TEMPERATURE DEPENDENCE OF THE F.I.R. ABSORPTION
SPECTRUM IN AMORPHOUS DIELECTRICS

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Abstract

The temperature dependence of the absorption coefficient in amorphous dielectrics below 10 cm^{-1} enables us to identify energy level configurations from population changes at liquid helium temperatures. Over a well defined frequency range a two level mode has been identified.

The thermal properties of glasses at low temperatures have provided experimental evidence that anomalous low frequency modes occur in amorphous materials.^{1,2} The linear temperature dependence of the specific heat which occurs in glasses below a few degrees K is interpreted as arising from these anomalous modes whose density can be specified in the energy range below 4 cm^{-1} . Both the non-linear ultrasonic attenuation³ around 0.1 cm^{-1} and the anomalous sound velocity measurements⁴ around 0.01 cm^{-1} at very low temperatures have established that the modes at those frequencies are very anharmonic and that the density of modes is consistent with the specific heat measurements.^{1,2} In addition to these special modes, Brillouin scattering experiments⁵ have shown that there are regular well behaved transverse and longitudinal phonons in this frequency region as well. To account for these special modes a tunneling model has been proposed^{6,7} in which atoms, ions, or groups of particles quantum mechanically tunnel between two or more equivalent sites. The linear dependence of the specific heat has been obtained from this model by including a statistical distribution of barrier heights and asymmetries for the local potential. One straightforward prediction which this model makes is that the temperature dependence of the absorption coefficient should be determined by the occupation numbers of a small number of energy levels associated with the tunneling manifold.

In this paper we describe the first measurements of the temperature dependent absorption coefficient of amorphous dielectrics in the far infrared at frequencies between 2 and 10 cm^{-1} . Four different glasses, namely, GeO_2 , PMMA, SiO_2 and SiO_2 with 600 ppm H_2O have been studied between 1.2 and 4.2°K . This frequency region cannot be probed with the ultrasonic technique. We find complex temperature dependences which identify the energy level manifold associated with some of the anomalous modes. Our preliminary results indicate that energy levels can be identified from population changes with temperature and a two level

transition can account for the temperature dependent component of the absorption coefficient at low frequencies. The density of these infrared active modes is comparable with the values obtained from specific heat measurements.

For the spectroscopic measurements we have used a lamellar interferometer together with a liquid He^3 cooled germanium bolometer detector.⁸ The PMMA samples were obtained from commercial stock. Both SiO_2 (Optosil) and SiO_2 with 600 ppm H_2O (Infrasil) were obtained from Valprey Corporation while the GeO_2 samples were grown at the Cornell Crystal Growing Facility. The absorption coefficients were obtained from transmission measurements on samples of differing lengths. The incident power on the samples was estimated to be less than 10^{-9} watts. The absorption coefficient for PMMA and SiO_2 (Optosil) at room temperature and at 4.2°K is shown in Figure 1. Our room temperature absorption coefficient agrees satisfactorily with the higher frequency data previously obtained on SiO_2 ^{9,10} and with the few frequencies measured for PMMA.¹¹ Using discrete laser frequencies, Strom et al.¹¹ have reported temperature independent structureless far infrared absorption from 300°K to 4.2°K for eight different glasses. (PS, SiO_2 and PMMA were not included in these studies.) Our experimental measurements below 10 cm^{-1} in Figure 1 demonstrate that some structure in the frequency dependence of the absorption coefficient exists at room temperature and becomes quite pronounced at 4.2°K, a very different result from that obtained by Strom et al.¹¹

In order to separate the temperature dependence of the anomalous modes from the anharmonic temperature dependence associated with difference band processes for regular phonons we have restricted our spectroscopic studies to glasses at low temperatures (1.2 to 4.2°K). Our temperature dependence measurements of the absorption coefficients for the four different glasses are summarized in Figure 2. The absorption coefficient was measured at many intermediate temperatures between 1.2 and 4.2°K but for clarity Figure 2

only indicates the experimental results at the temperature extremes. Although the magnitudes of the absorption coefficient are very different for these glasses the temperature dependence is remarkably similar. This temperature dependence of the absorption coefficient (at low temperatures) can be divided into three frequency regions: 1) For frequencies larger than 10 cm^{-1} no temperature dependence is observed, 2) Between 7 and 9 cm^{-1} the absorption coefficient increases with increasing temperature and 3) Below 6 cm^{-1} the absorption coefficient decreases with increasing temperature. The decrease in absorption coefficient with increasing temperature is described quantitatively for all these glasses by the population dependence of a two-level model in the restricted frequency region designated by the dashed curves in Figure 2¹². We now consider this restricted frequency region in more detail.

Two-level modes: The absorption coefficient, α_t , associated with a statistical distribution of optically active two-level systems with a level spacing $\hbar\omega$ can be written quite generally as

$$\alpha_t(\omega, T) = g(\omega, T) \tanh \frac{\hbar\omega}{2kT} \quad (1)$$

Because the local potential and hence the wavefunctions are not expected to change with respect to a small temperature change near 4.2°K , $g(\omega, T)$ is approximated by $g(\omega)$. However the amorphous solid is known to contain regular harmonic phonons in addition to the anomalous modes; thus the absorption coefficient of a glass which has both components may be written in the low temperature limit as

$$\alpha(\omega, T) = g(\omega) \tanh \frac{\hbar\omega}{2kT} + h(\omega) \quad (2)$$

where $h(\omega)$ represents the temperature independent harmonic phonon component.

Experimentally we have measured

$$\Delta\alpha(\omega, T) = \alpha(\omega, T_R) - \alpha(\omega, T) \quad (3)$$

where our lowest experimental temperature is defined as T_R . To determine $g(\omega)$ at each frequency in Eq. 2 we plot $\Delta\alpha(\omega, T)$ vs. $(\tanh \frac{\hbar\omega}{2kT_R} - \tanh \frac{\hbar\omega}{2kT})$ for various intermediate temperatures. Good fits to straight lines are obtained in the frequency region below 6 cm^{-1} . The slope of such a line gives $g(\omega)$ at one frequency. Because ω , T and T_R are all experimentally measured there are no adjustable parameters in this fit. The dashed lines in Figure 2 designate $h(\omega)$ in the frequency interval where a good fit for Eq. 2 is observed. To better illustrate the unique temperature dependence in the restricted frequency region given by the dashed curves in Figure 2 we have plotted in Figure 3 a universal curve of $D(\omega, T)$ versus the difference in the population factor with

$$D(\omega, T) \equiv \frac{\Delta\alpha(\omega, T)}{g(\omega)} \quad (4)$$

the normalized absorption difference. In Figure 3 all of the experimental data points cluster around the straight line appropriate to a two-level system. The significance of the scatter in the data can be judged by comparing the experimental data with the predicted dependence for a three-level with equal energy spacing. Such a dependence occurs in the shaded region bounded by curve B in Figure 3. The limiting case of an infinite ladder of equally spaced energy levels is given by curve C.

From specific heat measurements Stephens has estimated the number density of anomalous mode to be $D \sim 5 \times 10^{16}/\text{cc}$. The density of infrared active two level modes in the frequency interval designated by the dashed curve in Figure 2 can be estimated from the sum rule on the absorption coefficient which at $T = 0^\circ\text{K}$ is¹³

$$\int_0^\infty \alpha_t(\omega) d\omega = \frac{\pi e^2}{\sqrt{\epsilon} c} \left(\frac{\epsilon + 2}{3} \right)^2 \frac{Df}{M^2} [\text{cm}^{-2}] \quad (5)$$

where f is the oscillator strength of the transition, D the density of modes, M' the effective mass of the mode and ϵ the dielectric constant of the medium. We approximate the integral in Equation 5 by $\int g(\omega) d\omega$ over the frequency interval designated by the dashed curves in Figure 2. If we assume $f = 1$ (electric dipole transition) and $M' =$ mass of a formula or polymer unit then $D \approx 5 \times 10^{15}/\text{cc}$ for GeO_2 and PMMA and $D \approx 10^{14}/\text{cc}$ for fused quartz. These number densities are smaller by one or two orders of magnitude than the number estimated from specific heat but smaller numbers are to be expected since specific heat measures both infrared and noninfrared active modes. Considering the rough parameters used in our sum rule and the restricted range of the integral the agreement is satisfactory.

Harmonic modes: Because we have also measured the absolute absorption coefficient at 4.2°K the $g(\omega)$ found above can be used to obtain $h(\omega)$ the temperature independent contribution to the absorption coefficient in Eq.2. This contribution, then, must represent the harmonic oscillator contribution to the absorption coefficient of these glasses. Just why the harmonic contribution should produce structure in the absorption coefficient at such low frequencies is not yet understood, but may be associated with a particular kind of low frequency motion such as harmonic bending modes. Even more surprising is the large temperature independent low frequency contribution for Infrasil (see Fig. 2). The water dopant in Infrasil definitely enhances the low frequency absorption coefficient but does not change significantly the contribution of the two level component.

Complex modes: The most intriguing experimental results are associated with the temperature dependence in the 7 to 9 cm^{-1} region in Figure 2. The increase in absorption strength with increasing temperature over such a narrow frequency region indicates that we are observing excited state not ground state transitions. A unique energy level diagram must be assigned to these anomalous modes and must consist of a very low lying set of levels with

splitting greater than 1.2°K (0.84 cm^{-1}) but less than 4.2°K (2.7 cm^{-1}) with an additional excited state transition about 10 cm^{-1} above the ground state. This energy level diagram is shown schematically in Figure 2. Because at still higher frequencies the absorption coefficient is temperature independent, the manifold does not contain any additional higher energy states. Although this measurement has identified the excited states for only one type of anomalous mode it is now evident that the entire excited state spectrum can be mapped out by measuring the absorption spectrum as a function of temperature starting with much lower sample temperatures, say, 0.3°K . Low temperature hydrostatic pressure measurements may also provide a complementary technique for separating these excited state transition energies from those associated with the harmonic background absorption.

From our experiments we conclude that one group of anomalous modes in these glasses can be represented by a two level system in a restricted frequency range. Most of the experimental evidence which we have given here substantiates this claim. This energy level scheme is suggestive of a tunneling configuration for centers with orthorhombic or lower symmetry. In addition we have provided evidence that some of the centers with transition energies in the microwave region also contain a third and perhaps more levels at much higher energies, namely in the far infrared spectral region. Finally a third group of modes and the one with the largest absorption coefficient can be represented by temperature independent harmonic modes of some type. To understand quantitatively our experimental results on the low frequency properties of these amorphous dielectrics, a heterogeneous mixture of different types of modes is necessary.

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make precise measurements over the low frequency region and the two level model has been verified only over a one wavenumber interval centered around 5 cm^{-1} .

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Figure 1

Absorption coefficient at two temperatures for PMMA and vitreous silica. Curve A is the absorption coefficient of PMMA at 300°K; A' is at 4.2°K. The triangles represent the experimental data of Strom et al.¹¹ Curve B is the absorption coefficient of SiO₂ at 300°K, B' is at 4.2°K. The dot-dash curve represents the experimental data of Ref. 9. No single power law can fit the data over this frequency interval. Experimental error is less than $\pm 10\%$.

Figure 2

Temperature dependence of the absorption coefficient versus frequency for four different glasses. The solid curve gives the absorption coefficient at 4.2°K and the dotted curve the absorption coefficient at 1.2°K. The dashed curve, $h(\omega)$, is the extrapolated temperature independent absorption obtained by fitting the two level model (see Eq. 2 of text). Below 7 cm^{-1} the temperature dependence is fit by a two level model as indicated in the diagram in the Figure. Above 7 cm^{-1} a more complex energy level scheme is required, and is shown schematically in the Figure. Spectral resolution is $.7 \text{ cm}^{-1}$.

Figure 3

Comparison of the experimental temperature dependence with the theoretical dependence predicted by different models. $D(\omega)$ versus $\frac{\omega}{T}$ on a tanh scale for four different glasses (See Eq. 4 of text). Using $T_R = 1.2^\circ\text{K}$, A is the theoretical two level system, B and C bound the region for a three level system with equal energy spacing, ω . Curve C represents a temperature independent harmonic oscillator model.

TEMPERATURE DEPENDENCE OF DISORDERED SYSTEMS IN F.I.R.

NORMALIZED ABSORPTION DIFFERENCE $D(\omega, T)$

- = GeO_2
- = SiO_2 (Vitreous) Optosil
- △ = SiO_2 (Vitreous) Infrasil II
(H_2O , 600ppm)
- ◇ = Plexiglass

- a = 2.5 cm^{-1}
- b = 3.0 cm^{-1}
- c = 3.5 cm^{-1}
- d = 4.0 cm^{-1}
- e = 4.5 cm^{-1}
- f = 5.0 cm^{-1}
- g = 5.5 cm^{-1}
- h = 6.0 cm^{-1}