Is There a Correlation between the First Sharp Diffraction Peak and the Low Frequency Vibrational Behavior of Glasses?

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Neutron diffraction and light scattering studies have been performed on a network glass subject to structural modifications. Large changes of the first sharp diffraction peak (FSDP) and the low frequency dynamics (the boson peak) are demonstrated by gradually changing the intermediate range structural ordering, the short range order being preserved. A recently suggested "universal" correlation for glasses between the positions of the FSDP and the boson peak is shown to fail; in fact opposite trends are observed.

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It is well known that amorphous solids exhibit universal characteristics in their low frequency vibrational behavior not found in their crystalline counterparts [1]. The anomalous low frequency behavior of glasses is observed in low frequency Raman [2–4], infrared absorption [5], and inelastic neutron scattering [6,7] spectra. It is also demonstrated in an excess specific heat of glasses in the temperature range 5–30 K [8] as compared to the Debye behavior of crystals, and in the anomalous thermal conductivity plateau of glasses [9]. The origin of these low frequency vibrations, though presently much debated [10–14], is still not known. However, it is apparent that they play a key role for the properties of glasses and, from their universality, seem to be the result of the disorder as such.

In Raman spectra of glasses the anomalous low frequency behavior is demonstrated by a broad peak, the boson peak, in the frequency range 10–100 cm^{-1} [2–4]. The low frequency spectrum of glasses is commonly ascribed to disorder induced scattering from acoustic modes and related to the density of vibrational states $g(\omega)$, through $I(\omega)=c(\omega)g(\omega)[n(\omega)+1]/\omega$ where $c(\omega)$ is the light-vibration coupling constant and $n(\omega)+1$ represents the Bose-Einstein thermal factor. The origin of the boson peak has been much debated and recently shown to be due to a maximum in $g(\omega)$ rather than in $c(\omega)$ [7]. It is suggested to reflect a crossover from long wavelength vibrations propagating in a continuous medium to localized vibrations on length scales where the molecular structure of the glass becomes important [2]. A characteristic length can be attributed to the crossover using the boson-peak frequency ν_m and the sound velocity v according to $2R_c \sim v/\nu_m$ [2–4,11–14]. The characteristic lengths ($\sim$5–50 Å) have been ascribed to various specific structural arrangements such as chemical ordering [11], microcrystalline regions [14], layered structures [4], etc. The universality of the phenomenon, however, suggests that it originates from some general feature of the disordered solids rather than due to specific molecular structures.

Another characteristic of amorphous solids, likewise related to the intermediate range structure, is the "first sharp diffraction peak" (FSDP) of the static structure factor $S(Q)$ [15]. X-ray and neutron diffraction studies of oxide and chalcogenide glasses show a distinct peak at a momentum transfer, Q, of about 1.5 $\mathrm{Å}^{-1}$ which reflects molecular correlations beyond the nearest-neighbor distances (see Refs. [15–17] and references therein). Several attempts have been made to explain the FSDP in terms of different characteristic structural units as in the case of the boson peak. However, again the universality of the phenomenon seems to require a more general explanation. It has for example been proposed that the FSDP is the result of a random packing of structural units [15], later further developed into a conditional packing of units taking into account charge neutrality and excluded volume effects [18].

Recently, it has been suggested that the FSDP and the anomalous low energy vibrational spectrum of glasses are related [11]. The boson-peak frequency ν_m was then used to define a wave vector $\Omega=2\pi\nu_m/v$ that represents the inverse of some "dynamic characteristic length." Similarly the momentum transfer Q_1 of the FSDP was taken to represent the inverse length scale of structural correlations. The results from a wide variety of glasses indicated a linear relation between Q_1 and ν_m/v, shown as a dashed line in Fig. 1 [11]. An explanation has recently been offered in terms of density-fluctuation domains giving rise to phonon localization in the structure [12]. In the model the domains represent the chemical ordering of interstitial voids around cation centered structural units (e.g., $\mathrm{SiO_4}$ tetrahedra). The domain size $2R$ is defined by the distance R at which features of the atom-void density function $\rho_{\mathrm{av}}(r)$ are no longer discernible. Thus, for distances larger than R from an arbitrary atom the material appears homogeneous and isotropic. The domain size can be related to the nearest-neighbor cation-cation distance d by $R \approx kd$ where k is found to be a constant with a value of 3–4. The FSDP position is in the model given approximately by $Q_1 \approx 3\pi/2d$ [12,16]. At small wave-

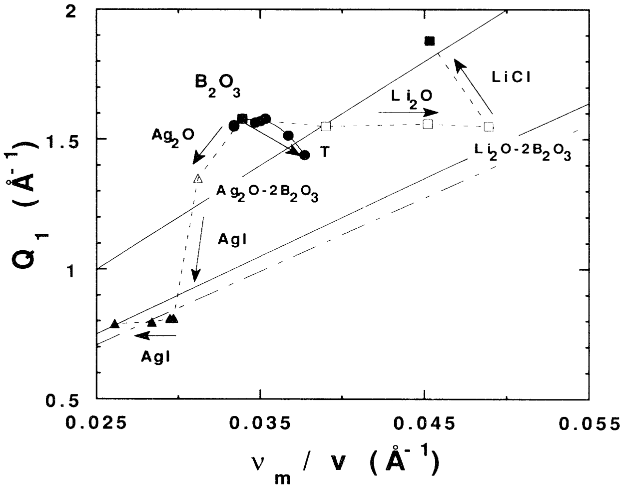

FIG. 1. Data for ν_m/v and Q_1 in borate glasses; (●) B_2O_3 at temperatures $293 < T < 1273$ K (Q_1 from Ref. [27]); (□) $Li_2O + nB_2O_3$ for $n = 2,4,8$; (■) $(LiCl)_x$-$(Li_2O + 2B_2O_3)_{1-x}$ for $x = 0.6$; (△) $Ag_2O + 2B_2O_3$; (▲) $(AgI)_x$-$(Ag_2O + 2B_2O_3)_{1-x}$ for $x = 0.2$, 0.3, 0.4, 0.5, 0.6. Dashed line represents the linear relation suggested in Ref. [11] and solid lines depict the correlation range of Eq. (1) [12].

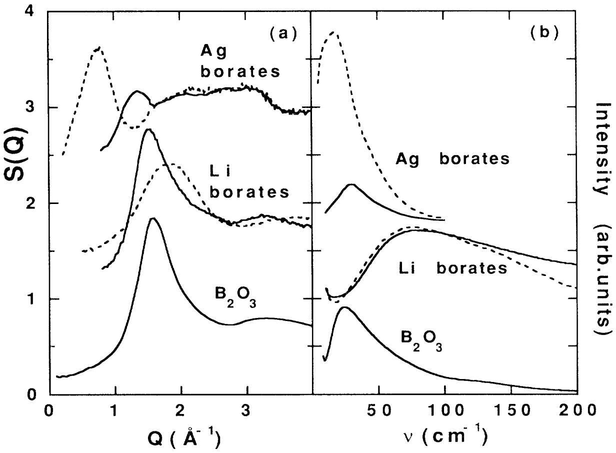

FIG. 2. (a) Structure factors in the low-Q range 0–3 $Å^{-1}$ and (b) low-frequency Raman spectra for B_2O_3 [24], $(LiCl)_x$-$(Li_2O + nB_2O_3)_{1-x}$, and $(AgI)_x$-$(Ag_2O + nB_2O_3)_{1-x}$. For the Ag and Li containing glasses solid lines represent the modified glasses ($n = 2$; $x = 0$) and dashed lines represent the salt doped glasses ($n = 2$; $x = 0.6$). The curves have been shifted vertically for clarity.

lengths these domains will act as scattering centers of elastic phonon scattering which, if sufficiently strong, can lead to phonon localization. From the Ioffe-Regel condition for phonon localization the frequency ν_m at which localization occurs is given by $\nu_m \approx v/2R$, assuming a linear dispersion relation for propagating phonons. The correlation between ν_m and Q_1 is then obtained from this relation and the above expressions for Q_1 and R as

$$Q_1 \approx 3\pi k \nu_m/v . \qquad (1)$$

Experimental data represented in a Q_1 vs (ν_m/v) plot are reported to fall between the straight lines of slopes 9π, 12π, respectively (see solid lines in Fig. 1). v is here taken as the average sound velocity.

The present study is devoted to an investigation of the validity of a linear relation between Q_1 and (ν_m/v). The relations in Fig. 1 [11,12] are based on literature data taken from disparate results of a wide variety of glasses. We have investigated a specific system, B_2O_3, as it has been subject to systematic structural changes induced by temperature, network modifier M_2O, and by a dopant salt MX ($M \approx$ Li,Ag and X=Cl,I). In most cases we have obtained the data for Q_1, ν_m, and v needed to test Eq. (1) by using neutron diffraction, Raman, and Brillouin scattering on the same samples. We believe that by systematically changing a specific system and investigating it by all the necessary experimental tools we remove uncertainties related to previous data. Neutron diffraction experiments were performed at the liquid-amorphous diffractometer at ISIS, Rutherford-Appleton Laboratory, U.K. [19]. Sound velocity data were obtained by Brillouin scattering [20,21]. Low frequency Raman scattering data were collected using standard double-grating spectrometers [22]. The samples, B_2O_3, M_2O-nB_2O_3, and $(MX)_x$-$(M_2O$-$nB_2O_3)_x$, were prepared with conventional melt-quenching methods [19,20].

Starting with B_2O_3 we show in Fig. 2 the low frequency Raman spectrum, and in Fig. 3 the peak positions of the reduced spectra $\{I(\omega)\omega/[n(\omega)+1]\}$ versus temperature. The peak frequency is almost constant below T_g, thereafter it drops rapidly and at ~850 K crosses over to another constant region. A similar behavior is demonstrated by the transverse v_T and longitudinal v_L sound velocities obtained from Brillouin spectra, also plotted in Fig. 3. The close correspondence implies that the characteristic

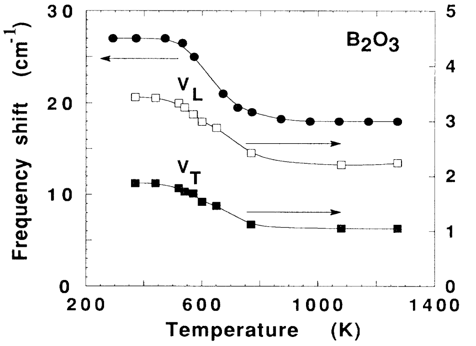

FIG. 3. Frequency shifts vs temperature of the reduced $\{I_T(\omega) = I(\omega)\omega/[n(\omega)+1]\}$ low frequency Raman band of B_2O_3 (left), and (right) longitudinal (v_L) and transverse (v_T) sound velocity data vs temperature for B_2O_3 [21].

length changes very little; R decreases less than 6% over the studied 800 K temperature range. The observation may be explained by the fact that B_2O_3 is a "strong" glass former [23]; it is formed by randomly connecting BO_3 units into a continuous irregular network which contains a large amount ($\sim 60\%$) of six-membered B_3O_6 boroxol rings [22,24]. Although the ring structure gradually breaks up above T_g [22] the covalent-bonded network is to a large extent preserved even at temperatures well above the melting temperature [21,22]. In contrast to the dynamic results neutron data for the FSDP in B_2O_3 [25] indicate an expanding correlation length (Q_1 decreases) as temperature is raised. Within the chemical ordering model [16] Q_1 is expected to decrease as the density decreases, as has also been found in experiments [17,26] and simulations [18] of other glasses. The downshift of the position of the FSDP for B_2O_3 is therefore likely due to the decreased density [27] as the rings break up. Thus, we conclude that while the behavior of the FSDP can be explained by density effects this is not the case for the low frequency dynamics. Results for Q_1 and v_m/v are shown in Fig. 1 and they clearly violate the correlation suggested in Eq. (1).

Next we examine the effects of adding network modifiers M_2O to B_2O_3 (M =Ag,Li). With increasing M_2O content an increasing amount of borons change their coordination number from three to four. Various complicated structural units containing BO_3 and BO_4 groups are then formed, such as di-, tri-, and tetraborates [28], without changing the short range order (B-O distance is kept). In Fig. 2(a) we show $S(Q)$ for the compositions of the largest Ag_2O and Li_2O concentrations investigated ($n=2$). Comparing the Li_2O modified glass with B_2O_3 [24], also shown in Fig. 2(a), it can be seen that the position and also the shape of the FSDP are preserved. In contrast, modification by Ag_2O causes large changes in the low-Q range; the FSDP splits and the sharpest component appears at a considerably lower value (1.32 $Å^{-1}$) than in B_2O_3 (1.58 $Å^{-1}$). The different low-Q behavior for Ag_2O and Li_2O modification indicates different arrangements of their molecular building blocks, although NMR and ir experiments show a similar number of the basic molecular groups [28,29]. Density data also suggest considerable structural differences caused by Ag_2O and Li_2O modifiers. The initial B_2O_3 network expands by about 20% for a modification by $n=2$ Ag_2O [28], whereas there is hardly any volume change of the B-O network for Li_2O modification (0.7% densification for $n=2$) [29] from the chemical ordering model [16]; this implies that Q_1 for the Ag_2O glasses should decrease whereas it should be constant for the Li_2O glasses, i.e., in agreement with our observations. We want to point out that despite the large differences in the intermediate range order between the Ag_2O and Li_2O modified glasses, the short range order of both glasses is almost identical to that of B_2O_3, as evident from the radial distribution functions [30]. A completely different scenario is revealed by the low frequency Raman spectra shown in Fig. 2(b); Li_2O introduces large changes while Ag_2O hardly affects the low frequency vibrational behavior at all, i.e., the opposite to the neutron diffraction observations. Combining the neutron diffraction and Raman data with sound velocity results [20,22] it is evident that the proposed relations [11,12] between Q_1 and v_m/v are violated, see Fig. 1. Thus, while the density well explains the behavior of the "structural" characteristic lengths for increasing Ag_2O or Li_2O modifier content, this is not the case for the "vibrational" correlation lengths.

Finally, we consider the salt doped systems, $(MX)_x + (M_2O+nB_2O_3)_{1-x}$, starting with the glasses containing the largest concentration ($x=0.6$) of AgI and LiCl. The two glasses show opposite shifts in the position Q_1 of the FSDP, see dashed curves in Fig. 2(a). In the case of the AgI doped glass it is related to a new feature observed at an extremely low Q_1 value of about 0.8 $Å^{-1}$ which is not present either in $Ag_2O+2B_2O_3$ or in B_2O_3 [Fig. 2(a)]. The component is observed at about the same position for AgI concentrations in the range $0.2 < x < 0.6$ and with an intensity which increases with the amount of AgI. Reverse Monte Carlo simulations combined with neutron and x-ray diffraction results show that the low-Q peak is due to density fluctuations of the host glass network induced by the introduction of AgI [30]. Interconnected units of AgI expand voids of the network, while the B-O short range order is preserved [19,31]. At the other extreme, the $S(Q)$ of the $(LiCl)_{0.6}$-$(Li_2O+2B_2O_3)_{0.4}$ is only slightly modified from that of Li_2O-$2B_2O_3$; the FSDP simply broadens and shifts to a higher value ≈ 1.9 $Å^{-1}$, see Fig. 2(a), and there is no sign of any new feature or change of the short range order of the B-O network. The observations imply a random introduction of Li^+ and Cl^- into interstices of the borate network; the random arrangement of BO_3 and $BO_4{}^-$ groups of the binary glass is more or less preserved, however, slightly more disordered. Thus, overall disordering in the LiCl doped glass in contrast to the expansion of the BO network in the AgI doped glass can explain their opposite Q_1 behavior. Next we turn to the low frequency Raman behavior of the two glasses with the highest concentrations of LiCl and AgI, see dashed curves in Fig. 2(b). It can be seen that their boson peaks are only slightly shifted from the undoped glasses (solid curves) in contrast to the positions of the FSDP in Fig. 2(a). Using the data for v_m and Q_1 together with values for the sound velocity [20] we present the results in Fig. 1, where we also include data for the samples of lower AgI concentrations. Clearly, the results cannot be represented by the suggested linear relations [11,12].

The present study covers a wide window in the Q_1 vs v_m/v plot (see Fig. 1). This is the range discussed in Refs. [11,12] and we find that the complete data set indeed clusters around the suggested correlations. More important, however, is to note that the routes followed for the specific and systematic modifications of the glass system do not agree with the proposed linear relations [11,12]. In fact, even opposite behavior is revealed as demonstrated by temperature and LiCl induced changes. This indicates that the model of Ref. [12] is oversimplified. In the model only two length scales are introduced and they are coupled; the distance d between characteristic structural units of the material and the distance R at which density fluctuations are smeared out. The shape of these structural units is not discussed but was shown in other models to be significant both for the FSDP [15] and the low frequency dynamics [14]. It is also reasonable that one should consider the coupling of the structural units, both in terms of geometrical connectivity and types and strengths of the bonding forces. Furthermore, it is not clear whether the boson peak is governed by transverse or longitudinal, or even torsional modes. This may be different in different types of glasses as is also the case for the form factors and the coupling of structural units.

In summary, for a borate glass system in which the short range order is kept intact while we introduce large changes on the intermediate range scale, we observe dramatic changes of both the low frequency dynamics (boson peak) and the low-Q range of the static-structure factor (FSDP). Thus, the boson peak and the FSDP, both features typical of glasses, are indeed related to properties of the intermediate range scale as has been discussed. The changes observed for the FSDP as the glass is systematically modified can qualitatively be understood in terms of density changes while we find that this is not the case for the boson peak. Attempts to correlate a structural length scale related to the position of the FSDP to a dynamic length scale related to the position of the boson peak are shown to fail. This is contradictory to recent suggestions of a linear relation [11,12]. We propose that the suggested relation is too simple and that also the dynamical/geometrical coupling between structural units, their form factors, and the type of vibrational modes that dominate the low frequency dynamics should be considered.

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