

Anomalous Sound Velocity in Vitreous Silica at Very Low Temperatures

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The temperature dependence of the longitudinal sound velocity has been measured in vitreous silica between 0.28 and 4.2 K and at frequencies between 30 and 150 MHz. With decreasing temperature the sound velocity does not increase monotonically towards its value at $T=0$ K, but reaches a maximum around 2 K and decreases steadily at lower temperatures. This new result, unique for a pure dielectric solid, gives further evidence for the existence of two-level systems in glasses.

At very low temperatures remarkable anomalies of the thermal properties in amorphous materials have been observed recently by several authors.^{1,2} To explain these observations it was suggested that the anomalous high specific heat can be attributed to two-level systems showing a broad distribution of their energy splitting.³ These systems should strongly scatter resonant thermal phonons, thereby leading to the observed short thermal mean free path. This resonant-scattering process also has a very pronounced effect on the ultrasonic attenuation below 1 K as was demonstrated recently.⁴ Already at very low acoustic intensities (> 50 nW/cm²) the attenuation becomes intensity dependent indicating a saturation of the two-level systems. At higher intensities or higher temperatures a relaxation process between the two-level systems determines the attenuation.^{5,6} So far this nonlinear ultrasonic attenuation has been the main experimental evidence for the existence of two-level systems having a strong resonant coupling to phonons. These two-level systems could be described as tunneling states,^{3,5} but so far no direct evidence for the tunneling nature has been found. Therefore we restrict ourselves here to a phenomenological description, not discussing the question of the atomic origin of these two-level systems.

In order to study the influence of the two-level systems on the elastic properties directly, we have measured the variation of the sound velocity of longitudinal waves in vitreous silica Suprasil I⁷ between 0.28 and 4.2 K at frequencies between

30 and 150 MHz. Applying an acoustic intensity of about 1 mW/cm²—an intensity where the ultrasonic attenuation is completely saturated—we obtain an accuracy of 2×10^{-5} for the relative variation of the velocity $\Delta c/c = [c(T) - c(T_0)]/c(T_0)$. Here $T_0 = 0.28$ K, the lowest temperature attained in our experiment, is our reference temperature.

Our results are shown in Fig. 1 where $\Delta c/c$ is

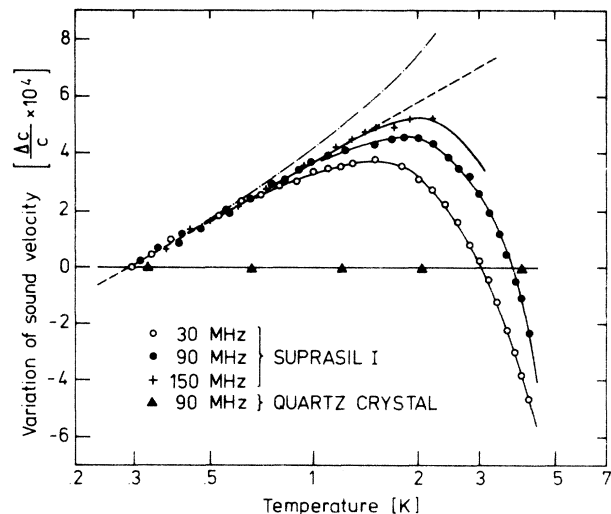


FIG. 1. Relative variation of the longitudinal sound velocity $\Delta c/c$ plotted as a function of temperature. Straight dashed line, a variation proportional to $\ln T$; solid lines, the theoretical prediction for the sum of the contribution of the resonant interaction and the relaxation process; dashed-dotted line, the contribution of the resonant interaction alone, assuming a density of states $n(E) = n_0 [1 + a(E/k_B)^2]$.

plotted as a function of temperature. The sound velocity shows a strong and unexpected temperature dependence. At higher temperatures the velocity increases with decreasing temperature and is frequency dependent (for still higher temperatures see Anderson and Bömmel, and Krause⁸). Below 1.5 K, however, the velocity is not frequency dependent, decreases steadily, and does not tend towards a constant value even at temperatures as low as 0.28 K. We have also observed in water-free vitreous silica results similar to those from Suprasil I. Such a temperature dependence cannot be explained by thermal expansion and is in striking contrast to that of pure dielectric crystals where the expected variation⁹ is well below the sensitivity of our experimental setup. The experimental check of the sound velocity in quartz crystal indeed yielded a constant value as indicated in Fig. 1.

This very unusual behavior can be explained in terms of a distribution of two-level systems. As in the case of the ultrasonic attenuation there are two contributions of the two-level systems to the sound dispersion: one due to the resonant interaction and the other due to relaxation. While relaxation generally leads to a decrease of the sound velocity with increasing temperature, it is the resonant interaction that leads to an increase. We will show that the different temperature dependence of the measured sound velocity below and above its maximum value (around 1.5 K) can be explained by the sum of these two different contributions. A relaxation mechanism alone cannot¹⁰ describe our data.

The contribution of the *resonant* interaction to the sound velocity can be derived by using the Kramers-Kronig relation between the sound absorption $\alpha(\omega)$ and the sound dispersion $\Delta c(\omega)$,

$$\frac{\Delta c}{c} = P \int_0^\infty d\omega' \frac{c}{\pi} \frac{\alpha(\omega', T) - \alpha(\omega', T_0)}{\omega^2 - \omega'^2}, \quad (1)$$

and the expression for the resonant absorption⁵

$$\alpha(\omega, T) = \pi \frac{n_0 M_l^2}{\rho c^3} \omega \tanh\left(\frac{\hbar\omega}{2k_B T}\right). \quad (2)$$

Here P indicates the principal part of the integral (1), n_0 is the constant part of the density of states derived from the linear term of the specific heat,² ρ is the density of the glass, and M_l is the coupling energy for the resonant interaction between a two-level system and a longitudinal phonon.¹¹

The frequency and temperature dependence of

the resonant absorption predicted by Eq. (2) have been confirmed experimentally in the frequency range $\hbar\omega \ll k_B T$ where $\alpha_{\text{res}}(\omega) \propto \omega^2/T$.⁶ We assume that the expression (2) is valid for all frequencies below a certain cutoff frequency ω_{max} and that $\hbar\omega_{\text{max}} \gg k_B T$ holds. This implies that the energy splitting of the two-level systems extends well beyond $k_B T$. Inserting Eq. (2) into the Kramers-Kronig relation [Eq. (1)], the contribution of the resonant interaction to the sound velocity at low frequencies ($\hbar\omega \ll k_B T$) is found to be

$$\frac{\Delta c_{\text{res}}}{c} = \frac{n_0 M_l^2}{\rho c^2} \ln\left(\frac{T}{T_0}\right). \quad (3)$$

Note that this result does not depend on frequency. The contribution to the Kramers-Kronig integral which determines the logarithmic temperature dependence comes from the frequency range $\hbar\omega \sim k_B T$. This explains why the effect of the resonant interaction on the sound velocity—in contrast to the resonant attenuation⁶—is not affected by the saturation of those two-level systems with an energy splitting $E = \hbar\omega$.

The logarithmic temperature dependence agrees well with our experimental data below 1 K. Fitting our data (see straight line in Fig. 1) by Eq. (3), and using $n_0 = 7.8 \times 10^{32} \text{ erg}^{-1} \text{ cm}^{-3}$,¹² $\rho = 2.2 \text{ g/cm}^3$, and $c = 5.8 \times 10^5 \text{ cm/sec}$, we derive a value of $M = 0.32 \text{ eV}$. This is in good agreement with the value obtained from ultrasonic attenuation⁶ and thermal conductivity.^{2,3}

Alternatively, our results as described by Eq. (3) can be understood directly from the well-known coupled-modes picture in analogy with the spin-phonon problem.¹³ We consider a set of two-level systems with an energy splitting E interacting with the phonon field. Their dispersion curves without interaction are indicated by the dashed lines in Fig. 2. From elementary perturbation theory we know that the resonant coupling between these excitations causes a repulsion between both modes. The strength of this repulsion is proportional to the difference in the population of the levels of the two-level systems¹³ and is therefore zero at very high temperatures but increases as the temperature decreases. This repulsion reduces the phonon energy $\hbar\omega$ at low frequencies ($\hbar\omega < E$), and hence the sound velocity. Because of the temperature dependence of the repulsion strength the sound velocity effectively increases with increasing temperature. Though we have to take into account a broad distribution of the energy splitting of the two-level

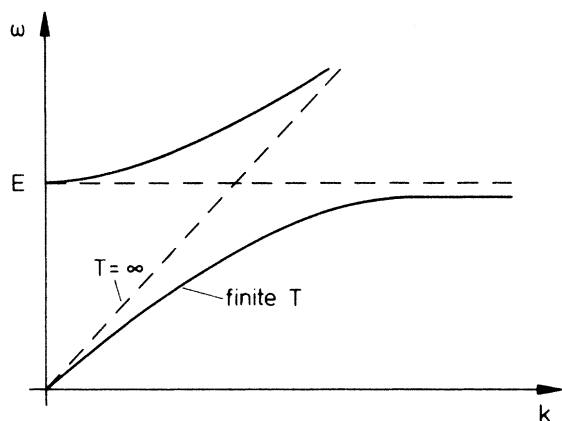


FIG. 2. Schematic representation of the acoustic dispersion curve in the presence of a set of two-level systems with an energy splitting E . Dashed lines, the situation for $T = \infty$; full lines, the behavior of the dispersion curves at a finite temperature.

systems this effect subsists, since the energy splitting of most of them is large compared to the energy of the ultrasonic phonon.

We shall now describe the effect of the *relaxation* mechanism which offers an explanation for our velocity data at temperature above 1.5 K. This process occurs since a sound wave disturbs the ensemble of thermal excitations by shifting their excitation energy. At higher temperatures (~ 50 K) the influence of relaxation on the sound propagation is well known in glasses,⁸ where thermally activated structural relaxation is observed.

To calculate the contribution of the relaxation process we assume that at temperatures around 1 K the relaxation of two-level systems¹⁴ is governed by the resonant one-phonon interaction. The relaxation time $\tau(E)$ of a two-level system with energy splitting E is then given as in Ref. 5 by

$$\tau^{-1}(E) = \left(\frac{M_t^2}{c_t^5} + \frac{2M_t'^2}{c_t^5} \right) \frac{E^3 \coth(E/2k_B T)}{2\pi\rho\hbar^4}. \quad (4)$$

Here $c_t = 3.8 \times 10^5$ cm/sec is the velocity of transverse phonons and M_t is the coupling energy between these phonons and the two-level systems. The relaxation contribution to the variation of the velocity of sound is described by the following equation¹⁵:

$$\frac{\Delta c_{rel}(\omega)}{c} = -\frac{2(M_t')^2}{\rho c^2} \int_0^{\hbar\omega_{max}} dE n(E) \frac{df(E)}{dE} \frac{1}{1 + \omega^2 \tau^2(E)}, \quad (5)$$

where $f(E) = [\exp(E/k_B T) + 1]^{-1}$ and M_t' is the shift of the energy splitting E per unit strain¹¹ and is assumed to be constant. Integrating this equation numerically by fitting it to our experimental data we obtain values for M_t' and M_t .

Specific-heat measurements have given evidence for excitations in addition to the constant distribution of the two-level systems. Assuming these excitations to be also two-level systems we write for the total density of states $n(E) = n_0 [1 + a(E/k_B)^2]$, where $a = 0.078 [K^{-2}]$.¹² Our calculations show that in order to find good agreement with our experimental results we must indeed take into account the energy-dependent density of states. To be consistent we have to replace n_0 by $n(E)$ also in Eq. (2) (see Fig. 1).

Adding the values found by integrating Eqs. (2) and (5) we obtain the final results as plotted in Fig. 1 for different frequencies. For M_t' we obtain a value $M_t' = 0.37$ eV and estimate $M_t = 0.13$ eV even though the fit is not very sensitive to the exact value of M_t . Nevertheless these results indicate that the coupling between the two-level systems and transverse sound waves is weaker than that of longitudinal phonons. A more detailed analysis of the experimental and theoretical aspects of the relaxation process including the ultrasonic absorption will be published elsewhere.

We conclude that our results on the unusual temperature dependence of the velocity of sound at the lowest temperatures can be explained by the resonant interaction between the acoustic wave and a broad distribution of two-level systems. This gives further evidence for the existence of such excitations in glasses although their microscopic nature is not yet fully understood. At slightly higher temperatures the relaxation of these two-level systems becomes predominant and leads to the decrease of the sound velocity with temperature. Its interpretation supports the idea that the density of states of the two-level systems is not constant but includes a quadratic term in accordance with specific-heat data.

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Evidence for Critical-Field Switching in Amorphous Semiconductor Materials

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We have investigated the role of thermal and electronic effects in threshold switching in an amorphous semiconductor of memory composition. Evidence is presented to show that switching is a bulk field effect, and that, if thermal effects are discounted or eliminated, the switching field is independent of pulse width for pulses longer than 1 nsec. This was the shortest pulse width measured. Short-pulse (1.5 nsec) measurements indicate that a previously unreported conduction region is established at the critical switching field.

Threshold switching mechanisms¹ in amorphous semiconductors have been studied intensively for several years. Attempts to explain the switching mechanism theoretically can be divided into thermal models, which interpret switching as a result of a thermal instability, and electronic models, which assume a breakdown of the electronic equilibrium as a result of an applied field or current. In order to account, at least qualitatively, for much of the experimental data, simple thermal models were inadequate, and it became necessary to include a field-dependent electrical conductivity. Several electronic models have been proposed and have recently received support because of the observation of polarity, contact, and critical-field effects.² In particular, Haberland and Stiegler³ reported evidence for bulk switching based on charge accumulated prior to switching. Henisch and Smith⁴ concluded, from high-field photoconductivity measurements, that switch-

ing occurred at a critical uniform field. Switching models were generally reviewed recently by Adler⁵ and Fritzsche.⁶

Investigation of the threshold switching phenomenon is subject to a number of experimental difficulties due to compositional and geometric uncertainties which limit the usefulness of some of the experimental data previously gathered. Some of these difficulties are discussed below.

Amorphous semiconductors generally exhibit monostable switching for structurally stable compositions, and memory switching for compositions which exhibit a reversible phase change. In memory compositions, threshold switching precedes the structural transformation. The tendency of many compositions to undergo phase separation on heating, together with the known filamentary nature of the conducting state, causes further experimental difficulties. As a result, data gathered by repetitive switching of single de-