PHYSICAL REVIEW B VOLUME 51, NUMBER 17 1 MAY 1995-I

Nature of the first diffraction peak in glassy selenium

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(Received 29 August 1994; revised manuscript received 19 December 1994)

The physical significance of the first diffraction peak in glassy Se is discussed in the light of recent experimental results regarding the temperature dependence of the parameters characterizing the first peaks in the elastic $S(Q,\omega = 0)$ and static $S(Q)$ structure factors. The rather different behavior with temperature of both peaks as well as a comparison with the behavior observed for a polycrystalline (trigonal) sample serves to clarify their relationships with physical magnitudes such as thermal-expansion coefficients and temperature-dependent correlation lengths.

The existence of medium-range-order (MRO) scales in glasses (i.e., structural or dynamic regularities involving distances beyond those corresponding to second nearest neighbors, that is, $\geq$ 5–10 Å) has been discussed for several decades without reaching any generally accepted conclusion. The topic has received a renewed attention in more recent times,[1–3] sometimes in connection with the apparently anomalous dependence with temperature of the first peak in $S(Q)$,[1] usually referred to as the first sharp diffraction peak (FSDP), or its possible relationship with finite-frequency features in the spectra of inelastically scattered radiation,[2] or with the existence of chemical medium-range order (i.e., the nonrandom disposition of atoms and voids over such a length scale).[4]

In most cases, the presence of MRO has been inferred from the appearance of peaks in the $S(Q)$ static structure factors of chalcogenide and some other covalent glasses (SiO_2, $GeSe_2$, As_2S_3, P) at momentum transfers $Q \approx$ 1–1.5 Å^{-1}, although some other widely studied glasses such as g-Se and g-Ge seem to be devoid of it. Such an interpretation seems difficult to reconcile with the fact that most of such FSDP's survive well into the normal liquid phase, where the existence of MRO is difficult to visualize, and also it is by no means clear why glasses of not too different "fragilities" such as As_2S_3 and g-Se (Ref. 5) exhibit such disparate ordering properties.

The physical interpretation of the origin of such a peak (and therefore the basis for discussing the existence of MRO) becomes strongly dependent upon the approach followed to analyze the data. For glasses formed by "molecular" entities[6] (i.e., SiO_2 is supposed to consist of $Si(O_4)_{1/2}$ units) a form factor for those can be subtracted from the measured $S(Q)$, thus separating short-range correlations from those involving larger distances[7] which are then lumped together within a structure factor reflecting the strong orientational correlations between such "molecules." Alternatively, the structure factors from different temperatures can be subtracted, thus removing the Fourier components arising from short-range correlations which tend to show a mild dependence with temperature. None of these two approaches can be sensibly applied to other glasses such as Se, S, some forms of amorphous (red) phosphorus, or mixed chacogenates, where such "molecular" entities cannot be found, and therefore the discussions regarding these materials cannot go beyond the phenomenological characterization of such peaks, which is often carried in broad terms.

A point which has mostly been overlooked in the current discussions on this topic regards the relationships between the location in Q of the FSDP and the characteristic lowest reflections of some crystalline polymorphs of the same materials. As a matter of fact and taking as case examples those of vitreous silica[8] and red phosphorus[9] one can see that the FSDP in amorphous samples of both materials basically appears at momentum transfers close to those characteristic of the lowest-angle reflections of a good number of their crystalline modifications. Such a close relationship between the characteristic location of the first diffraction peak in disordered and crystalline forms goes well beyond the amorphous-crystalline case since the same coincidence has been repeatedly reported regarding some molecular liquids and their plastic (rotator) crystalline phases.

In consequence, the structural relevance of the first peak in $S(Q)$ seems difficult to assess unless some additional data are brought forward. Our purpose here is to illustrate a procedure devoted to inquire into the physical meaning of the first diffraction peak in glassy Se (g-Se) by means of a comparison of temperature-dependent properties such as the $\alpha(T)$ thermal-expansion coefficients as calculated from the characteristic Q values corresponding to the location of the diffraction peaks $[Q_p(T)]$ with the same quantities measured by macroscopic means. In analogy with the case of red P,[9] where the existence

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of MRO has been inferred from diffraction data alone, the Q_p of g-Se comes close to those of the lowest-angle reflections of polycrystalline (trigonal) Se. A comparison between the crystal $\alpha(T)$ derived from diffraction and macroscopic measurements and that for the glass is therefore carried in parallel in order to explore whether $R = 2\pi/Q_p$ can rightly be interpreted in terms of a characteristic length scale.

On the other hand and as shown in our recent work,[10] the shape of the elastic $S(Q,\omega = 0)$ and static $S(Q)$ structure factors of g-Se become remarkably different as the temperature is raised, which leads to significantly different values for Q_p and the peak widths Δ_Q, especially at relatively high temperatures where the inelastic contribution to $S(Q)$, $I_{\rm inel}(Q) = S(Q) - S(Q,\omega = 0)$, becomes important. This makes crucial the separation of the elastic $S(Q,\omega = 0)$ response, especially if the temperature dependence of Q_p is discussed in terms of a length scale R and also if some correlation length $R_c = 2\pi/\Delta_Q$ is to be found from the peak widths.

Some measurements additional to those reported in our previous paper[10] have been carried out using the same experimental setup which provided a resolution in energy transfers of 0.05 THz [full width at half maximum (FWHM)] and a resolution in momentum transfers of ≈ 0.04 Å^{-1}. In particular, both $S(Q,\omega = 0)$ and $S(Q)$ were measured for a sample of trigonal (polycrystalline) Se, covering a range of temperatures 15 K $\leq T \leq$ 300 K and momentum transfers up to $Q = 2.7$ Å^{-1}. The region of the crystal structure factors accessible to our measurement comprises the [100] and [101] reflections which, in terms of d spacings are linked to the a and c unit-cell dimensions through $d_{hkl} = [4(h^2 + k^2 + kh)/(3a^2) + l^2/c^2]^{-1/2}$, thus enabling a direct measurement of the crystal expansion. As shown in Fig. 1(a), both crystal structure factors consist of two sharp lines which can be modeled in terms of Lorentzians (convoluted with the Gaussian resolution function) plus a constant background. Figure 1(b) displays the temperature dependence of the a lattice constant as derived from the lower-Q reflection as well as an estimate of the temperature dependence of the α thermal-expansion coefficient, which is compared with macroscopic high-purity single-crystal data taken from Ref. 12. Both $S(Q)$ and $S(Q,\omega = 0)$ lead to basically the same result and the differences between the present estimates for $\alpha(T)$ and the macroscopic ones can be accounted for in terms of sample composition (i.e., high-purity Se shows enhanced values for most of the elastic constants due to piezoelectric effects and $\alpha \propto 1/\chi$, where χ stands for the linear compressibility), as well as to the polycrystalline nature of our sample. On the other hand, the structure factors for the glass have been analyzed in terms of a single Gaussian fitted to the measured intensities, which gave a reliable account of the experimental measurements down to $Q \approx 1$ Å^{-1}, from where the presence of a small hump at $Q \approx 0.7$–0.8 Å^{-1}, the meaning of which has already been discussed,[13] deviates from such simple behavior [see Fig. 1(a)]. The crucial point thus regards how the peak maxima, widths, and intensities of the glass structure factors behave with temperature. In particular, the temperature dependence of quantities derived from Q_p regarding $S(Q)$ or $S(Q,\omega = 0)$ may unravel some thermal expansion effects, thus lending support to the interpretation of R as a physical length scale. Also, if R_c as derived from the widths of the peaks was to be interpreted as a correlation length, it can be expected that, due to thermal disorder, such a quantity decreases with increasing temperature. Finally, the amplitudes of $S(Q,\omega = 0)$ and $S(Q)$ are expected to follow markedly dissimilar behaviors with temperature as discussed in our previous paper.[10] The temperature dependences of R, R_c, and the peak amplitudes as derived from the parameters fitted to both structure factors are shown in Fig. 2. First and foremost, the most remarkable result regards the disparate behavior followed by the R's as calculated from the static or elastic structure factors which show basically no (within statistical errors) thermal-expansion effects in the quantity derived from $S(Q)$, whereas relatively large increases in R are seen for that regarding $S(Q,\omega = 0)$. As done with the polycrystal, the best way to assess such a result consists in the comparison of the

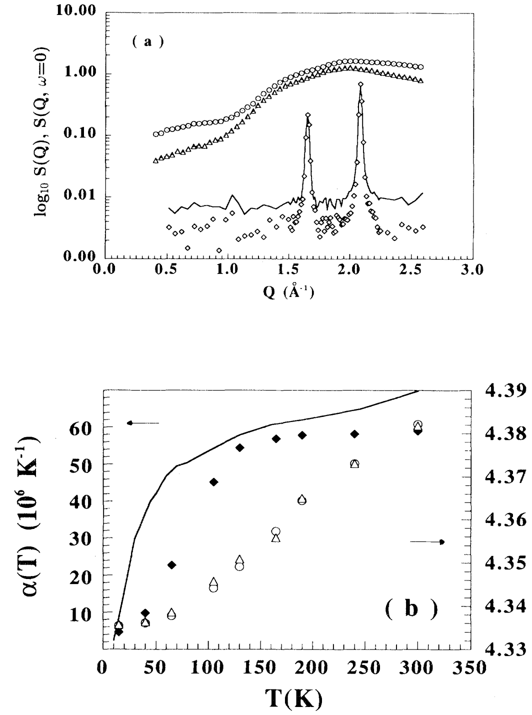

FIG. 1. (a) Static, $S(Q)$ (circles) and elastic (triangles) $S(Q,\omega = 0)$ structure factors for glassy Se at T=300 K. The lower traces show $S(Q)$ (solid line) and $S(Q,\omega = 0)$ for the trigonal polycrystal and the same temperature. (b) Temperature dependence of the in-plane lattice constant as derived from the peak positions of the static (circles) and elastic (triangles) structure factors. The present values can be favorably compared with those derived by Hamilton *et al.* (Ref. 11) for a single crystal at T=77 and T=298 K. The solid line shows the results of the thermal expansion coefficient for a direction normal to the crystal c axis (i.e., normal to the Se chains) measured from high-purity single crystals (Ref. 12). The solid lozenges depict the values of the same function as derived from the temperature dependence of the a lattice constant.

temperature derivatives $1/R\partial R/\partial T$ with those available from macroscopic measurements on a sample of glassy (quenched) Se.[12] As shown in Fig. 2(a), the quantity calculated from data regarding $S(Q,\omega)$ after approximating the experimental points by a smoothing spline follows a trend alike to that of the macroscopic $\alpha(T)$ although the values of the expansion coefficient at temperatures above 150 K are about twice the macroscopic ones. The origin of such discrepancy is not understood at present although it could be tentatively ascribed to differences in sample preparation, and above all, in annealing times. At any rate, what seems clear from such a comparison is the fact that only the peak position in $S(Q,\omega=0)$ should serve as an indication of an underlying length scale, unless the measurements are carried out at temperatures low enough that both structure factors become coincident. A distinct behavior is also found regarding the R_c correlation lengths as shown in Fig. 2(b). Notice, however, that the quantity calculated from the elastic structure factor remains basically constant about a value of $R_c \approx 9.1$ Å common to both structure factors at the lowest explored temperature, whereas the R_c function derived from $S(Q)$ evidences a behavior which conforms to that expected for a correlation length, showing a decrease with temperature caused by the increased thermal disorder and also evidencing a fast drop in the vicinity of the glass transition ($T_g \approx 313$ K). Finally and for the sake of completeness, the temperature dependence of the intensities of both peaks is shown in Fig. 2(c), where a decrease in peak intensity of $S(Q,\omega=0)$ which follows a quasilinear behavior above 65 K contrasts with the scarce variation in the intensity of $S(Q)$, and the interested reader is directed to our previous paper[10] where the dependence of both intensities with temperature and wave vector are discussed in more detail.

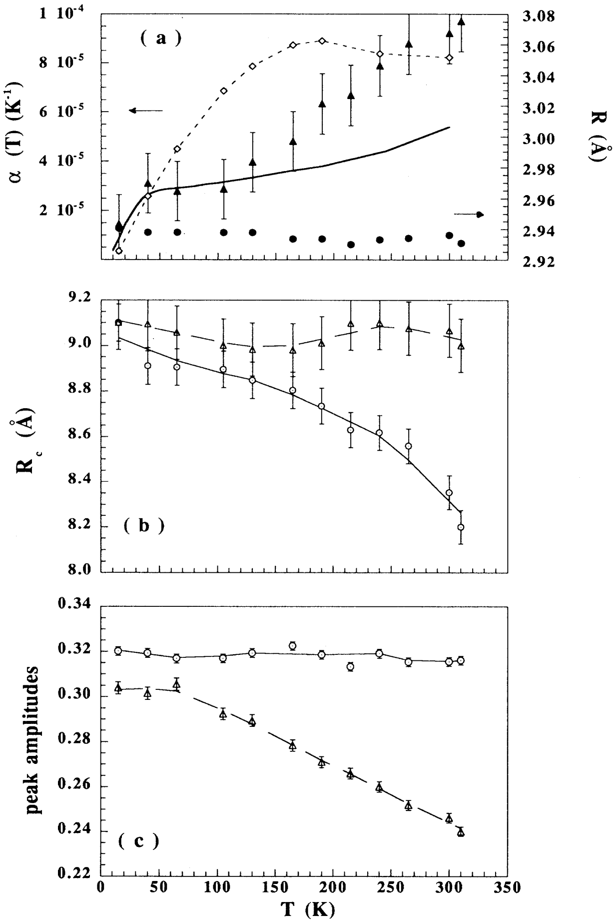

FIG. 2. (a) Solid circles and triangles show the temperature dependence of the quantity $R = 2\pi/Q_p$ corresponding to the static and elastic structure factors, respectively (see text). The solid line shows the macroscopic isotropic thermal expansion coefficient of a sample of glassy Se (Ref. 12), and the open lozenges show estimates for this quantity derived from the temperature dependence of the maxima in $S(Q,\omega=0)$. (b) Temperature dependence of the "correlation lengths" R_c as derived from the widths of the peak in $S(Q)$ (circles) and $S(Q,\omega=0)$. The lines have been drawn as guides to the eye. (c) Dependence with temperature of the peak intensities. Same symbols that before are used.

In consequence, the temperature dependence of both static and elastic structure factors evidences that the characteristic period R as derived from the maxima of $S(Q,\omega=0)$ and that R_c derived from the width of the first peak in $S(Q)$ can be rightly interpreted as a characteristic distance and correlation length, respectively, on similar grounds as those of polycrystals. Notice that reliable estimates for such a length scale and "correlation length" cannot be derived from diffraction measurements [of $S(Q)$] only, since the glass dynamics begins to contribute to the diffracted intensities in a way strongly dissimilar to that observed for the polycrystal. Although changes in R or R_c with temperature may not be dramatic, and therefore some estimates for both quantities could be derived from a single diffraction measurement, some care should be exercised if correlations of these quantities with others of dynamic nature (see Ref. 2) are sought.

The present results can also help to clarify some results which have been the focus of controversies such as the temperature dependence of the first sharp diffraction peak in vitreous silica.[1] In agreement with such data, no substantial reduction in the peak intensity of $S(Q)$ within the explored temperature range was found. On

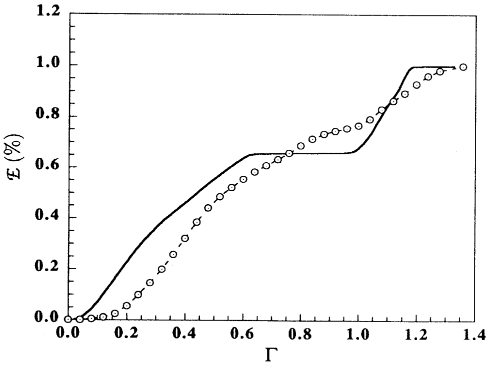

FIG. 3. Running integrals for the average kinetic energy [see Eq. (1)] for g-Se (solid line) and vitreous SiO_2 (circles).

the other hand and contrary to the present case, no significant variation in R_c was detected for vitreous SiO_2, even at the highest explored temperature ($\approx$ 1300 K, that is, $0.9T_g$). Once scaled by T_g, the decrease in R_c at $0.9T_g$ shown in Fig. 2(b) represents $\approx 8\%$ of the value found at $T = 15$ K, and since such a decrease is caused by thermal disorder, a scaling additional to T_g which accounts for the vibrational dynamics should also be sought in order to compare data of different glasses. In this respect, recent experimental results[14] point to the average kinetic energy per atom, E_{kin}, as measured by neutron Compton scattering or, equivalently, to the quantity calculated from realistic models (or experimentally determined) for the vibrational $Z(\omega)$ density of states[15] from

$$\mathcal{E} = \frac{3}{4}\int_0^\infty d\omega \hbar\omega Z(\omega) \coth\left(\hbar\omega/2k_BT\right) \tag{1}$$

as a quantity encompassing relevant information regarding the vibrational frequency distribution which can serve as the required scaling variable. In fact, the percentual values of the running integral in Eq. (1) plotted against the dimensionless parameter $\Gamma = \hbar\omega/T_g$ shown in Fig. 3 may serve to provide a tentative explanation for the markedly different behavior of R_c when approaching T_g from below. Notice that for g-Se, most of the contributions to $\mathcal{E}$ arise from the lower-frequency and high-amplitude motions (translations, bond torsions, and bendings), and that these exhaust the integral for energies up to k_BT_g, whereas a more smooth behavior is followed by g-SiO_2, where only a small dip at T_g is apparent. Such a different behavior will obviously translate into significantly different amounts of dynamic disorder present in both samples at such a reference temperature. In fact, a calculation of the average atomic mean-square displacements at $0.9T_g$ from $\langle u^2\rangle = \hbar/2M_{\mathrm{av}}\int_0^\infty d\omega Z(\omega)/\omega \coth\left(\hbar\omega/2k_BT\right)$, where M_{av} stands for the average mass of the chemical unit, yielded values of 0.274 and 0.023 Å^2 for g-Se and g-SiO_2, respectively, which are close to experimental estimates from other sources (i.e., Lamb-Mössbauer factors[10] or peak widths in the radial distributions[1]), and in the case of g-Se, such a value is not too far from the ≈ 0.5 Å decrease in R_c. It seems then clear that because of large spread in frequencies of g-SiO_2, temperatures well above T_g would be required to match the values of $\langle u^2\rangle$ found for g-Se, leading to a concomitant reduction in R_c.

This work has been supported in part by DGICYT Grant No. PB92-0114-C04.

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