Medium-Range Order in Glasses: Comparison of Raman and Diffraction Measurements

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The correlation lengths of vitreous structures estimated from the low-frequency (boson) peak in Raman spectra and from the width of the first sharp diffraction peak are compared. This first comparison shows that the two estimates, which are based on dynamic and static properties, respectively, are in good quantitative agreement. The present result supports the concepts that (a) a decisive scale for structural order in glasses is ~10 Å, and (b) the low-frequency excitations are defined by the characteristic length in vitreous structures.

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Peculiarities of vitreous structures on a medium-range scale have been studied for more than fifty years. The main question is whether a regularity of the structural order exists beyond second nearest neighbors. It is supposed that the arrangement of structural units (for example, SiO_4 tetrahedra in SiO_2) is not completely random but has some correlations on a scale of ~10-15 Å. This is in contradiction with the ideal continuous-random-network (CRN) model. Experimentally there are several arguments in favor of the existence of these structural correlations: pronounced peaks in the radial distribution function (out to ~8 Å in SiO_2 [1]), and the presence of rings of atoms with concentration much higher than expected for an ideal CRN [2]. Also, the first sharp diffraction peak (FSDP) of the x-ray or neutron structure factor $S(Q)$ and the low-frequency peak of the Raman spectrum, the so-called boson peak, are frequently ascribed to structural correlations over an intermediate-range scale.

From the dynamical point of view the boson peak as well as other low-frequency (~10-100 cm^{-1} or 1-10 meV) anomalies of vibrational properties of glasses appear as a result of quasilocal excitations. The nature of these quasilocal vibrations is still under discussion [3-5], but most authors suppose that they are connected with some correlation radius of the vitreous structure, $R_c \approx 10$ Å [5-8]. It was shown in Ref. [6], starting from plane acoustic waves, that fluctuations of elastic and/or elasto-optical constants over some range R_c will produce a peak in the Raman spectrum at a frequency

$$\omega_{\max} \approx V_t/2\pi c R_c \approx 0.32 V_t/c2R_c\,. \qquad (1)$$

Here V_t is the velocity of transverse sound waves and c is the velocity of light. However, it was later shown that some of the predictions or assumptions about this model are wrong: The density of vibrational states has no Debye behavior and the spectral dependence of the light-to-vibration coupling constant has no maximum in the frequency range of the boson peak [5,9]; the value and spectral dependence of the depolarization ratio estimated in the frame of the model significantly differ from the experimental results [7,10]. On the other hand, results of recent model calculations [11] and computer simulations [12] support the basic idea of the model: The number of atoms involved in low-frequency quasilocal vibrations is not small and may be approximately equal to 30-100. Strong arguments in favor of the size character of the boson peak have been obtained from Raman spectra of nanocrystals of size $D \approx 50$-200 Å embedded in glassy matrices [13,14]. It was shown in Refs. [13,14] that the frequency of the Raman peak is inversely proportional to the nanocrystal size and coincides well with the estimates of the lowest frequencies of surface vibrational modes of spherical particles:

$$\omega_{\max} \approx 0.85 V_t/cD \qquad (2)$$

for torsional modes and

$$\omega_{\max} \approx 0.7 V_l/cD \qquad (3)$$

for spherical modes (V_l is the longitudinal sound velocity). It was also shown that the appearance of a torsional or spherical mode is determined by conditions on the boundary between the nanocrystal and the surrounding matrix [14].

Another characteristic feature of glasses is the FSDP in $S(Q)$, but its origin also is not as yet clearly understood. Various models have been suggested for a description of the FSDP [15-18]. All of them ascribe it to some manifestation of medium-range order in the vitreous structure. An estimation of correlation lengths obtained by fitting the structure factor $S(Q)$ gave a value of $R_c \approx 10$ Å for As_2Se_3 [15] and $R_c \approx 11$ Å for Se [16]. The analysis of partial contributions of Ge-Ge, Ge-Se, and Se-Se correlations in $S(Q)$ for $GeSe_2$ has shown [17] that in this glass the FSDP arises from correlations between the positions of Ge atoms with a characteristic correlation length ~4-8 Å. So, it is obvious that the FSDP in glasses is connected with peculiarities of their structure on an intermediate-range scale, and a correlation with the boson peak is to be expected.

An analysis of the data on various glasses has been made in Ref. [19], and it was found that indeed strong correlations exist between the properties of both the boson peak and the FSDP. These are correlations between changes of their intensities, and also correlations between the position of the FSDP, Q_1, and the value of $\omega_{\max}$ nor-

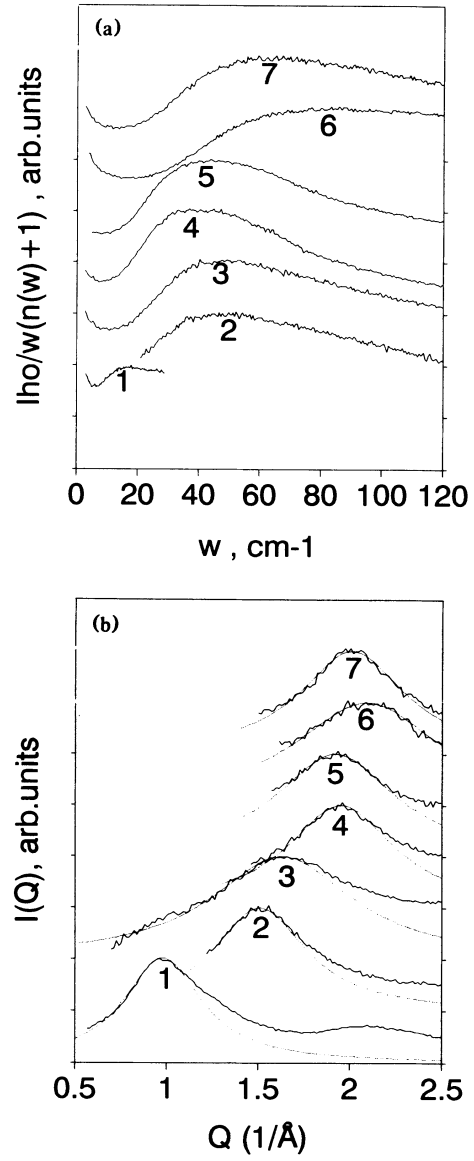

FIG. 1. (a) Low-frequency normalized Raman spectra and (b) x-ray diffraction pattern in the glasses (the numbers correspond to the numbers in Table I) and approximations of FSDP by Lorentzian curves. Each curve has been shifted upwards by one scale unit with respect to the preceding one.

malized to the sound velocity, $\Omega=\omega_{\max}c/V$ [19]. The meaning of these correlations is not yet clear. In particular, the length scale defined by Q_1, $R\approx 2\pi/Q_1$, is approximately 4-6 times smaller than the value of $1/\Omega$ and so it corresponds to a much smaller size of the structural units.

The true issue, however, is that the position of a peak in the diffraction pattern reflects some repetitive characteristic distance between structural units, whereas a correlation length produces a broadening of the peak. There is the well-known Scherrer equation for microcrystalline samples, which connects the width of Bragg peaks in diffraction patterns with the average size of microcrystals. For estimations of the correlation length of disordered structures, D, a simple expression $D\approx 2\pi/\Delta Q$ (ΔQ is the half-width of the FSDP) is often used [20,21].

So, for an analysis of the correlation length one must compare the position of the boson peak in a Raman spectrum with the width of the FSDP, ΔQ. For this purpose x-ray diffraction, Raman, and Brillouin spectra of different oxide glasses [F1, SF1, BaSF64, and LaSF9 (all from Schott), SiO_2, GeO_2-5.4%Na_2O] and the polymer glass PMMA-XT have been investigated. All measurements have been performed at room temperature. Right-angle depolarized Raman spectra have been measured using a U-1000 double monochromator at $\lambda=514.5$ nm [22]. The spectral slit width was 1 cm^{-1}. The frequency of the boson peak has been determined as the maximum of the normalized Raman spectra $I_n=I/\omega[n(\omega)+1]$ [see Fig. 1(a)], where $n(\omega)+1$ is the boson factor for the Stokes component. Sound velocities have been derived from Brillouin scattering spectra which were obtained using the setup described in [23]. X-ray diffraction has been measured on flat samples in a focusing reflection geometry using Cu $K\alpha$ radiation and a slit width corresponding to $\Delta\Theta\approx 0.1°$. The geometrical correction for the sample size was taken into account and the small-angle background was subtracted; see Fig. 1(b). Careful measurements of the FSDP in SiO_2 have shown [1] that it can be approximated well by a Lorentzian curve. To evaluate the width ΔQ of the FSDP we also used a Lorentzian approximation $I(Q)\sim\Delta Q/[(Q-Q_1)^2+\Delta Q^2]$ fitted to the small-Q side of the peak [Fig. 1(b)]. The results obtained are presented in Table I. The values

TABLE I. Frequencies of the boson peak maximum, sound velocities, and parameters of FSDP in oxide glasses.

Samples	$\omega_{\max}$ (cm^{-1})	V_t (km/s)	V_l (km/s)	Q_1 ($Å^{-1}$)	ΔQ ($Å^{-1}$)
(1) PMMA	16.5(5)	1.42	2.78	0.98	0.26(3)
(2) SiO_2	51.5(10)	3.79	5.92	1.51	0.31(2)
(3) GeO_2-5.4% Na_2O	48.5(10)	2.46	4.1	1.63	0.47(4)
(4) SF1	38.5(10)	2.22	3.77	1.95	0.36(5)
(5) F1	43.5(10)	2.47	4.15	1.92	0.40(4)
(6) BaSF64	83.5(15)	3.51	6.23	2.09	0.49(3)
(7) LaSF9	64.0(10)	2.98	5.43	2.01	0.35(5)

of $\omega_{\max}$, V, Q_1, and ΔQ for SiO_2 coincide well with the literature data.

In Fig. 2 we plot the correlation length estimated from ΔQ against that from the boson peak, $V_t/c\omega_{\max}$. Analysis of the present results shows that indeed a good correlation is observed. A linear approximation of this correlation gives the ratio

$$D = 2\pi/\Delta Q \approx (0.90 \pm 0.11) V_t/c\omega_{\max} . \tag{4}$$

This ratio is very close to the ratio of Eq. (2) obtained for the torsional mode of nanocrystal vibrations and significantly larger than the prediction given by Eq. (1). The estimates of R_c which have been obtained earlier for many glasses using Eq. (1) gave much smaller values than those obtained from x-ray data, as was mentioned previously in [7]. The present result seems to favor a mechanism for the strong localization of low-frequency vibrational excitations in glasses that follows more the picture of eigenstates of nanocrystalline subunits [8,13] than that of damped plane waves [6].

From Fig. 2 one can see that the point for LaSF9 deviates significantly from the general dependence. The reason for this deviation is not clear, but if Eq. (3) is used for the estimation of R_c from the Raman data, the ratio between $2\pi/\Delta Q$ and R_c will be the same as that for the other glasses. It may be significant that among oxide glasses LaSF9 has a smaller value of V_t/V_l (Table I) and, possibly, this leads to the appearance of another type of localized vibration in its structure.

The observed correlation suggests that in vitreous materials structural order on a scale of ~10–20 Å exists. These structural correlations determine the width of FSDP in $S(Q)$ and strongly influence other properties of glasses. In particular, they lead to the appearance of quasilocal vibrational excitations, which contribute substantially to specific-heat and Raman spectra, determine the thermal conductivity, and so on. The estimation of the correlation length obtained from analysis of thermal conductivity [24] gives 33 Å for SiO_2 and 42 Å for PMMA. While these values are higher than ours, their ratio is close to that of our data.

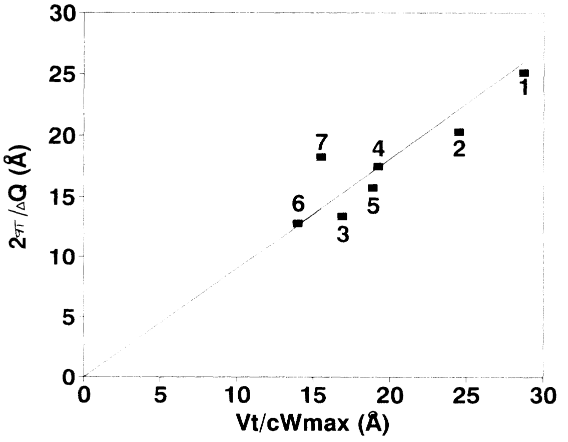

FIG. 2. Correlation length as obtained from the width of the FSDP vs that from the frequency of the boson peak maximum; the numbers correspond to Table I.

An analysis of the results (Table I) shows that in most glasses the width of the FSDP correlates with its position $\Delta Q \approx (0.3\text{–}0.2) Q_1$. This means that the correlation length $2R_c$ of vitreous structures, i.e., the scale of intermediate-range order, is closely related to some characteristic distance L between the underlying structural units which produce the FSDP in the diffraction pattern. Apparently, $2R_c$ amounts to $(3\text{–}5)L$. This explains the above-mentioned correlation of Q_1 and $\Omega \sim 1/R_c$, which had been observed earlier for a wide variety of glasses [19]. Recently an attempt has been made [18] to explain this correlation with a model which ascribes the appearance of FSDP to an interstitial volume in the vitreous structure. The author shows that if one free parameter of this model (the coefficient between the nearest-neighbor atom-void distance and the correlation length of density fluctuations) is equal to ~3–4, then we will have quantitative agreement between Q_1 and Ω. Now, our results strongly suggest that we have a correlation between ΔQ and Ω and this quantity, 3–5, is simply the ratio of $Q_1/\Delta Q$, which, in principle, may then be seen as the ratio between the correlation length and the atom-void distance.

We turn finally to a comparison of various glasses. From an analysis of our results as well as literature data we can conclude tentatively that R_c is larger in simple glasses (like SiO_2), while the addition of other chemical elements leads to a decrease of R_c (like in F1 or in GeO_2-Na_2O glass). This decrease happens in many cases without significant variation of the structural units, and thus of Q_1, but rather only with a loss of correlation in their arrangement, i.e., a decrease of the correlation length. Probably the introduction of additional chemical elements destroys the SiO_2 or GeO_2 network, and gives an additional chemical disorder. But there exist some exceptions, when chemical additives lead to an increase of R_c, for example, AgI in Ag_2O-B_2O_3 glass [20,25] and Cs_2O in B_2O_3 glass [26]. In the AgI case it may be explained by the appearance of structural units with large size (this glass has an anomalously small value of $Q_1 \approx 0.8$ Å^{-1} [20]).

Analysis of the low-frequency Raman spectra of glass-forming liquids and of rapidly quenched glasses shows [22,27,28] that the correlation radius of the vitreous structure is formed in the supercooled melt and does not depend on the cooling rate. Thus the correlation length is essentially a thermodynamic equilibrium property, which is, however, strongly dependent on the chemical composition of the glasses.

In summary, we have for the first time demonstrated a close correlation between the width of the first sharp diffraction peak from x-ray scattering and the low-frequency (boson) peak in Raman scattering. Both are considered typical signs of intermediate-range order in glasses, and correlation lengths derived from them agree well. This agreement depends, however, on the use of the nanocrystalline interpretation of the boson peak. In view of the general interest in intermediate-range structure of disordered systems, it appears urgent to remove ambiguities which still exist in the procedures by which parameters of intermediate-range order may be derived from different experiments.

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