PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 52, NUMBER 14 1 OCTOBER 1995-II

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Comparison of Raman- and neutron-scattering data for glass-forming systems

A. P. Sokolov*
Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

U. Buchenau
Institut für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, D-52425 Jülich, Germany

W. Steffen
Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

B. Frick
Institut Laue-Langevin, Boîte Postale 156 X, F-38042 Grenoble Cedex, France

A. Wischnewski
Institut für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, D-52425 Jülich, Germany

(Received 15 May 1995)

Low-frequency Raman- and neutron-scattering spectra are compared for the three glass formers polybutadiene, polystyrene, and SiO_2 at different temperatures. One finds similar neutron and Raman spectra in the frequency range where the quasielastic (relaxational) contribution dominates, but a marked quasilinear increase of the light-scattering sensitivity above the vibrational boson peak. Analysis of the data shows that there is some intrinsic relation between the quasielastic contribution and the boson peak vibrations. These results are compared with predictions of different models.

Low-frequency ($\nu \sim 1-100$ cm^{-1}) Raman spectra of disordered materials have been intensively investigated during the last two decades. The spectra have two main contributions:[1] quasielastic scattering, which is usually ascribed to some kind of relaxational motion, and the so-called boson peak, a vibrational contribution. The mechanism of light scattering at these frequencies is still controversial.

The general approach for the description of the spectra is disorder-induced scattering, assuming that excitations in disordered systems have no well-defined wave vector **q**. For this reason they may all contribute to the light-scattering spectra. The Raman intensity is supposed to be proportional to the density of states of these excitations $g(\nu)$:[1,2]

$$I(\nu)=C(\nu)g(\nu)\{n(\nu)+1\}/\nu, \qquad (1)$$

where $n(\nu)+1=\{1-\exp(-h\nu/\mathrm{kT})\}^{-1}$ is the temperature Bose factor and $C(\nu)$ is the light-to-excitation coupling coefficient. The coupling coefficient depends on the motional eigenvector of the excitation. In particular, it was shown that for slightly damped acoustic vibrations $C(\nu)\propto \nu^2$.[1] According to a second approach, the soft-potential model, the main contribution to the Raman spectra comes from localized excitations in soft potentials.[3] The latter have been postulated to have $C(\nu)=\text{const.}$[3] A third approach, dipole-induced-dipole (DID) scattering, suggests[4] that the main contribution to the light-scattering spectra appears due to a second-order process and the intensity may be expressed as a convolution of the dynamic structure factor $S(q,\nu)$ with itself: $I(q,\nu) \propto \int dQ\, d\Omega S(Q,\Omega)S(q-Q,\nu-\Omega)$. Taking into account that $S(q,\nu)$ is essentially a δ function in ν (as long as the broadening of the elastic line does not reach the spectral window),

0163-1829/95/52(14)/9815(4)/$06.00

one arrives at the conclusion that $I(\nu)\propto S(q_0,\nu)$, where q_0 is the main peak in $S(q)$.[4] Thus light- and neutron-scattering spectra should have similar frequency dependence. In terms of Eq. (1), this means that $C(\nu)$ should be essentially frequency independent.

Thus the present theoretical background gives different predictions for the frequency dependence of $C(\nu)$. Experimental results presented so far are contradictory. There are several papers claiming experimental observations of $C(\nu)\propto\nu^2$ at lower frequencies (see, for example, Refs. 1 and 5). Another group of papers reports that $C(\nu)$ around the boson peak frequency can be well approximated by a linear function.[5–8] However, as was shown in[3,9] $C(\nu)\approx$const may be a good approximation at low frequencies. There, the light-scattering spectra look similar to the neutron ones.[9]

In this paper we compare neutron- and Raman-scattering data for three different glass formers at different temperatures. The comparison shows some general features of $C(\nu)$ in different systems. In particular, $C(\nu)$ of the quasielastic contribution seems to be related to $C(\nu)$ of the boson peak. These results are compared to predictions of different models.

Right-angle Raman spectra were measured using a double monochromator (U-1000, FU-Berlin) and normalized in intensity at high frequencies. Neutron-scattering spectra were measured using the cold neutron time-of-flight spectrometer IN6 at the Institut Laue-Langevin, Grenoble. Two of the samples (the two polymers polystyrene and polybutadiene) were predominant incoherent scatterers. These were treated in the usual way, subtracting the empty container, normalizing to vanadium, correcting for absorption and for multiple scattering, and finally determining an effective vibrational density of states from the Q^2 dependence at low Q and finite-energy transfer. The third sample, vitreous silica, a coherent scatterer, was evaluated in terms of a model for the eigenvectors as described in an earlier publication.[10] The effective vibrational density of states obtained in that way still contains both vibrational and relaxational contributions.

The details of the experimental and data treatment procedures will be described in a more extended paper.[11] The measurements have been done at different temperatures. Since the quasielastic scattering is much more strongly temperature dependent than the vibrational scattering, one thus has different relative contributions of the boson peak and the quasielastic scattering to the spectra.

Figure 1 shows the comparison of $g(\nu)/\nu^2$ as obtained from the neutron spectra with depolarized Raman spectra. As usual, both spectra show the boson peak at $\nu_{\max}\sim 12$–50 cm^{-1} and quasielastic scattering at lower frequencies. The latter strongly increases with T. Both the Raman and neutron spectra have the same frequency dependence at low ν, but differ at $\nu>\nu_{\max}$ (Fig. 1). For PS and SiO$_2$ the Raman spectra at $T<10$ K are also shown, though there are no neutron data at these low temperatures. These spectra illustrate the strong quasielastic contribution even at fairly low temperatures, $T=35$ K for PS and $T=50$ K for SiO$_2$.

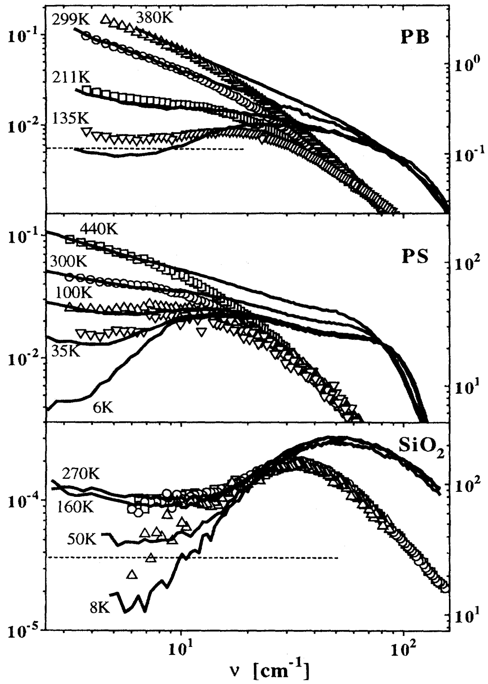

FIG. 1. Comparison of $g(\nu)/\nu^2$ from neutron data (symbols) and normalized Raman intensity (solid lines) at different temperatures for PB, PS, and SiO$_2$. Dashed lines show the Debye level at lowest T (135 K for PB and 50 K for SiO$_2$).

It is evident that different kinds of excitations (sound waves, localized vibrations, relaxation, etc.) may have different $C(\nu)$. An effective $C_{\rm eff}(\nu)$ can be directly estimated if one divides the Raman spectra by the neutron ones: $C_{\rm eff}(\nu)=I(\nu)\nu/g(\nu)\{n(\nu)+1\}$. The results (Fig. 2) show the same general behavior for all three substances: (i) at low frequencies $C_{\rm eff}(\nu)\approx$const with a weak temperature dependence at lower T; (ii) at higher ν $C_{\rm eff}(\nu)$ has a nearly linear frequency dependence; (iii) the crossover between these two regions happens just around $\nu_{\max}$; (iv) at still higher ν $C_{\rm eff}(\nu)$ reaches a maximum just at the frequency of the first maximum in the vibrational $g(\nu)$. A softening of that maximum with increasing temperature is observed for PB and PS. However, in order to separate different contributions to the spectra one should use some additional model assumptions.

For the analysis of $C_{\rm eff}(\nu)$ let us assume that both neutron and Raman spectra can be written as a sum of the relaxational and the vibrational contributions, i.e., $g(\nu)=g_r(\nu)+g_v(\nu)$ and $I(\nu)\propto C_r(\nu)g_r(\nu)+C_v(\nu)g_v(\nu)$. Then, using Eq. (1), one can write

$$C_{\rm eff}(\nu)=C_r(\nu)+[C_v(\nu)-C_r(\nu)]g_v(\nu)/[g_v(\nu)+g_r(\nu)]. \tag{2}$$

The frequency dependencies of both $C_v(\nu)$ and $C_r(\nu)$ are not known. However, in the frequency range where the quasielastic contribution dominates (low frequencies and high temperatures) the second term in Eq. (2) is negligible and $C_{\rm eff}(\nu)\approx C_r(\nu)$. Thus $C_r(\nu)\approx$const (Fig. 2). At $\nu>\nu_{\max}$ the vibrational contribution dominates and $C_{\rm eff}(\nu)\approx C_v(\nu)$. Figure 2 shows that in that interpretation $C_v(\nu)$ has a strong frequency dependence, at least at frequencies above the boson peak maximum.

How can one describe the temperature variation of $C_{\rm eff}(\nu)$? Let us assume that the main temperature variation in the spectra is an increase of the quasielastic intensity and

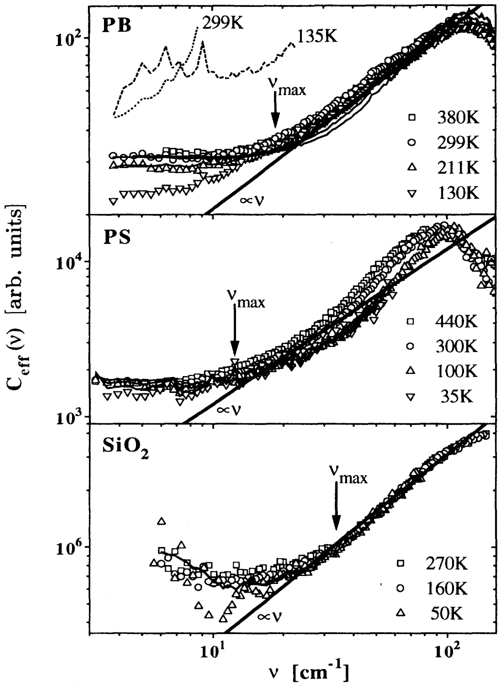

FIG. 2. $C_{eff}(\nu)$ at different temperatures (symbols) for PB, PS, and SiO_2. Arrows show the position of ν_{max}. Thick solid lines show the linear frequency dependence. Thin solid lines show estimated $C_{eff}(\nu)$ using Eq. (3) with $C_r=22$ for PB, $C_r=1800$ for PS, and $C_r=10^6$ for SiO_2. Dashed lines show $C_{eff}(\nu)$ for PB calculated after subtraction of the Debye contribution from the neutron spectra for two temperatures.

that the vibrational contribution has a nearly harmonic behavior, i.e., $C_v(\nu)$ and $g_v(\nu)$ are essentially temperature independent. In this case one can rewrite Eq. (2):

$$C_{eff}(\nu,T)=C_r+[C_{eff}(\nu,T_1)-C_r]g(\nu,T_1)/g(\nu,T), \quad (3)$$

where $C_{eff}(\nu,T_1)$ and $g(\nu,T_1)$ are the coupling coefficient and the effective density of states at some temperature T_1. We calculated $C_{eff}(\nu)$ for all temperatures using Eq. (3) and the data at the lowest temperature ($T=130$ K for PB, 35 K for PS, and 50 K for SiO_2). At these temperatures, one has the smallest quasielastic contributions (Fig. 1). A reasonable agreement with the experimental data was obtained using $C_r=\text{const}$, independent of temperature and frequency. Obviously, the temperature variation of $C_{eff}(\nu)$ at low frequencies can be ascribed to the variation of the quasielastic contribution relative to the vibrational one. Some deviations of the calculated $C_{eff}(\nu)$ from the experimental data appear at $\nu>\nu_{max}$ for PB and PS. We ascribe this deviation to a softening of the vibrational spectra with T, contrary to the assumption of Eq (3).

The value of C_r was found approximately equal to the value of $C_{eff}(\nu=\nu_{max})\approx C_v(\nu=\nu_{max})$ for all three substances under investigation (Fig. 2). This is an important result; it supports the idea of some intrinsic relation between the quasielastic scattering and the boson peak. This idea is independently supported by earlier findings on the depolarization ratio $\rho(\nu)=I_{dep}/I_{pol}$. This is an important parameter for the light-scattering spectrum and was analyzed for many glass-forming systems. It was found that in the low-frequency range ρ varies from ~ 0.24 for ZBLAN20 (ZrF_4:53%, NaF:20%, BaF_2:20%, LaF_2:4%, AlF_3:3%) (Ref. 12), ~ 0.3 for SiO_2 up to a maximum value ~ 0.75 for most of the organic systems (including PB and PS).[1,11] However, in all cases investigated so far it was found that $\rho(\nu)$ has the same value for the boson peak and for the quasielastic contribution. Thus the depolarization ratio and the analysis of $C_{eff}(\nu)$ (Fig. 2) both show that the boson peak and the quasielastic-scattering contribution could have some intrinsic relation.

Now let us compare our results with the predictions of different model approaches. We do not find the $C_{eff}(\nu)\propto\nu^2$ behavior predicted for the slightly damped plane waves.[1] Our results do not support previous publications where authors claimed a ν^2 behavior for the frequency range $\nu<\nu_{max}$ (see, for example, Refs. 1 and 5). It is known that the vibrational $g(\nu)$ around ν_{max} is significantly higher than the one expected for sound waves and increases faster than ν^2 (as it should for sound waves) at $\nu<\nu_{max}$. The presented neutron-scattering spectra at low temperatures, where the vibrational contribution dominates, also show that the vibrational $g(\nu)$ at $\nu<\nu_{max}$ increases faster than ν^2 (Fig. 1): there is a slight increase of $g(\nu)/\nu^2$ for PB and PS, which is additionally masked by the quasielastic contribution at lower frequencies, and a strong increase can be seen for SiO_2. Thus the theoretical basis of an analysis in terms of sound waves is already questionable. The expected ν^2 behavior should appear (if it exists at all) at low frequencies, where vibrations are certainly plane waves with small damping. However, we cannot reach this region because at lower ν (~ 4 cm^{-1} for PB and PS and ~ 6 cm^{-1} for SiO_2) at all analyzed temperatures the spectra are dominated by the quasielastic contribution (Fig. 1). Thus the question remains open.

The soft-potential model,[3] in contrast, assumes that the contribution of sound waves is negligible and that the main contribution to the low-frequency Raman spectra comes from localized excitations in soft potentials. The latter may be relaxationlike, which gives quasielastic scattering, or quasiharmonic vibrations, which show up as the boson peak.[3] Thus a relation between the quasielastic scattering and the boson peak is expected in the framework of the soft potential model. The simplest assumption[3] is to take $C(\nu)=\text{const}$ for both kinds of excitations and independent of temperature. In this scheme, the depolarization ratio should be the same for quasielastic scattering and for the boson peak. The latter is in agreement with experimental observations. However, our results show that $C_{eff}(\nu)$ is frequency dependent and has a weak temperature dependence (Fig. 2). Of course, for a correct comparison with the predictions of the soft potential model one should subtract the Debye-like contribution (sound waves, shown by the dashed line in Fig. 1) from the neutron spectra. The results of the comparison of the Raman spectra with $g(\nu)-g_D(\nu)$ for PB are shown in Fig. 2. The weak temperature and frequency dependencies observed at $\nu<\nu_{max}$ for $C_{eff}(\nu)$ are not removed, but rather enhanced. Thus the subtraction does not improve the situation and we cannot make conclusions about the sound wave contribution from the presented data. In any case, the observed strong frequency dependence of $C_{\mathrm{eff}}(\nu)$ at $\nu > \nu_{\max}$ (Fig. 2) is in contradiction with the prediction.[3]

According to another approach, DID,[4] the Raman spectra $I/\nu(n+1)$ should be similar to $S(q,\nu) \sim g(\nu)/\nu^2$. This prediction is in good agreement with the obtained results at $\nu < \nu_{\max}$, where the quasielastic contribution dominates, but it is not correct in the frequency region where the vibrational contribution dominates (Fig. 1). The DID mechanism also predicts that the depolarization ratio $\rho \approx 0.75$. This is certainly not the case for SiO_2, where $\rho \approx 0.3$.[1] Thus the DID explains the frequency dependence of the quasielastic scattering, but fails to describe the depolarization ratio.

The intrinsic relation between the two contributions is also explained in the framework of another phenomenological model.[13,14] The model assumes that the low-frequency vibrations are damped due to some relaxation channel. As a result every vibration (with some frequency Ω) gives two contributions to the spectrum: an inelastic one at $\nu \approx \Omega$, and a quasielastic one. The depolarization ratio is the same for both contributions and is defined by the depolarization ratio of the vibrational contribution. The contribution of every vibration to the Raman spectra differs due to $C(\Omega)$. However, this does not change the spectral shape of the quasielastic part and only changes its amplitude according to $C(\Omega)$. As a result the vibrational (inelastic) contribution will have some frequency-dependent $C_v(\nu)$, while the quasielastic one will have $C_r(\nu) \approx \mathrm{const}$. The model assumes that all vibrations around the boson peak contribute to the quasielastic spectrum. In this case C_r is some averaged value of $C_v(\nu)$ and, consequently, $C_r \approx C_v(\nu = \nu_{\max})$. Thus the observed relation between the quasielastic and the boson peak contributions are explained. However, the model does not explain the frequency dependence of $C_v(\nu)$. Our results show (Fig. 2) that $C_v(\nu)$ has a nearly linear frequency dependence at least for $\nu > \nu_{\max}$ (it deviates significantly from this behavior only in PS). The same quasilinear behavior has been found for Se, As_2S_3, B_2O_3, SiO_2, PB, and Sm_2O_3-P_2O_5 glasses.[5,7,8] Thus this frequency dependence seems to be universal. It is not explained by either one of the theoretical approaches discussed above. Some explanation for this behavior in terms of fractonlike models has been suggested,[5,6] assuming linearlike eigenvectors. However, in the present paper we are not able to discuss these models because of the limited space.

The existence of the quasilinear frequency dependence is even more striking in view of the experimental evidence[10] for a frequency-independent eigenvector of the vibrations in vitreous silica between 10 and 100 cm^{-1}, interpretable in terms of coupled librations of corner-connected SiO_4 tetrahedra. From that evidence, it seems that the quasilinear increase of $C_{\mathrm{eff}}(\nu)$ can hardly be related to a change of the eigenvector.

As a conclusion, the above analysis shows that there is a general behavior for $C_{\mathrm{eff}}(\nu)$ in different kinds of glass forming systems: $C_{\mathrm{eff}}(\nu) \approx \mathrm{const}$ at low ($\nu < \nu_{\max}$) frequencies and a nearly linear frequency dependence at higher ν. The crossover between these two regions appears just around $\nu_{\max}$. At low frequencies and temperatures $C_{\mathrm{eff}}(\nu)$ has a weak temperature dependence, mainly due to the increase of the relaxational scattering with increasing temperature. In all cases it was found that $C_r \approx C_v(\nu = \nu_{\max})$. These results together with the depolarization ratio ρ show that there is some intrinsic relation between the boson peak and the quasielastic contribution. This holds for organic and covalent systems, for systems which have $\rho \approx 0.75$ and $\rho \approx 0.3$. The intrinsic relation is expected in the soft potential model[3] and in the model found in Refs. 13 and 14, but not in the DID mechanism.[4] However, the frequency dependence of $C_{\mathrm{eff}}(\nu)$ deviates strongly from the prediction in Ref. 13 and is not discussed at all in Refs. 13 and 14. It shows a quasilinear increase, setting in at the boson peak, which seems to be a universal feature of all glass formers.

The authors are grateful to Professor D. Quitmann, Dr. V. Novikov, and Professor D. Parshin for helpful discussions. This work was supported by DFG through SFB 262. The partial financial support by EC, HCM-Network project (No. CHRX-CT92-0009) is gratefully acknowledged. A.P.S. is grateful to Max-Planck-Gesellschaft and INTAS (Grant No. INTAS-93-2185) for partial financial support and to FU-Berlin and, personally, to Professor D. Quitmann for hospitality.

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*Permanent address: IA&E Russian Ac.Sci., Universitetsky pr.1, 630090, Novosibirsk, Russia.

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