PHYSICAL REVIEW B VOLUME 48, NUMBER 10 1 SEPTEMBER 1993-II

Evaluation of density of vibrational states of glasses from low-frequency Raman spectra

A. P. Sokolov,* A. Kisliuk, and D. Quitmann
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D14195 Berlin, Germany

E. Duval
Laboratoire de Physicochimie des Matériaux Luminescents, Université Lyon I, 69622 Villeurbanne, France

(Received 23 December 1992; revised manuscript received 31 March 1993)

Low-frequency Raman spectra of some glasses have been measured at low temperature. Comparison of the spectra with heat-capacity data shows that in a broad frequency range the Raman intensity is simply proportional to the number of vibrational excitations [density of the vibrational states $g(\nu)$ multiplied by the Bose factor]. The conclusion is reached that $g(\nu)$ up to half of the Debye frequency may be evaluated from the low-frequency Raman spectra of disordered solids.

The main part of vibrational excitations in amorphous solids has no well-defined wave vector because of the structural disorder. As a result, conservation of momentum between the excitation and the photon is no longer a restrictive selection rule for the process of Raman scattering and all vibrational modes contribute to the Raman spectra. It was shown in Ref. 1 that the intensity of the Raman spectra in disordered solids is proportional to the density of vibrational states $g(\nu)$ multiplied by light-to-vibrations coupling coefficient $C(\nu)$:

$$I(\nu)=g(\nu)C(\nu)[n(\nu)+1]/\nu\ ; \tag{1}$$

here $[n(\nu)+1]$ is the Bose factor for the Stokes component. So, it is possible to find $g(\nu)$ from Raman spectra, if one knows the frequency dependence of $C(\nu)$. In the first discussion[1] it was supposed that $C(\nu)=\text{constant}$, but this dependence does not lead to the correct $g(\nu)$.[1] Later in the framework of a plane wave approximation for acoustic-like vibrations, it was shown[2] that $C(\nu)$ may have a complicated spectral dependence which is

$$C(\nu)\sim\nu^2 \tag{2}$$

at very low ν and then has a maximum at some frequency $\nu_{\max}\sim V/R_c$, where V is a sound velocity and R_c is a correlation radius of amorphous structure. It was found in Refs. 3 and 4 that with some modifications this model gives a good description of the spectral form of the so-called boson peak in Raman spectra of glasses, and correlations of $\nu_{\max}$ with the size of structural inhomogeneities were established.[4–6]

Nevertheless, comparison of the Raman spectra with inelastic neutron scattering data [which yield in the incoherent approximation directly $g(\nu)$] have shown[7–10] that $C(\nu)$ has no maximum and varies nearly linearly in the low-frequency region. For various materials Raman spectra were measured at low temperature, where the contribution of quasielastic light scattering is negligible.[11,12] The experiments showed[10,13,14] that at low frequencies $\nu<20-30$ cm^{-1} the spectral dependence of Raman intensity is

$$I/[n(\nu)+1]\sim g(\nu)C(\nu)/\nu\sim\nu^3\ . \tag{3}$$

Supposing in addition a Debye behavior for the vibrational density of states $g(\nu)\sim\nu^2$, one arrives at a conclusion of a quadratic spectral dependence of $C(\nu)$, as in Eq. (2). But inelastic neutron scattering measurements and especially low-temperature heat capacity data give overwhelming evidence that $g(\nu)$ in amorphous solids does not follow a Debye behavior at low frequencies.[7,8,12,15–17] So, the spectral dependence of $C(\nu)$ is still an unsettled problem, and this lack of knowledge limits the possibility for determining $g(\nu)$ from Raman measurements.

In the present work Raman spectra of various glasses have been measured down to low temperature. The comparison of these data with heat capacity data leads to the result that in a broad frequency range $C(\nu)$, as defined by Eq. (1), has a linear dependence on frequency, and has no quadratic behavior down to 5–8 cm^{-1}. It is shown that from the Raman spectra one may obtain $g(\nu)$ for frequencies up to about half of the Debye frequency ν_D, and besides the shape, $g(\nu)$ can be estimated in absolute units. If this result is of general validity, Raman spectroscopy may be a useful method for the determination of the vibrational density of states in disordered solids, thus allowing a much easier determination than by the traditional inelastic neutron scattering method.

The right angle depolarized Raman spectra of four glasses have been measured at two temperatures $T\sim50$ K and $\sim5-10$ K. The temperatures were estimated using the Stokes–anti-Stokes intensity ratio. The spectra of chalcogenide glasses, Se and As_2S_3, were measured using a double monochromator (U-1000) with spectral slit width ~1 cm^{-1} and a Kr laser at $\lambda=752$ nm; the laser beam power at the sample was 20 mW for Se and 150 mW for As_2S_3. The spectra of the oxide glasses, B_2O_3 and SiO_2 (suprasil), were measured using a quintuple (Dilor) monochromator with spectral slit width ~1.5 cm^{-1} and an Ar laser at $\lambda=514$ nm; the power was 200 mW for B_2O_3 and 300 mW for SiO_2.

The obtained spectra are shown in Fig. 1 in a log-log plot. For this presentation the special normalization $I/\{[n(\nu)+1]\nu^2\}$ was used in order to stress two points.

(i) The contribution of quasielastic light scattering to the Raman spectra at $\nu < 10$ cm^{-1} is not negligible even at $T \sim 50$ K.

(ii) The spectral dependence of $I/[n(\nu)+1]\nu^2$ at very low frequencies is linear, or perhaps even somewhat stronger. This is especially clear from the spectra of As_2S_3 and B_2O_3 in the frequency range from 5–6 to 15 cm^{-1} [Figs. 1(b) and 1(c)].

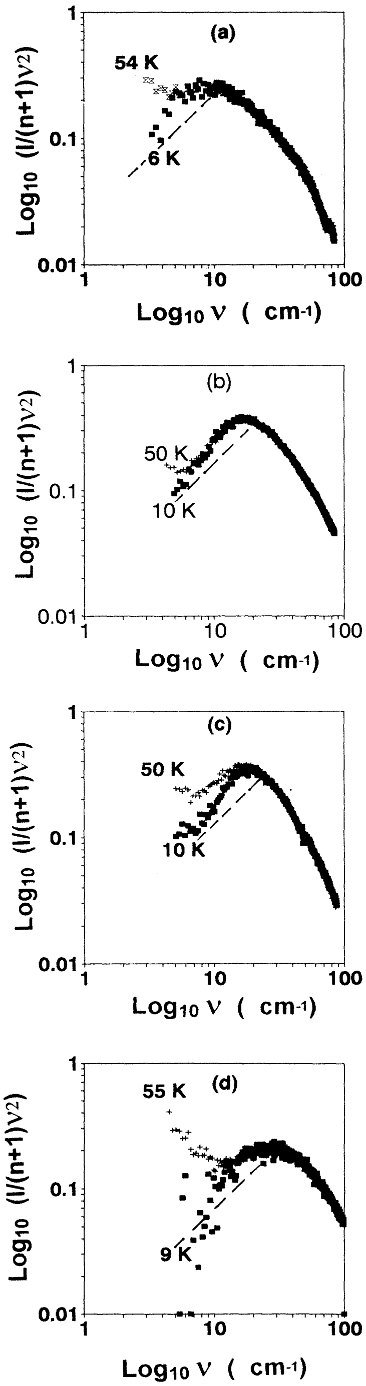

FIG. 1. Normalized Raman spectra of glasses in a log-log scale: (a) Se, (b) As_2S_3, (c) B_2O_3, (d) SiO_2 (suprasil). Dashed lines correspond to a linear dependence on frequency.

The last result means, if one assumes a Debye behavior for $g(\nu)$, that $C(\nu)$ varies with frequency at least like ν^2. However, the spectra of $g(\nu)$ in this very low-frequency region are not known. Analysis of heat-capacity data shows[16,17] that $g(\nu)$ varies faster than ν^2. Thus, one would expect that $C(\nu)$ varies with frequency slower than ν^2. The problem for this frequency range is that the inelastic neutron scattering spectra have some uncertainties, especially due to contribution of quasielastic scattering.[18] So, for a correct comparison with light scattering data one would have to use low-temperature (as it follows from our results, $T < 50$ K) neutron measurements, which we have not found in the literature.

Another idea is to compare the Raman data directly with heat-capacity data. It is a usual way for testing of $g(\nu)$ obtained from inelastic neutron scattering measurements. We can use it for evaluation of $C(\nu)$ through the testing of $g(\nu)$ obtained from the Raman spectra. For this purpose the spectral dependence of $g(\nu)$ down to 4–5 cm^{-1} was calculated from low-temperature Raman spectra (Fig. 1) using Eq. (1) with the only assumption that $C(\nu)$ has linear dependence on frequency:

$$g(\nu) = G_0 I(\nu)/[n(\nu)+1] \ . \tag{4}$$

Here G_0 is a constant which was used as a fitting parameter in further calculations. Below $\nu < 4$–5 cm^{-1} $g(\nu)$ was approximated by the Debye density of states $g_D = 3\nu^2/\nu_D^3$ estimated from known parameters of the glasses under investigation (Table I). Now the temperature dependence of the heat capacity was calculated using the obtained density of vibrational states and the well-known equation:

$$C_v = 3Nk_B \int_0^{\nu_D} g(\nu)(h\nu/k_BT)^2 \frac{\exp(h\nu/k_BT)}{[\exp(h\nu/k_BT)-1]^2} d\nu \ . \tag{5}$$

Here N is the number of atoms per gram, k_B is Boltzmann's constant, and ν_D is the Debye frequency $\nu_D = k_B T_D/h$. The analysis shows that for the temperature range from 2 K up to 20 K the calculated values of C_v do not show a dependence on the detailed spectral shape of $g(\nu)$ at $\nu < 4$–5 cm^{-1} and at $\nu > 80$ cm^{-1}. At $T < 1$–2 K the heat capacity is dominated by the linear term. This term is not related to the vibrational excitations and usually is ascribed to tunneling centers.[12] Their contribution to the Raman spectra at low temperatures has been searched but was not found (see, for example,

TABLE I. Parameters of glasses used in calculations: T_D, Debye temperature; M_a, averaged atomic weight; ρ, mass density. All data from Ref. 19, except * from Ref. 20. G_i is the integral (up to $\nu_D/2$) of the density of vibrational states obtained from Raman spectra, Eq. (6), as a fraction of the total number of vibrations.

	T_D, K	M_a	ρ, g/cm^3	G_i
1. Se	123	79	4.3	0.17
	113*			0.15
2. As_2S_3	170	49	3.2	0.13
3. B_2O_3	259	14	1.8	0.07
4. SiO_2	492	20	2.2	0.14

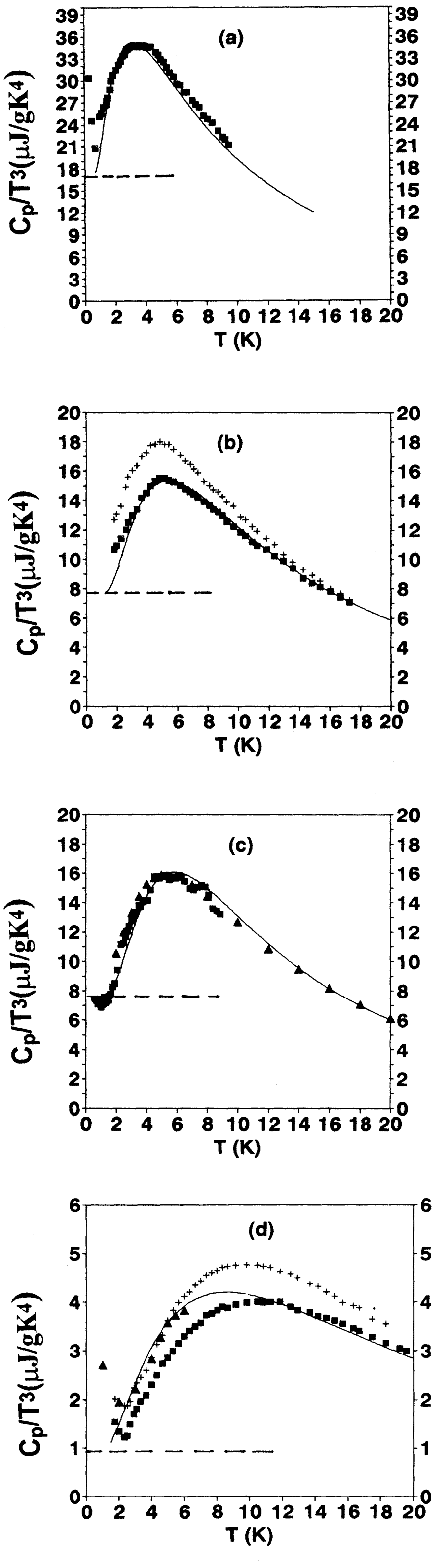

FIG. 2. Heat capacity of glasses calculated from Raman spectra (lines), and from experiment (points): (a) Se (data from Ref. 21), (b) As_2S_3 (Ref. 16), (c) B_2O_3 (■) from Ref. 22 and (▲) from Ref. 23, (d) SiO_2 (■)—heralux and (+)—spectrosil from Ref. 17, (▲)—suprasil (Ref. 24). Dashed lines correspond to values expected from the Debye model.

Refs. 12 and 14). So, we limit our fitting procedure to the temperature range $T > 2$ K, where the main contribution to C_p is given by vibrational excitations, and where contribution of tunneling centers cannot influence our conclusions.

The results are shown as lines in Fig. 2. The calculated heat capacities C_v reproduce well the existing experimental data C_p for all glasses under investigation (the difference between C_v and C_p can be neglected here). Small deviation from experimental temperature dependence of C_v is observed only for As_2S_3 glass at $T < 3$ K. Only this region may be a sign of superlinear dependence of $C(\nu)$. For all other frequency regions and all glasses under investigation the linear frequency dependence of $C(\nu)$ in Eq. (1) is a very good approximation for calculating C_v (Fig. 2).

This linear behavior of $C(\nu)$ seems to be a general regularity for the low-frequency Raman scattering in glasses, because it was also found from the comparison with neutron data for SiO_2 and B_2O_3,[10] as well as for polymer glasses PMMA,[9,10] polybutadiene, and DGEBA.[10] The same may be found from analysis of the earlier data for As_2S_3.[7] But the question is again how far is this regularity valid down to the low frequencies? From the experimentally observed frequency dependence of the Raman spectra [Eq. (3); see also Fig. 1], and assuming $g(\nu) \sim \nu^2$, many authors[10–14] reached the conclusion that $C(\nu) \sim \nu^2$ at $\nu < 20\ \mathrm{cm}^{-1}$. But up to now the real behavior of $g(\nu)$ in this frequency range is not known. For SiO_2 at frequencies $\nu < 20\ \mathrm{cm}^{-1}$,[25] and for B_2O_3 at $\nu < 15\ \mathrm{cm}^{-1}$,[26] a quadratic dependence of $g(\nu)$ has been derived from inelastic neutron scattering measurements. However, the quoted neutron $g(\nu)$ is significantly higher than expected in the Debye model [by a factor of four in SiO_2 [Ref. (25)] and will not give a correct temperature dependence of the heat capacity (i.e., the pronounced peak for C_p/T^3 will be missing). In order to obtain agreement with $C_p(T)$ near and below 5 K, the authors of Ref. 15 used for SiO_2 an extrapolation of $g(\nu)$, which varies faster than ν^2 in this frequency range. Moreover, the direct analysis of $C_p(T)$ also shows[16,17] that $g(\nu)$ must vary faster than ν^2 even at very low frequencies (5–20 cm^{-1}). Thus, $C(\nu)$ in this frequency range has variations slower than ν^2.

Analysis of our data also shows that assumption of quadratic dependence for $C(\nu)$ at $\nu < 15$–$20\ \mathrm{cm}^{-1}$ will not give a correct temperature variation of heat capacity: In comparison with the results presented in Fig. 2, the calculated C_v will increase ~2–3 times at $T \approx 2$–3 K, while values at $T > 10$ K will remain approximately the same. It also means that $C(\nu)$ in this frequency range varies slower than ν^2 and in fact the results presented here (Fig. 2) show that one can reproduce well the heat-capacity data if one uses a linear approximation of $C(\nu)$ down to 5–8 cm^{-1}.

Thus in a wide frequency range (from 5–8 cm^{-1} up to ~100 cm^{-1}) $C(\nu)$ is well approximated by a linear frequency dependence. Some recently proposed models,[10,27] using an assumption that the localization length of vibrational excitations $l_\nu \sim 1/\nu$, predict this dependence, but only in some special cases. In Ref. 10 the linear dependence results only if l_ν is smaller than the radial correlation radius, and much larger than a (newly introduced) angular correlation radius. In Ref. 27 the linear dependence of $C(\nu)$ is explained using the assumption that the vibrational excitations are essentially linear. A linear dependence $C(\nu)$ has also been found in a special computer model calculation for the two- and three-dimensional percolating clusters,[28] though other dependencies have been obtained for similar conditions (see, e.g., Ref. 29). The experimental results discussed here, as well as previously published results,[7-10,16,17] suggest that $C(\nu)\sim\nu$ is a more general property of low-energy vibrational excitations, which was observed for oxide, chalcogenide, superionic, and polymer glasses. Moreover, $C(\nu)\sim\nu$ was found in the spectral region where the estimate of the phonon mean free path l_ν from thermal conductivity data shows a variation $l_\nu\sim\nu^{-4}$.[20] So, a more general model is necessary for a description of the essentially linear spectral dependence of $C(\nu)$.

One of the ideas may follow from the fact that for $\nu>5-8$ cm^{-1}, l_ν estimated from thermal conductivity data of glasses is usually much shorter than light wavelength ($\lambda\sim1$ μm).[20] So, we have incoherent scattering and, probably (as it follows from our data), that for vibrations with $l_\nu \ll 1/q\sim\lambda$ (q is a scattering wave vector) the Raman intensity is simply proportional to the number of these vibrations. On the other hand, at much lower frequencies l_ν becomes larger than λ and the coherent scattering process appears as Brillouin scattering.

Another important question is the following: Is it possible to estimate the absolute value of $g(\nu)$ from the Raman spectrum? For that one must know G_0 [Eq. (4)]. The latter was estimated for spectra of all glasses under investigation as a fitting parameter in the heat-capacity calculations. If G_0 is estimated correctly by this procedure, we will have the correct normalization of $g(\nu)$. The integral of the density of states was calculated:

$$G_i=\int_0^{\nu_D/2} g(\nu)d\nu \tag{6}$$

up to $\nu_D/2$, because at higher frequencies the contribution of optical vibrational modes in the Raman spectra become important. The latter may have coupling coefficients $C(\nu)$ which differ significantly from the value for low-frequency acoustic-like vibrations. Of course, the estimate Eq. (6) strongly depends on ν_D (the quoted values of which have a big scatter in the literature) and on the redistribution of the vibrational states between low (10–30 cm^{-1}) and higher energy regions. Nevertheless the calculated G_i, presented in Table I, are not too far from the value $\sim$12.5% expected in the Debye approximation. A particularly large deviation is found for B_2O_3 glass, which may be connected with a strong non-Debye behavior of $g(\nu)$ in this glass. It remains to be checked whether the method of analysis of low-frequency Raman spectra (boson peak) which we have discussed here can be applied to amorphous substances in general.

In summary, we have compared the low-frequency Raman spectra of different glasses with heat-capacity data. This comparison has shown that the Raman intensity in the frequency range 5–8 cm$^{-1}<\nu<100$ cm^{-1} is simply proportional to the number of vibrational excitations, or, in terms of Eq. (1), that the light-to-vibrations coupling coefficient has an essentially linear dependence on frequency. So, low-frequency Raman spectroscopy may be used as a technique for evaluation of density of the vibrational states in disordered solids and may become competitive with traditional inelastic neutron scattering spectroscopy.

One of the authors (A.P.S.) is grateful to Laboratoire de Physico-Chimie des Materiaux Luminescents, Université Lyon I, for hospitality, to Bernard Varrel for technical assistance, and to the Alexander von Humboldt Foundation for financial support. This work was supported by DFG through SFB 337.

---

*Permanent address: Institute of Automation & Electrometry, Russian Ac. Sci., Novosibirsk, 630090, Russia.

[1] R. Shuker and R. Gammon, Phys. Rev. Lett. **25**, 222 (1970).

[2] A. J. Martin and W. Brenig, Phys. Status Solidi B **64**, 163 (1974).

[3] V. K. Malinovsky and A. P. Sokolov, Solid State Commun. **57**, 757 (1986).

[4] M. Krüger *et al.*, J. Chem. Phys. **96**, 7352 (1992).

[5] E. Duval *et al.*, Phys. Rev. Lett. **56**, 2052 (1986).

[6] A. P. Sokolov *et al.*, Phys. Rev. Lett. **69**, 1540 (1992).

[7] V. K. Malinovsky *et al.*, Europhys. Lett. **11**, 43 (1990).

[8] A. Fontana *et al.*, Phys. Rev. B **41**, 3778 (1990).

[9] M. G. Zemlyanov *et al.*, Zh. Eksp. Teor. Fiz. **101**, 284 (1992) [Sov. Phys. JETP **74**, 151 (1992)].

[10] E. Duval, N. Garcia, A. Boukenter, and J. Serughetti, J. Chem. Phys. (to be published); T. Achibat, A. Boukenter, and E. Duval, *ibid.* (to be published).

[11] G. Winterling, Phys. Rev. B **12**, 2432 (1975).

[12] *Amorphous Solids: Low-Temperature Properties,* edited by W. A. Phillips (Springer, Berlin, 1981).

[13] J. S. Lannin, Solid State Commun. **12**, 947 (1973).

[14] R. J. Nemanich, Phys. Rev. B **16**, 1655 (1977).

[15] U. Buchenau *et al.*, Phys. Rev. B **34**, 5665 (1986).

[16] N. Ahmad *et al.*, J. Phys. C **19**, 3765 (1986).

[17] N. Ahmad and Matiullah, Solid State Commun. **76**, 433 (1990).

[18] U. Buchenau *et al.*, Phys. Rev. Lett. **60**, 1318 (1988).

[19] R. B. Stephens, Phys. Rev. B **8**, 2902 (1973).

[20] J. E. Graebner *et al.*, Phys. Rev. B **34**, 5696 (1986).

[21] J. C. Lasjaunias and R. Maynard, J. Non-Cryst. Solids **6**, 101 (1971).

[22] M. A. Ramos *et al.*, in *Proceedings of the Second International Workshop on Non-Crystalline Solids,* edited by J. Colmenero and A. Alegria (World Scientific, Singapore, 1990), p. 515.

[23] G. K. White *et al.*, Phys. Rev. B **29**, 4778 (1984).

[24] H. v. Löhneysen *et al.*, Z. Phys. B **60**, 323 (1985).

[25] A. J. Dianoux, Philos. Mag. B **59**, 17 (1989).

[26] A. Hannon *et al.*, in *Proceedings of the VIIth International Conference of the Physics of Non-Crystalline Solids,* edited by L. D. Pye *et al.* (Taylor and Francis, London, 1992), p. 67.

[27] V. N. Novikov, Pis'ma Zh. Eksp. Teor. Fiz. **51**, 65 (1990) [JETP Lett. **51**, 77 (1990)].

[28] M. Montagna *et al.*, Phys. Rev. Lett. **65**, 1136 (1990).

[29] E. Stoll *et al.*, Phys. Rev. Lett. **68**, 2472 (1992).