Unlike the BP, the properties of which are quite well investigated and explained, the nature of the QEP has not found a consistent theoretical interpretation till now. For example, the double-level system model [8] leads to unsatisfactory interpretation of the experimental data [7] for the temperature dependence of the QEP intensity. Another approach [9], relating QEP with a light scattering at overdamped acoustic modes in the glass, can be hardly considered as consistent, because no physical model has been suggested in [9] for justification of presence of such the modes.

On the contrary, the idea about the cluster structure of glass-like materials allows one to arrive at an adequate (even on a quantitative level – see below) treatment of the low-frequency RS in the above media. Essential argument in favour of the mentioned idea is a well-known fact that the crystallization process in the glass, as a matter being in a metastable state, takes some time. As it is known, the process is realized with appearance of small agglomerates of crystalline phase within the metastable phase of the glass. It is just these agglomerates that should be associated with the NC, which produce the two intensity peaks – the BP and the QEP – in the low-frequency RS of glass-like materials.

Among the glass-like systems, one can distinguish a class of compounds containing the ion-conductive inclusions AgI. According to the experimental data [10], the latter represent a part of the glass in the form of NC (or “microdomains”, in terms of [10]), weakly connected with the glass-forming matrix. It has been shown in [11] that the QEP shape in such the materials is well described with the ideas of local dynamic fluctuations of the concentration of mobile ionic defects inside the NC. In this situation, the contribution of the individual NC to the QEP intensity is determined by a Lorentzian, whose width is equal to the inverse

relaxation time of the mentioned dynamic fluctuations. The resulting frequency dependence of the QEP intensity is obtained with averaging the local Lorentzians over the NC size distribution.

In principle, one could perform theoretical analysis of the QEP in dielectric glasses of $\text{Sm}_2\text{O}_3\text{-P}_2\text{O}_5$ type, basing on the model of relaxation of structural defects inside the NC. However, simple estimations show that the defect activation energy required for the agreement with the experimental data [7] is much lower, in comparison with the values known for those materials from the literature [12].

It means that, most likely, the QEP in dielectric glasses is caused by the relaxation phenomena at the boundary NC/matrix. An important fact demonstrated by Frenkel (see the monograph [12]) is that the activation energy for the surface defects is several times lower than the corresponding bulk value. Then the dynamical variations of the surface tension at the boundary NC/matrix cause dynamical deformations inside the NC, due to the Laplace pressure effect. Through the elasto-optic effect, these deformations will induce the appearance of QEP in the RS of glasses. Within this formulation, the role of the surface becomes crucial, as it should be naturally expected for the NC.

On the basis of the ideas formulated above, in the present paper we have suggested for the first time a natural approach to description of both the frequency and temperature dependences of the QEP intensity in the dielectric glassy materials. We shall show that the theoretical calculations can be quantitatively coordinated with the experimental data for the QEP at quite realistic values of the parameters appearing in the theory, which have an apparent physical meaning.

2. Theoretical model

Similar to earlier works [6, 11], we shall model the NC in the glass by spheres, the radii R of which are distributed according to the

logarithmic-normal law. For the quantitative description of the fluctuation processes at the NC surfaces we shall use the Frenkel's concepts [12]. Let us suppose that the atoms at the NC surface layer can pass into the adsorbed state (i.e., they "partially evaporate", in terms of [12]) by means of the activation, forming a so-called "subsurface" layer of "adatoms". Let us denote the time-dependent numbers of the adatoms and "non-evaporated" atoms at the NC surface as $N_{ad}(t)$ and $N_s(t)$, respectively. Let N be the number of positions occupied by both the "non-evaporated" atoms and the adatoms. Since the whole number of the surface atoms remains conserved, the relation $N_{ad}(t) + N_s(t) = N$ must fulfil. The free energy of the adatoms is defined by the expression

$$F[N_{ad}(t)] = EN_{ad}(t) - TS[N_{ad}(t)], \quad (1)$$

where E is the energy of "partially evaporated" atom (or the energy needed for forming the adatom) and T the temperature,

$$S[N_{ad}(t)] = 2 \ln \left[\frac{N!}{[N - N_{ad}(t)]! N_{ad}(t)!} \right] \quad (2)$$

denotes the entropy of independent distribution of the adatoms and "non-evaporated" atoms over their possible positions. $N_{ad}(t)$ can be presented as a sum of the two components: (i) the equilibrium (static) number of adatoms

$$N_{ad}^{(eq)} = \frac{N}{\exp(E/2T) + 1}, \quad (3)$$

where ω is the frequency and the summation is performed over all NCs in the scattering volume. Eq. (5) must describe either the BP or the QEP occurring in the low-frequency domain of RS in the glass-like system. As for the BP, its shape will be determined by the dynamic fluctuation strain tensor $u_{ij}(\vec{r}_1^{(n)}, t)$ inside the NC (see Introduction), so that we have

determined by the minimum of the free energy (1), and (ii) the dynamical fluctuation term $\delta N_{ad}(t)$ leading to appearance of the QEP. $\delta N_{ad}(t)$ can be determined from the next obvious condition: the changing rate for the number of adatoms is equal to the difference between the numbers of atoms passing per unit time from the surface to the subsurface layer and backwards. Performing elementary mathematical calculations, we come to the expression

$$\delta N_{ad}(t) = \delta N_{ad}(0) e^{-t/\tau}, \quad (4)$$

where $1/\tau = 1/\tau_{ev} + 1/\tau_{con}$, $\tau_{ev} = \tau_{\infty} \exp(E/T)$ is the characteristic time of "partial evaporation" (the time for appearance of the adatom) and $\tau_{con} = \tau_{\infty} \exp(E_1/T)$ the characteristic time of the adatom's "condensation". Below, we put $E_1 = 0$ for simplicity, considering the condensation time that coincides with the characteristic vibration period $\tau_{\infty} \propto 10^{-12}$ s.

In order to find the RS tensor, it is necessary to calculate thermodynamic averages $\langle \delta \varepsilon_{ij}(\vec{r}_1^{(n)}, t) \delta \varepsilon_{kl}(\vec{r}_2^{(n)}, 0) \rangle$ from bilinear combinations of the dynamic permittivity tensor at the points $\vec{r}_1^{(n)}$ and $\vec{r}_2^{(n)}$ of an individual (n th) NC, supposing uncorrelated fluctuation processes for different NCs. Then the RS tensor is determined by

$$I_{ijkl}(\omega) = \sum_n \int_0^{\infty} dt \int d\vec{r}_1^{(n)} \int d\vec{r}_2^{(n)} \langle \delta \varepsilon_{ij}(\vec{r}_1^{(n)}, t) \delta \varepsilon_{kl}(\vec{r}_2^{(n)}, 0) \rangle e^{-i\omega t}, \quad (5)$$

$$\delta \varepsilon_{ij}(\vec{r}_1^{(n)}, t) = a_1 u_{ij}(\vec{r}_1^{(n)}, t) + a_2 \delta_{ij} u_{ll}(\vec{r}_1^{(n)}, t), \quad (6)$$

where a_1 and a_2 are the elasto-optic constants of the NC. The procedure for calculating the frequency dependence of the RS intensity in the BP region, using Eq. (6) and taking explicitly into account the effects of dissipation and surface tension at the NC/matrix boundary, is

described in [6]. In the present paper, we use the relation for the BP intensity taken from [6] and neglect for simplicity the dissipation effect (such the neglect does not affects essentially the accuracy for description of the experimental data – see below).

When calculating the frequency dependence of the QEP intensity, it is necessary to consider the fluctuation permittivity tensor that accounts for the contribution corresponding to the fluctuation processes at the boundary NC/matrix discussed above. As mentioned in Introduction, it would be natural to connect the QEP with the NC permittivity variations, owing to the fluctuations $\delta p(t)$ of the Laplace pressure caused by curvature of the NC surface. In view of a small size of the NC, one can neglect the effects of acoustic retardation of the pressure fluctuations and represent the fluctuation permittivity tensor inside the NC as

$$\delta \varepsilon_{ij}(t) = \delta_{ij} \left(\frac{\partial \varepsilon}{\partial p} \right)_{p=0} \delta p(t), \quad (7)$$

where the pressure derivative of the permittivity

$$\langle \delta \sigma_{ad}^2(0) \rangle = \frac{\int d(\delta \sigma_{ad}(0)) \delta \sigma_{ad}^2(0) e^{-F[\delta \sigma_{ad}(0)]/T}}{\int d(\delta \sigma_{ad}(0)) e^{-F[\delta \sigma_{ad}(0)]/T}}, \quad (10)$$

where we have kept the term $\propto \delta \sigma_{ad}^2(0)$ in the fluctuation part $F[\delta \sigma_{ad}(0)]$ of the functional (1). The resulting relation for the QEP intensity may be obtained with calculating the appearing Gaussian integrals and replacing the summation over individual NCs with integrating in the R space with the logarithmic-normal distribution function.

Introducing the dimensionless frequency $\tilde{\omega} = \omega / \omega_{\max}$, where ω_{\max} stands for the frequency of the BP intensity maximum, we can write

$$I_{ijkl}(\tilde{\omega}) = \delta_{ij} \delta_{kl} (I^{QEP}(\tilde{\omega}) + I^{BP}(\tilde{\omega})). \quad (11)$$

Here we obtain

is written out using the assumption of isotropic continuum. The variation of the Laplace pressure is given by

$$\delta p(t) = \frac{2\delta\kappa(t)}{R}, \quad (8)$$

where $\delta\kappa(t)$ represents the fluctuation part of the surface tension coefficient at the boundary NC/matrix. One can link $\delta\kappa(t)$ with the dynamical part of the adatoms' surface density $\delta\sigma_{ad}(t) = \delta N_{ad}(t) / (4\pi R^2)$ through the relation

$$\delta\kappa(t) = b\delta\sigma_{ad}(t), \quad (9)$$

where the constant b , in its meaning, is of the order of the adatom formation energy.

Substituting Eq. (7) into Eq. (5), taking Eqs. (8) and (9) into account and integrating over the time and coordinates of the individual NC, we obtain that its contribution into the QEP intensity will be proportional to the square of NC volume and the Lorentzian having the width $1/\tau$. After that, the thermodynamic averaging in Eq. (5) is reduced to calculating the normalized functional integral

$$I^{QEP}(\tilde{\omega}) = A \frac{1 + 2e^{E/2T}}{(1 + e^{E/2T})^2} \times \frac{1 + e^{-E/T}}{\tilde{\omega}^2 + (1 + e^{-E/T})^2 / (\tau_{\infty} \omega_{\max})^2} \quad (12)$$

for the QEP intensity. The BP intensity can be calculated as described in [6]. If the NC oscillation damping is neglected (processing of the experimental data testifies that the neglect does not influence notably the accuracy of agreement between the theory and experiment), we finally arrive at

$$I^{BP}(\tilde{\omega}) = BT \frac{\tilde{\omega}^2 e^{-\frac{1}{2\Delta^2} \ln^2[\lambda \tilde{\omega} \Lambda(\tilde{\omega})]}}{1 + \frac{\xi}{\tilde{\omega} \Lambda(\tilde{\omega})}}, \quad (13)$$

where $\lambda = 2, 3c_L / (\omega_{\max} R_0)$, c_L is the longitudinal

sound velocity in the NC material, Δ and R_0 the parameters of the logarithmic-normal distribution, $\xi = \left[\frac{\omega_{\max}}{2,3c_L} \left(\frac{\partial \ln K}{\partial p} \right)_{p=0} 2\kappa \right]^{-1}$, K

denotes the bulk modulus for the NC material, and the function $\Lambda(\tilde{\omega})$ in Eq. (12) is given by a solution of a cubic equation and has the form

$$\Lambda(\tilde{\omega}) = \begin{cases} \sqrt[3]{\frac{\xi}{\tilde{\omega}}} \left(\sqrt[3]{1 + \sqrt{1 - \frac{\tilde{\omega}^2}{27\xi^2}}} + \sqrt[3]{1 - \sqrt{1 - \frac{\tilde{\omega}^2}{27\xi^2}}} \right); & \tilde{\omega} < 3\sqrt{3}\xi \\ \frac{2}{\sqrt{3}} \cos \left(\frac{\arctan \left[\sqrt{\tilde{\omega}^2 / 27\xi^2 - 1} \right]}{3} \right); & \tilde{\omega} > 3\sqrt{3}\xi \end{cases} \quad (14)$$

Here all the factors in Eqs. (12) and (13), which are unessential for the further analysis of

experimental data, are included in the constants A and B .

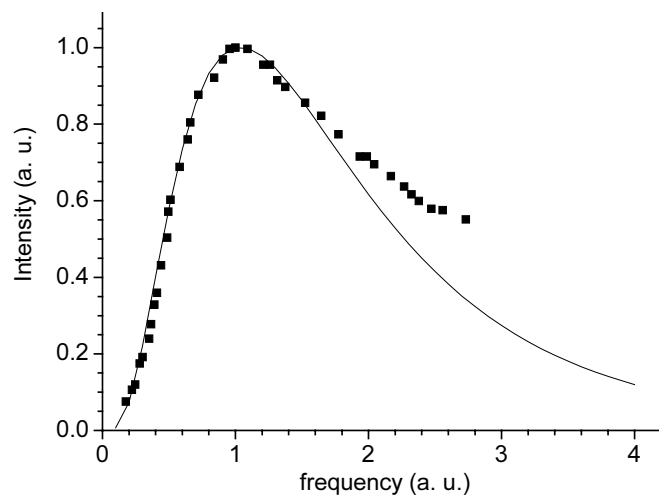


Fig. 1. Experimental low-frequency RS (■) for the glass $(\text{Sm}_2\text{O}_3)_{0.25}(\text{P}_2\text{O}_5)_{0.75}$ at $T = 15$ K [7]. The solid curve is calculated with formula (14). The parameters are given in Table 1.

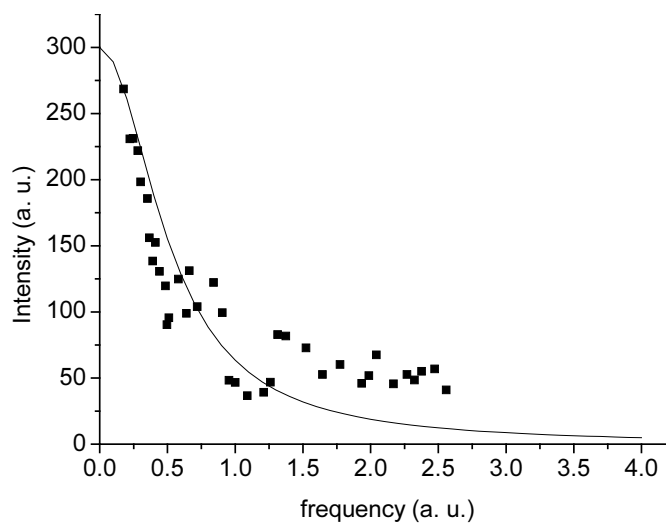


Fig. 2. Scaled experimental low-frequency RS (■) for the glass $(\text{Sm}_2\text{O}_3)_{0.25}(\text{P}_2\text{O}_5)_{0.75}$ at $T = 300$ K (see the text). The solid curve is calculated with formula (14). The parameters are given in Table 1.

3. Analysis of experimental data and discussion

Formulae (12) and (13) have been employed to describe the experimental RS data [7] for the glasses $\text{Sm}_2\text{O}_3\text{-P}_2\text{O}_5$. Being imposed by thermo-activation processes, the quasielastic scattering is negligible at low temperatures, so that only the BP is present in the low-frequency spectra. The results of processing of the experimental RS data at $T = 15$ K are shown in Fig. 1, where the solid line is constructed with the aid of Eq. (13) and the parameter values gathered in Table 1.

Table 1. Values of the parameters obtained from the best fit of the experimental data [7] and Eqs. (12) and (13).

Δ	λ	ξ	$\tau_\infty \omega_{\max}$	E, K
0.62	2	0.1	0.5	900

In order to select the effect of quasielastic scattering, we have subtracted the BP contribution (scaled using the Bose-factor for the case of room temperature) from the experimental data [7]. The graphs thus obtained are depicted in Fig. 2, together with the results of our calculations using Eq. (12) and the fitting

parameters from Table 1.

Besides, the experimental points for the glass $(\text{Sm}_2\text{O}_3)_{0.25}(\text{P}_2\text{O}_5)_{0.75}$ (the squares, see the data [7]) and the theoretical line (calculated using Eq. (12)) depicted in Fig. 3 show the temperature dependence of the quasielastic scattering intensity at $\tilde{\omega} \approx 0.25$. For comparison, we show also the results [7] calculated within the double-level system model (see the dashed line in Fig. 3). It is seen that the latter model does not reflect the experimental situation, even on a qualitative level. On the contrary, the calculation results based on our formula (12) agree very well with the experiment. Thus, one can consider the approach developed in the present paper as being adequate to the actual situation occurred in the glasses such as $\text{Sm}_2\text{O}_3\text{-P}_2\text{O}_5$.

In summary, let us formulate the main conclusions of this work. Basing on physically clear ideas about the dynamic fluctuations of the adatom density at the NC/matrix boundaries, we have put forward a consistent theory for the low-frequency RS in glass-like materials. The results of the theory can be made quantitatively consistent with the experimental data for the

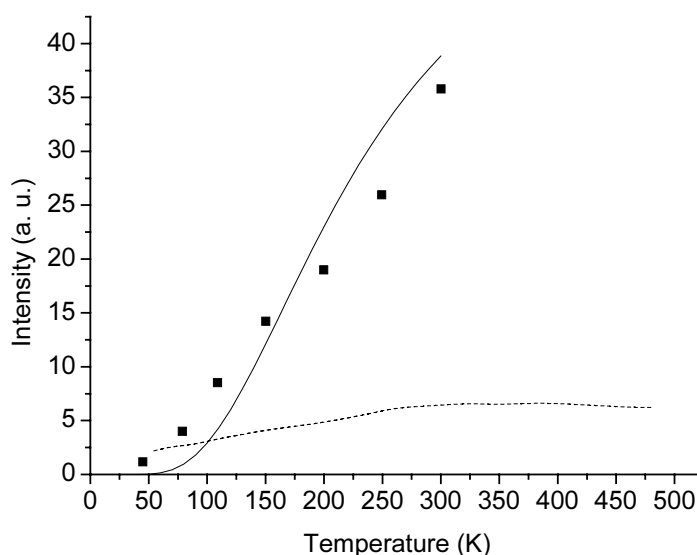


Fig. 3. Experimental (■) temperature dependence [7] of quasielastic scattering intensity at the dimensionless frequency $\tilde{\omega} \approx 0.25$. The solid curve is calculated with formula (12) and the dashed curve with the double-level systems model [7].

glasses $(\text{Sm}_2\text{O}_3)_{0.25}(\text{P}_2\text{O}_5)_{0.75}$. On the contrary, the calculations that use the known double-level system model [7] do not describe the experimental data for such the glasses even qualitatively. At last, it seems worth noticing that one can extract the value of such important parameter of the glass as the adatom formation energy, while comparing the theory developed here with the available experimental data.

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