

## Anomalous Dielectric Dispersion in Glasses at Low Temperatures

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We have found a strong temperature dependence in the dielectric constant of three different glasses below 5 K, which we ascribe to the low-energy excitations of the amorphous state. From our data we can determine the electrical dipole moment associated with these excitations, which gives rise to resonant absorption of electromagnetic waves. The corresponding absorption coefficient is expected to saturate at electromagnetic intensities above a few milliwatts per square centimeter.

At very low temperatures, the thermal and acoustic properties of amorphous materials exhibit unexpected deviations from those of crystalline substances. The specific heat for example is anomalously high and nearly independent of the chemical composition.<sup>1</sup> It has been proposed that this could be described by assuming the existence of localized two-level excitations<sup>2</sup> or, more generally, of strongly anharmonic oscillators. These systems interact strongly with resonant phonons, an effect which leads to the very small thermal conductivity<sup>1,3</sup> and also to an ultrasonic attenuation which can be saturated already at very low acoustic intensity.<sup>4</sup>

Until now most experiments performed to demonstrate the existence of these two-level systems, and in particular ultrasonics, were related to the elastic properties of glasses. It appears that these elastic properties are rather insensitive to the chemical composition of the amorphous material. Therefore this type of experiment can give but little information on the nature of the two-level systems. In contrast, it can be expected that the ionic content of the substance, and thus its chemical composition, will have a more pronounced influence on the coupling to an electric field.

With this in mind we have measured very accurately the temperature dependence of the dielectric constant  $\epsilon$  by monitoring the shift in the resonant frequency (1.1 GHz) of a microwave cavity partially filled with the sample. We were able to detect a change in  $\epsilon$  of the order of  $10^{-6}$  in the temperature range between 0.28 and 5 K. Our results for vitreous silica Suprasil W and Suprasil I<sup>5</sup> are shown in Fig. 1 where we have plotted the relative variation of the velocity of light,  $\Delta c/c = -\Delta\epsilon/2\epsilon = -|\epsilon(T) - \epsilon(T_0)|/2\epsilon(T_0)$ , against temperature. Here  $T_0 = 0.3$  K has been chosen as a reference temperature. Suprasil W and Suprasil

I differ mainly by their "water content": 1.5 ppm OH<sup>-</sup> ions in the first and 1200 ppm in the latter. In Fig. 2 we show the results obtained for borosilicate glass BK7.<sup>5</sup>

The velocity of light increases on cooling and reaches a maximum at around 4 K for our frequency of 1.1 GHz; then at lower temperatures it decreases steadily without reaching a constant value. This behavior of the velocity of light shows a striking similarity to that of sound velocity observed recently.<sup>6</sup> We have carried out the same experiment on a quartz crystal and it yielded a constant value as indicated in Fig. 1. This confirms that the unusual temperature behavior of the dielectric dispersion is to be attributed to the glassy state. It is worth mentioning that in our

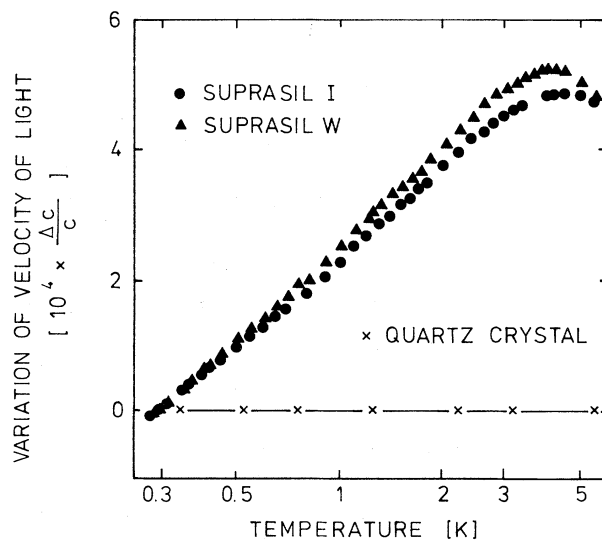


FIG. 1. Relative variation of the velocity of light  $\Delta c/c$  at 1.1 GHz in vitreous silica plotted versus temperature. Suprasil W contains 1.5 ppm and Suprasil I 1200 ppm of OH<sup>-</sup> ions.

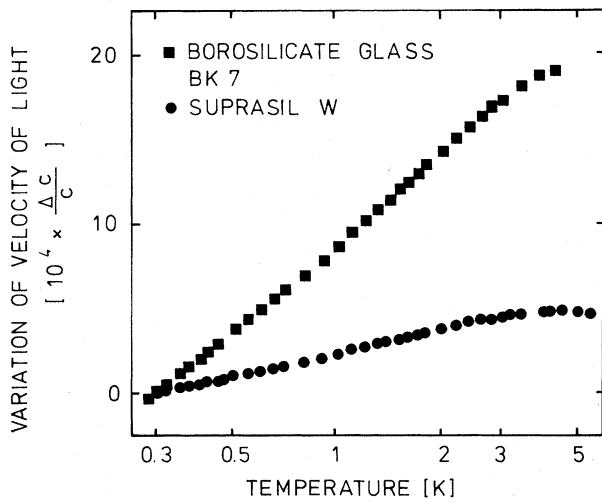


FIG. 2. Relative variation of the velocity of light  $\Delta c/c$  at 1.1 GHz in borosilicate glass BK7 plotted versus temperature. The values for Suprasil W from Fig. 1 are included for comparison.

temperature range the coefficient of thermal expansion implies a relative volume change of less than  $10^{-7}$ , a value far too small to explain our results. Consequently the variation of the velocity of light can be attributed to the presence of two-level systems and the problem can be treated in analogy to that of sound velocity.<sup>6</sup> At higher temperatures, above 4 K, the contribution of a relaxation process within the two-level systems predominates<sup>7</sup> and results in the increase of the velocity of light on cooling. Of greater interest here is the region of lower temperatures, where the resonant interaction between the microwave field and the two-level systems becomes dominant and leads to the observed decrease seen in Figs. 1 and 2.

For this process the microwave absorption<sup>8</sup> is given by

$$\alpha_M = (4\pi^2/c_0\sqrt{\epsilon})n_0p^2\omega \tanh(\hbar\omega/2k_B T), \quad (1)$$

where  $n_0$  is the constant density of states derived from specific-heat measurements below 1 K,<sup>1</sup>  $p$  is the electrical dipole moment associated with a transition between the two states,  $c_0$  is the light velocity in vacuum, and  $\omega$  is the microwave frequency. With use of Eq. (1) and the Kramers-Kronig relation between absorption and dispersion, the temperature dependence of the velocity of light becomes, in the case where  $\hbar\omega \ll k_B T$ ,

$$\frac{\Delta c}{c} = \frac{4\pi}{\epsilon} n_0 p^2 \ln\left(\frac{T}{T_0}\right). \quad (2)$$

The main contribution comes from two-level systems with an energy splitting  $E \approx k_B T$ , which are the ones responsible for the thermal anomalies observed at these temperatures. A microwave-absorption experiment, at the same frequency of 1.1 GHz, would have probed resonant two-level systems which do not give a significant contribution to the thermal properties.<sup>1,2</sup>

The logarithmic temperature dependence predicted by Eq. (2) corresponds to what is observed in Figs. 1 and 2. The quantity  $n_0 p^2$  is thus a constant, as  $n_0 M^2$  is in the case of ultrasonics,<sup>6</sup> where  $M$  is the mechanical coupling parameter. This leads to the conclusion that all three parameters ( $n_0$ ,  $p$ , and  $M$ ) are characteristic constants of a glass, independent of each other, within the limits given by the slight curvatures of the data seen in Figs. 1 and 2 and in the sound-velocity measurements.<sup>6</sup> From the slopes of our experimental results we measure directly the product  $n_0 p^2$ , and using a value of  $n_0 = 7.8 \times 10^{32} \text{ erg}^{-1} \text{ cm}^{-3}$  for the density of states,<sup>1</sup> we find for Suprasil W  $n_0 p^2 = 6.0 \times 10^{-5}$  in cgs units and  $p = 0.29 \text{ D}$ , and for Suprasil I  $n_0 p^2 = 6.7 \times 10^{-5}$  and  $p = 0.30 \text{ D}$ . Going to borosilicate glass BK7, the slope is much steeper, as can be seen in Fig. 2. We deduce for BK7 a value of  $n_0 p^2 = 3.1 \times 10^{-4}$  and a dipole moment  $p = 0.66 \text{ D}$ , assuming  $n_0$  in this case to be the same as for vitreous silica.<sup>1</sup>

This variation of a factor of 4 in  $n_0 p^2$  is very large compared to the variations observed in the acoustic and thermal properties. For example, the *elastic* dipole moment describing the coupling of elastic waves to two-level systems shows little difference between vitreous silica and borosilicate glass,<sup>6,9</sup> indicating that the spatial displacement is also of the same order of magnitude in the two materials. Obviously the *electrical* dipole moment is much more sensitive to the composition of the amorphous material. If the motion of groups of atoms is the origin of the two-level systems, the ions taking part in this motion carry a higher charge in BK7 than in vitreous silica.

The strong coupling to electrical fields should result in a contribution of the two-level systems to the microwave absorption of a glass. This absorption is expected to be intensity dependent in analogy to what has been found in the absorption of ultrasound in Ref. 4. With the values for  $n_0 p^2$  from our measurements we calculate that the intensity dependence should become observable at intensities above 2 mW/cm<sup>2</sup> in BK7.

In summary, we have observed a strong ther-

mal variation in the dielectric constant of glasses at very low temperatures. From our observations we have derived electric dipole moments associated with transitions within two-level systems in glasses. If one thinks of these two-level systems in terms of moving groups of atoms, our experiments show that the corresponding electrical charge is higher in borosilicate glass than in vitreous silica.

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## Spontaneous Magnetization Reversals in Magnetite in the Verwey Transition Region

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A magnetite rod has been observed to rotate suddenly at up to six discrete temperatures between 110 and 183 K in a weak magnetic field (1.5 Oe).

We have observed three, four, and sometimes six reversals in the direction of magnetization of samples of polycrystalline synthetic magnetite as well as of natural single crystals of the oxide as the temperature is raised through the Verwey temperature ( $T_V \approx 119$  K). We magnetize the sample along its long axis in a large field (about 10 kOe), cool it to liquid air temperature (while holding it in a keeping field of 50 Oe to maintain the remanent magnetization), and then lower the field ( $H$ ) to 1.5 Oe. The sample is placed within a cryostat and gradually warmed, over a period of up to 8 h at a rate of  $0.25 \pm 0.05$  K per minute. In the 1.5-Oe field, the sample rotates many times, coming to rest after swinging through any integral multiple of  $180^\circ$ . In general, the appearance of the discrete jumps of  $180^\circ$  varied from trial to trial. In some samples the jumps are accompanied by smaller rotations due to intermediate nonaligned orientations. Figure 1 exhibits typical angle-versus-temperature curves for four different samples. Figure 2 shows an example of the frequency of occurrence of the large discrete rotations of a sample of synthetic magnetite.

We think this is a unique phenomenon; so far as we know, there is no other material with more than one magnetization reversal. Magnetization reversal in magnetite is well known in the rock magnetization literature.<sup>1</sup> A single self-reversal in the direction of the remanent magnetization of a single crystal at 130 K was first reported by Yama-ai, Ozima, and Nagata.<sup>2</sup> These investigators found that the self-reversal was critically dependent on the shape of the sample; that is, the shorter the sample, the more pronounced was the self-reversal. In order to explain this reversal they assumed that there are two different kinds of magnetic domains which are coupled with each other by magnetostatic forces.

In our samples, which have a rod shape, we observe a large number of discrete  $180^\circ$  rotations only when they are many times as long as they are thick. We believe that our rods in their initial remanent states behave as single domains. The low frequency of observations of  $180^\circ$  rotations at higher temperatures (Fig. 2) may be due to the introduction of multiple domains in the samples after several successive reversals. Do-