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Dynamics of Glassy and Liquid Selenium

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Inelastic-neutron-scattering studies of glassy, liquid, and polycrystalline selenium have been performed at temperatures between 100 and 600 K. A self-consistent data evaluation, taking careful account of multiple and multiphonon scattering, shows that a complete interpretation is possible in terms of a temperature-dependent density of vibrational states, together with diffusion broadening of the elastic line. This density of states is used to calculate thermodynamic properties and to show that about one-third of the additional entropy of the liquid is vibrational. The results raise a number of questions concerning current theories of the glass transition.

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It has long been realized that a fundamental difference between a glass and a supercooled liquid is the presence in the latter of both conformational and vibrational motion. As an idealized example, motion in the liquid can be represented by an atom vibrating about an equilibrium position which is itself changing with time as a result of diffusion. What is not yet understood, however, is the way in which conformational motion freezes out at the glass transition temperature T_g and the way in which it influences thermodynamic properties. To take the particular example of interest here, there have been no direct measurements of the relative importance of conformational and vibrational contributions to the sudden (but not discontinuous) increase in the heat capacity $C_p(T)$ on passing from the glass to the supercooled liquid,[1] one of the most obvious signatures of T_g. That this increase in $C(T)$ is not simply a "release of degrees of freedom" can be seen in Se[2] where $C_p(T)$ increases from the classical value of $3R$ mole^{-1}K^{-1} in the glass to a value 50% higher just above T_g. (Se is a glass with a T_g sufficiently low for easy study, but without bonded H atoms or side groups which complicate the analysis in organic polymers.)

Recent mode-coupling theories[3,4] have attempted to understand conformational motion (also known as relaxation) by describing it in terms of a time-dependent particle-density correlation function. The predictions of these theories have encouraged a number of neutron studies of the dynamics of the glass transition:[5–9] Conformational and vibrational motion are distinguished by time scales of typically 1 ns (varying rapidly with temperature but set by the experiment) and 1 ps, respectively, and show up in quasielastic and spin-echo experiments, on the one hand, and in measurements of the Debye-Waller factor and inelastic scattering, on the other. Most experiments have been concerned with conformational motion above T_g and demonstrate the presence of relaxation with a temperature dependence similar to that shown by the bulk viscosity, and in reasonable agreement with theory. Vibrational motion has been examined less carefully, mainly because detailed analysis of the data is complicated by multiple and multiphonon scattering. In this Letter we adopt a self-consistent, model-independent procedure for data analysis and derive a temperature-dependent density of states $g(\nu)$ which serves to link neutron and thermodynamic measurements. The results have important implications for understanding vibrational states in glasses, and for theories of the glass transition.

Samples of 99.999% pure Se were melted in a sample cell which consisted of two thin (0.3 mm) disks separated by a 2-mm spacer and sealed using Al wire. The outer diameter was chosen to fit a standard furnace-cryostat on the IN6 time-of-flight spectrometer at the Institut Laue-Langevin in Grenoble. Measurements were made between 100 and 600 K using incident radiation of wavelength 4.1 Å, giving scattering vectors Q in the range $0.3 < Q < 2.6$ Å^{-1}. Initial neutron examination showed that the sample was partially crystalline, but heating to 600 K, equilibration, and *in situ* quenching gave an amorphous sample with no sign of crystallinity. No measurements were possible between 360 and 440 K because the sample crystallized, but this limitation was turned to advantage by using the crystalline sample at lower temperatures as a comparison. For calibration purposes measurements were also made on a dummy sample cell both empty and filled with vanadium powder.

The elastic structure factor $S(Q,0)$ shown in Fig. 1 is obtained by considering only those channels which correspond to no energy change, and agrees well with published results.[10] The pronounced peak at 2 Å^{-1} results from the well-defined second-neighbor distance of 3.7 Å in a selenium chain or ring, together with the "van der Waals shell" of interchain nearest neighbors at a similar distance. A detailed discussion of the changes in the structure factor through T_g will be left to a subsequent publication. The inelastic scattering $I(Q,\nu)$ is also shown for a frequency of 0.25 THz at 100 K. The similarity between $I(Q,\nu)/Q^2$ and $S(Q,0)$ demonstrates that at low frequencies neighboring atoms move in phase, to give an inelastic structure factor[11] proportional to $Q^2S(Q,0)$. Raw data for the complete frequency range are shown in Fig. 2.

At higher frequencies the inelastic peak broadens, as do both inelastic and elastic peaks at higher temperatures. In order to analyze the data without detailed structural and vibrational information, averages over the range $1.4 < Q < 2.4$ Å^{-1} were used, thereby allowing correlation to be ignored because over this range $S(Q)$ averages to unity.[10] For example, in the incoherent approximation the ratio $S(Q,0)/S(Q)$ gives e^{-2W}, where $2W$ is the Debye-Waller factor and $S(Q)$ is an integral of $S(Q,0)$ over all frequencies, but in general this is not true.[12] However, by taking an average over a range of Q where $S(Q)$ averages to unity, the incoherent result is retained to a good approximation. Similarly the inelastic factor averages to that expected in the incoherent limit. The procedure was checked by showing that it was not sensitive to the precise limits chosen for the average, and also by showing that the density of vibrational states at 100 K, where multiphonon processes are not important, was not significantly changed when coherence was included by using a procedure similar to that applied previously to silica.[13]

The data from IN6 were analyzed in a self-consistent way, dividing the total inelastic intensity into contributions from multiple scattering, one-phonon scattering, and multiphonon scattering in order to obtain a temperature-dependent density of states. At each temperature the multiple scattering at frequency ν was calculated from the total scattering intensity at ν integrated over Q, using a scaling factor which took into account the geometry of the experimental arrangement, and which was derived from the low-Q limit of the scattering. A consistent fit was obtained using the same constant at all temperatures provided that both elastic-inelastic and inelastic-inelastic multiple scatterings were included. After subtraction of multiple scattering the data were then analyzed into one-phonon and multiphonon terms, calculating the multiphonon contribution explicitly from $g(\nu)$. Typical results for the glass at 100 and 460 K, and also for the polycrystal, where the data were analyzed in a similar way, are shown in Fig. 3.

No broadening of the elastic line was detectable except at the highest temperatures, and so additional experiments were carried out using a cylindrical sample on the high-resolution spectrometer IN13. No broadening was detectable below 450 K but at 493 and 513 K the broadening increased as Q^2. Combined with the measurements on IN6 at 600 K, this temperature-dependent width could be interpreted in terms of a diffusion constant of $(2.2\times10^{-11}\ \text{m}^2\text{s}^{-1})\pm10\%$ at 500 K with an activation energy of 0.70 ± 0.02 eV. The magnitude of D is in good agreement with the results of Axmann *et*

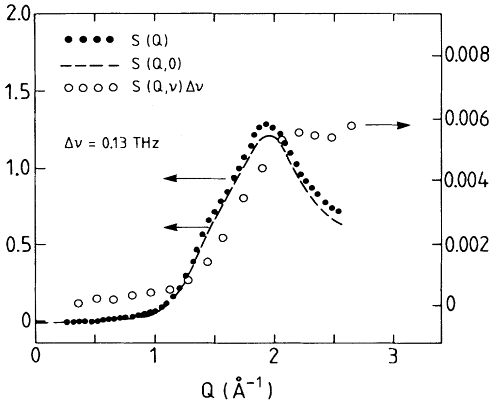

FIG. 1. The elastic structure factor $S(Q,0)$, the total scattering function $S(Q)$, and the inelastic scattering intensity at 0.25 THz for amorphous selenium at 100 K.

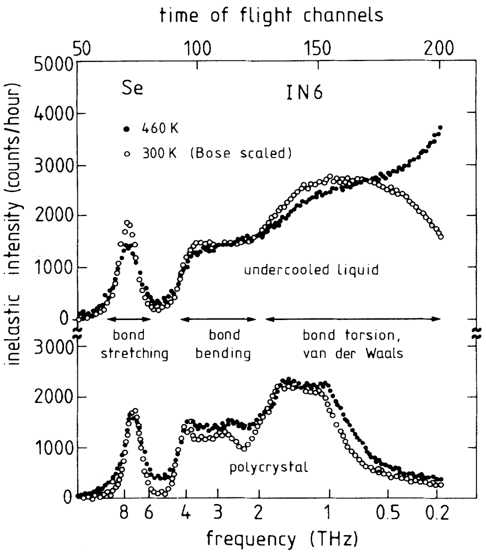

FIG. 2. The inelastic scattering intensity plotted as a function of frequency for (above) supercooled selenium and (below) polycrystalline selenium at 300 and 460 K.

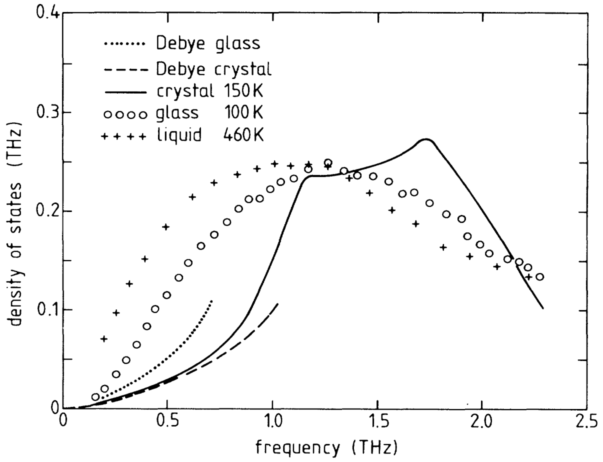

FIG. 3. The low-frequency density of states on an absolute scale for glassy, liquid, and polycrystalline selenium. The limiting Debye form is also shown.

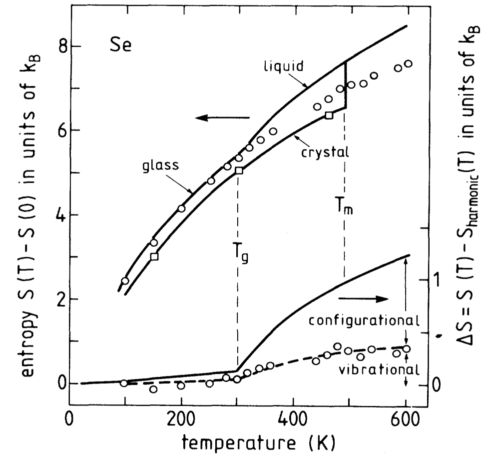

FIG. 4. The vibrational entropy calculated from the density of states for glassy, liquid, and polycrystalline selenium plotted as a function of temperature. Thermodynamic values are also shown. The lower curve gives the change in vibrational entropy arising from changes in the density of states.

al.[14] at 613 K, and the activation energy is identical to within experimental error with that derived from viscosity measurements[15] in the same temperature range.

The relatively small change of $g(\nu)$ with temperature shown in Fig. 3 makes it important to check the accuracy of the analysis. Vibrational states in the range $0.2 < \nu < 1$ THz dominate the heat capacity $C(T)$ in the range $2 < T < 12$ K, and direct calculation using $g(\nu)$ at 100 K shows agreement to within 2%, significantly better than that obtained using an earlier determination of $g(\nu)$ at room temperature.[16] Moreover, the crystalline density of states below 1 THz shows excellent agreement with the limiting Debye value deduced from the T^3 variation of the heat capacity below 10 K.

The overall form of $g(\nu)$ shown in Figs. 2 and 3 can be understood by using an argument based on constraints.[17,18] With one bond-stretching and one angle constraint per atom, $\frac{1}{3}$ of the modes should be dominated by stretching forces, $\frac{1}{3}$ by bending, and $\frac{1}{3}$ by torsional and van der Waal's interaction. This is shown in Fig. 2, where the separation between bending and stretching modes is obvious. The fact that the analysis gives the correct number of modes in the high-frequency peak (to 10%) is a further check of consistency.

$g(\nu)$ can be used to calculate thermodynamic properties, although in the presence of anharmonicity some care is needed in choosing the "fundamental" thermodynamic variable. It appears[19,20] that entropy is the best starting point, presumably because entropy essentially involves "counting." Using the harmonic form with experimentally measured frequencies the entropy $S(T)$ was calculated for the glass, for the supercooled and equilibrium liquids, and for the polycrystal. As shown in Fig. 4 the agreement with thermodynamic measurements[21] is excellent for the glass and crystal but not for the liquid. This is illustrated more clearly by subtracting the harmonic entropy calculated from the low temperature $g(\nu)$, as shown in the bottom half of the figure. This result provides, for the first time, direct experimental evidence that only one-third of the increased entropy in the liquid arises from vibrations, in agreement with the estimate made by Goldstein[22] from a comparison of quenched and annealed glasses.

The most marked feature of $g(\nu)$ is the increase in the density of modes below 1 THz on going from crystal to glass, and with increasing temperature in the liquid state. The data show a remarkable resemblance to the calculations on a model glass by Nagel *et al.*,[23] who show, using the equation-of-motion method to calculate $g(\nu)$ for a large random cluster, that the density of states increases at low frequencies as the physical density of the solid decreases, with the form of $g(\nu)$ changing from "concave" to "convex" just as shown in Fig. 3. However, it is not clear why this occurs, but it may result from the unusual, truncated, 6-12 interatomic potential used by Nagel *et al.* Calculations on other glasses using a Keating potential do not show a shift of the crystalline peak to lower frequencies.[24] It is worth emphasizing that the changes in Fig. 3 correspond to a softening rather than a broadening of the crystalline $g(\nu)$, and by comparison with density changes can be seen to give a Gruneisen parameter of about 2.

The Debye-Waller factor $2W$ varies more rapidly with temperature in the liquid than in the glass, a feature previously reported by a number of authors.[5,25] In the classical limit $2W$ is given in the quasiharmonic approximation by

$$2W = \frac{Q^2}{4\pi^2 M} \int_0^\infty \frac{g(\nu)}{\nu^2} d\nu ,$$

where M is the atomic mass, and so is dominated by low-frequency modes. The more rapid increase of $g(\nu)$ with temperature at low frequencies in the liquid is therefore sufficient to account for the observed behavior.

The work described here has a number of implications for theories of the glass transition and the liquid state.

(a) A temperature dependence of $g(\nu)$ must be included in any analysis of neutron scattering in the liquid. Although restricted to low frequencies, the weighting factor $1/\nu^2$ means that the increase in $g(\nu)$ has dramatic consequences for the Debye-Waller factor and for the form of the inelastic scattering. At first sight it might appear that low-frequency behavior similar to that shown by the supercooled liquid at 460 K in Fig. 2 is the result of the emergence of a broad quasielastic line, and indeed our data can be crudely represented by the sum of a temperature-independent $g(\nu)$ and a quasielastic line of constant width and with intensity increasing with temperature.[5] However, such a representation is not consistent with the more careful and detailed analysis presented here.

(b) Below 1 THz the density of states in the crystal is dominated by shear modes. The magnitude of $g(\nu)$ and the form of $I(Q,\nu)$ show that similar modes exist in the liquid and glass, but are sensitive to temperature. (At 600 K, the relaxation time derived from the diffusion constant D using $\tau \cong l^2/D$, where l is an atomic dimension, is approximately 1 ns, so that shear modes can exist in the liquid in the frequency range of these measurements.) This result suggests that current theories based only on density correlations should be extended to include more general mode behavior.

(c) The most important point of the analysis is that a complete self-consistent description of neutron scattering in the range $0.2 < \nu < 8$ THz is possible in terms of a temperature-dependent $g(\nu)$ which is consistent with other thermodynamic and neutron measurements. In this frequency range there is no evidence to suggest the existence of relaxation, although this is seen at much lower frequencies as a broadening of the elastic line.

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