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Excess Ultrasonic Attenuation in As_2S_3 Glass after Electric Field Removal

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Increased ultrasonic attenuation is found in As_2S_3 glass at 4.2 K after removal of a high electric field. The extra attenuation persists for a few minutes before disappearing, but can be reduced, or practically eliminated, by infrared radiation of moderate intensities. The effect is attributed to atomic relaxation accompanying electronic transitions in gap states where injected carriers have been trapped. The gap states may be valence-alternation pairs.

Microscopic understanding of the properties of disordered materials is still incomplete. Some of these properties, including the heat capacity,[1,2] thermal conductivity,[1-3] and the attenuation and velocity of ultrasonic waves,[4-6] exhibit behavior at low temperatures which has been explained in terms of tunneling in two-level systems[7] having various energy level separations and tunneling parameters. On the other hand, various electronic and optical properties of arsenic sulfide and selenide glasses, such as drift mobility, field effect, photoluminescence, and photoconductivity, have been explained in terms of the production, motion, and recombination of electron-hole pairs and the influence of localized states in the energy gap between valence and conduction bands.[8] The gap states have been associated with unfulfilled, or dangling, lone-pair bonds of the chalcogens which are occupied to various degrees so as to produce valence-alternation pairs[9] (VAP). In order to determine if there is a connection between the thermal-ultrasonic and electronic-optical phenomena, and thus between the two-level systems and the dangling-bond centers or VAP's, we have investigated the influence of high electric fields on the ultrasonic attenuation in As_2S_3 glass.

Our attenuation measurements were made with the sample immersed in liquid helium at 4.2 K contained in a double Pyrex Dewar vessel. We employed a pulse-echo method in which the attenuation of pulses of 30-MHz longitudinal ultrasonic waves was determined by averaging for 2.5 sec and recording the ratio of two echoes (usually 1 and 4) resulting from different numbers of round-trips in the sample. The minimum measurable change in attenuation amplitude was about 0.2%. We also applied dc voltages of up to 6 kV to the sample which was either in the dark or else in a beam of infrared (ir) radiation coming through a 1.0-mm-thick Ge filter in the path of light from a tungsten filament microscope lamp. The intensity of the ir radiation was measured with a Gen-Tec detector in place of the Dewar.

The samples were rectangular parallelepipeds of As_2S_3 glass (about 1.5 cm × 1.5 cm × 0.5 cm) purchased from the American Optical Company. Most of the data reported herein were obtained on sample 8 of Ref. 5 which contains details about its characteristics. In addition, the sample surfaces were oxidized in air at 100°C for 3 h. Electrodes to which the high voltages were applied usually consisted of a 0.70-cm-diam spot of silver paint on the bottom of the sample and the coaxial chrome-gold plating on the bottom of the 0.635-cm-diam, X-cut, quartz transducer which was attached to the top of the sample with 4-methyl-pentene-1 to make the acoustic bond. However, in one case we used silver paint electrodes opposite one another on the side faces of the sample while the transducer was atop the sample, as before. Although this arrangement was plagued by dielectric breakdown to the sample holder, at voltages below breakdown it gave

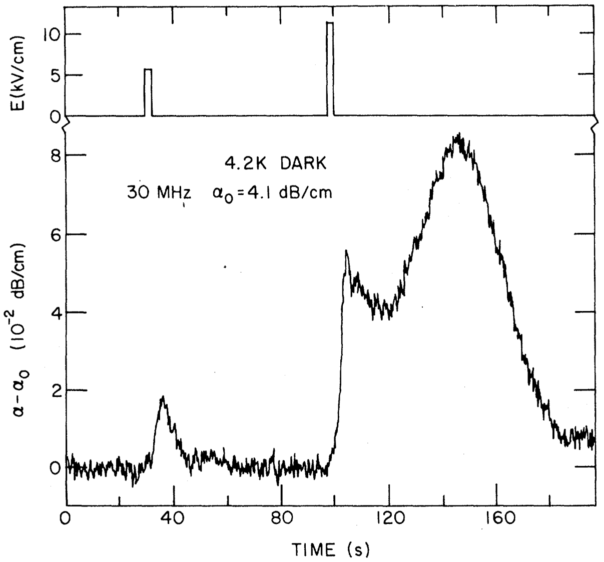

FIG. 1. Electric field (near the top) and excess attenuation of 30-MHz longitudinal ultrasonic waves vs time for amorphous As_2S_3, sample No. 8, in liquid helium in the dark.

results similar to those obtained with top and bottom electrodes.

We have discovered unusual changes in ultrasonic attenuation as summarized in Figs. 1–4. Figure 1 shows excess attenuation *versus* time during which electric fields of two different sizes have been applied and removed from an a-As_2S_3 sample in the dark at 4.2 K. As can be seen, while the dc field is on, the attenuation is changed very little, but after the field has been removed, it rises, goes through a maximum, and decays to about the value it had before field application. The effect occurred regardless of whether the Ag electrode was positive or negative relative to the

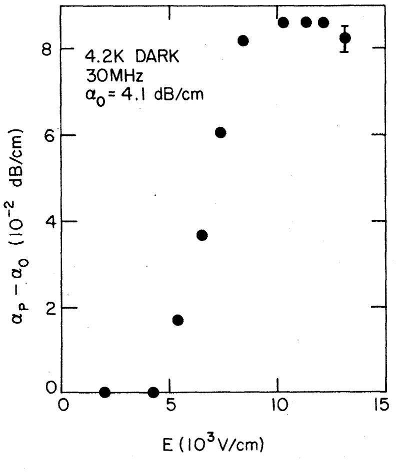

FIG. 2. Maximum excess attenuation occurring in amorphous As_2S_3, sample No. 8, during experiments like those in Fig. 1, for electric fields with various amplitudes. Uncertainty in each data point is like that shown for the last one.

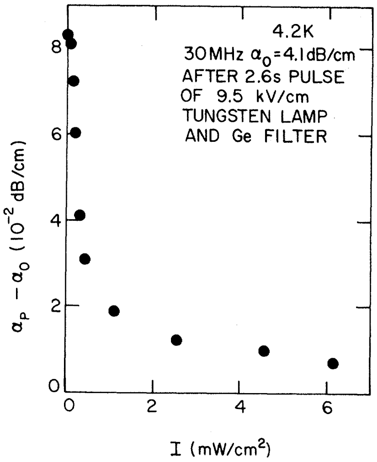

FIG. 3. Effect of infrared radiation of various intensities on the maximum excess attenuation occurring in a-As_2S_3, sample No. 8, during experiments like those in Fig. 1.

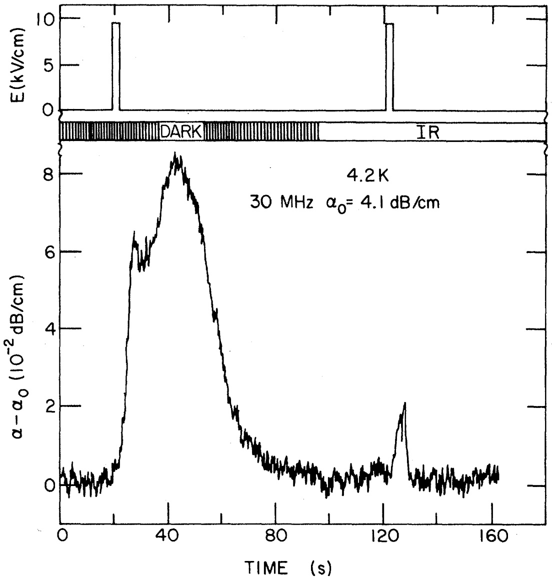

FIG. 4. Top to bottom: Electric field, illumination condition, and excess attenuation of 30-MHz longitudinal ultrasonic waves vs time for amorphous As_2S_3, sample No. 8, in liquid helium. The infrared illumination consisted of 5 mW/cm^2 of radiation coming from a tungsten-filament microscope lamp filtered with a 1-mm-thick plate of Ge.

grounded transducer.

The excess attenuation following the 11.3-kV/cm pulse in Fig. 1 and the 9.5-kV/cm pulse (in darkness) in Fig. 4 clearly has two components. One component grows in about 4 sec and begins to decay as a second, slower-rising, component becomes evident, reaches a peak and then decays with "time constants" of about 15 and 25 sec for the 9.5- and 11.4-kV/cm cases, respectively. The slow-rise component is not resolved after the 5.8-kV/cm pulse but does seem to be present since the decay time of the excess attenuation is definitely longer than the rise time. Although the data in Figs. 1–4 are for 2.6-sec-wide voltage pulses, we did employ much wider pulses occasionally. In each case the steep rise in attenuation did not occur until the voltage pulse was turned off, indicating that our measuring technique was not responsible for the rise in attenuation occurring only after removal of the 2.6-sec field pulses. The necessity of the oxide layer was indicated by the fact that measurements made after the oxide layer had been removed showed no post-field excess attenuation, but measurements made after reoxidation again showed the effect.

Figure 2 shows the maximum excess attenuation reached after removal of dc fields of various sizes. It is zero at low fields, increases almost linearly with field strength between 4 and 8 kV/cm and saturates above 10 kV/cm.

The induced attenuation can be reduced by infrared radiation with photon energies between about 0.35 and 0.69 eV as determined by the Pyrex Dewar walls and a Ge filter (see Fig. 3). Heating of the sample by the ir radiation was not responsible for the reduction of the excess attenuation since the temperature of a Ge thermometer mounted in the sample holder rose very little (less than 0.2 K) and an increase in temperature ordinarily[5] increases attenuation. The presence of ir radiation during application (and removal) of the electric field pulse causes a great reduction in the induced attenuation as seen in Fig. 4. It is interesting to note that photoinduced electron spin resonance in a-As_2S_3 is reduced by ir radiation.[10]

We do not think the post-field effects we observe are due simply to the electric field affecting the energy levels of the two-level systems which are involved in relaxation ultrasonic attenuation[11] in a-As_2S_3 in zero electric field.[5] It is true that some change in ultrasonic attenuation might be expected due to an applied electric field influencing how the two-level systems are distributed in energy[12] especially if the latter have dipole moments. The plausibility of such moments being present is indicated by dielectric dispersion measurements[13] on vitreous SiO_2 below 5 K. Perhaps an almost imperceptible increase in attenuation which occurs while the field is on (see Figs. 1 and 4) may be due to this cause. Even if this is true, the increase in attenuation after field removal cannot be due to subsequent dipole randomization since the post-field excess attenuation does not occur in a clean-surfaced sample. Neither can dipole relaxation in, or near, the surface layer be responsible since increased attenuation also occurs after fields applied to side electrodes which are far from the small central core of the sample where the ultrasound propagates.

We now offer an explanation of the effects we have discovered. Application of the electric field causes injection of mobile charge carriers at the surface of the sample (which is why an oxide layer is needed). The amount of injection into the bulk of the sample depends on the size of the electric field applied. While the field is on, the motion of the electrons and holes keeps them from being trapped at centers where they can interact strongly with the ultrasonic wave, but instead they recombine directly. After the field is turned off, there is trapping at defects which may be dangling-bond centers[8] or valence-alternation pairs.[9] While trapped, the carriers redistribute themselves between levels whose energies are shifted relative to each other by ultrasonic strain. Atomic relaxation accompanies the carrier redistribution. The relaxation lags the ultrasonic strain and causes dissipation of energy. Centers containing the trapped carriers are unstable configurations so that eventually the trapped carriers leave these centers and recombine, causing the ultrasonic attenuation to return to its preelectric field value. Infrared radiation liberates carriers from traps and thus eliminates the excess ultrasonic attenuation. The fact that Ge-filtered radiation is effective gives an indication that the depth of the traps must be less than about 0.7 eV. Involvement of both intimate and nonintimate valence alternation pairs may be the reason why there are two components in the extra attenuation.

In conclusion, investigation of the influence of rather large dc electric fields on the attenuation of ultrasonic waves in As_2S_3 glass has led to the discovery of temporary, post-field, attenuation increases which can be suppressed with infrared radiation. An interpretation of these effects is given which involves transitions of trapped carriers accompanied by atomic relaxation. The traps may be valence-alternation pairs.[9]

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"Compressibility Collapse" Transition in ReO_3

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We have used Fermi-surface pressure-derivative measurements at 2 K and single-crystal and powder x-ray studies as a function of pressure at room temperature to demonstrate that recently published anomalous Fermi-surface and lattice properties of ReO_3 are related to a novel second-order phase transition. This transition probably involves a tetragonal distortion of the lattice accompanying a displacement of the O atoms from the linear O-Re-O chains of cubic ReO_3 to a "hinged" arrangement at the oxygens and is characterized by an enormous increase in the compressibility of the high-pressure phase.

The compound ReO_3 has been shown to have many surprising properties. It is a bright red metal, with a conductivity within a factor of 6 of that of Cu at room temperature, which can be prepared in single crystals of sufficient perfection to permit observation of strong quantum oscillations in the magnetization[1] and thermal properties.[2] With some shifting of the bands, Mattheiss[3] was able to derive a band structure in agreement with both the Fermi-surface results and the optical data. Pressure studies[4] of the Fermi surface could be accounted for by a volume-dependent band structure by Myron, Gupta, and Liu.[5] Thus the electronic structure of this compound seemed to be rather well understood.

Razavi, Altounian, and Datars[6] recently reported an extension of the study of the pressure effect on the Fermi surface to higher pressures. The original work[4] gave only the initial derivatives determined by a method which requires pressures < 25 bars. Razavi, Altounian, and Datars found that the pressure derivatives for all the sheets of the Fermi surface suddenly increased at a much larger rate beginning at about 3 kbar. They speculated that this might be related to either (i) movement of the oxygens from their positions similar to the distortions that are observed in the related perovskites, or (ii) wave-function overlap changes with pressure, enhancing covalency in the compound and thus changing the Fermi surface.

Other investigators have reported anomalies in the lattice properties of ReO_3. Tsuda *et al.*[7] found that the elastic constants were very anisotropic, seriously violating the Cauchy relations. Pearsall and Coldren,[8] who also measured the elastic constants, suggested a phase transition might occur at low temperature although no di-