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Optically Induced Gap in the Atomic Tunneling Spectrum of As_2S_3 Glass

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Irradiation of the amorphous semiconductor As_2S_3 with band-edge photons opens a metastable gap in the low-energy density of states of atomic tunneling systems. Electric resonance studies at temperatures below 1 K indicate the annihilation of $\sim 10^{16}$ cm^{-3} tunneling centers, close to the density of metastable paramagnetic electronic defects created by low-level optical excitation. These findings link low-energy atomic tunneling systems to localized midgap electronic states.

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Low-energy tunneling systems dominate many of the properties of disordered solids at low temperatures.[1] Atomic tunneling between the two minima of a double-well potential results in two low-lying states with an energy splitting E. If the density of such two-level systems in glasses is approximately constant for energies <1 meV, the theory is in good agreement with the observed low-temperature properties. Nevertheless, a microscopic description of these centers has remained elusive.

It has often been suggested that there could be a connection between tunneling systems and electronic states in the gap of amorphous semiconductors, particularly the chalcogenide glasses.[2-8] However, wide disparities in the proposed densities of the two classes of defects as well as the different scale of excitation energies has made such an association rather tenuous. Irradiation with band-gap light forms electronic states which may be metastable at low temperatures, have an unpaired spin, and possess a broad optical absorption band in the gap.[9] The midgap absorption and spins can be removed by bleaching with light of an energy less than the band edge or by annealing above 150 K. These phenomena have been interpreted as the photoexcitation of charged defects to create neutral defects which have an energy near midgap.[3,10,11]

In this paper, we present the first experimental

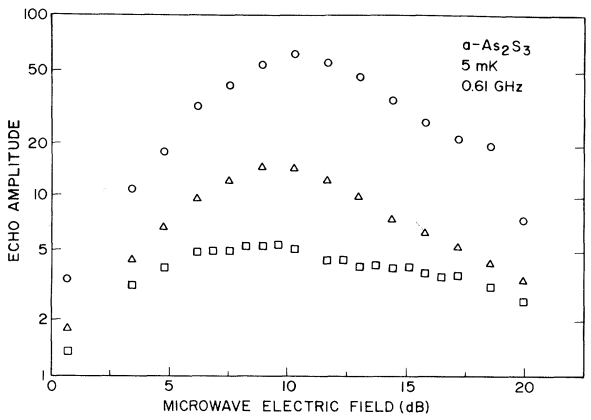
evidence that an intimate relationship exists between atomic tunneling systems and electronic gap states in a typical chalcogenide glass, As_2S_3. Our experiments measure the influence of optical radiation on microwave electric echoes emitted by tunneling systems, the electric dipole analog of spin echoes, and the dielectric constant of a-As_2S_3. These two techniques probe different regions of the spectrum of tunneling states and show dramatically different behavior when the electronic states are excited. Electric echo amplitudes at 0.6 GHz, proportional to the tunneling density of states $\bar{P}$ at this energy, are quenched by an order of magnitude when a-As_2S_3 is irradiated with 10^{18} photons at 2.18 eV. Echo suppression remains until the glass is bleached with midgap infrared radiation at 1.16 eV or until annealing above 150 K takes place. These phenomena thus show striking parallels to the well-known optical creation and manipulation of metastable paramagnetic centers in chalcogenide glasses.

In contrast to the large change in $\bar{P}$ at 0.6 GHz on irradiation, there appears to be no detectable change in $\bar{P}$ at energies greater than 5 GHz. This is inferred from the invariance after irradiation of the tunneling contribution to the dielectric constant above 0.1 K. We therefore propose that the band-gap optical radiation opens a reversible, metastable gap in the spectrum of tunneling levels at very low energies, $\lesssim 5$ GHz. Such a gap corresponds to the removal of $\approx 2\times10^{16}$ cm^{-3} tunneling systems, a number close to the density of metastable paramagnetic centers induced by light.[9]

The experiments were performed on samples of Servo As_2S_3 in the form of cylinders 2×14.5 mm in diameter. The sample resided in the uniform-electric-field region of a copper cylindrical reentrant microwave cavity. The bottom of the cavity adjacent to the sample consisted of a perforated disk, which functioned as a high-pass filter, i.e., passing light with 30% transmission but confining the microwaves to the cavity. The resonant structure was thermally linked to the mixing chamber of a dilution refrigerator. The temperature scale was established by calibrating the magnetic susceptibility of diluted cerium magnesium nitrate against U. S. National Bureau of Standards superconducting standards.

Light was brought into the refrigerator and cavity by low-loss multimode optical fibers which could be coupled to Kr^+ and Ar^+ ion lasers for excitation at 2.18 eV (568.2 nm), 2.34 eV (530.9 nm), and 2.41 eV (514.5 nm), and a neodymium-doped yttrium-aluminum-garnet laser for bleaching at 1.16 eV (1064 nm). All irradiations were carried out isothermally with the refrigerator between 150 and 200 mK, using intensities less than 200 μW/cm^2. The optical energy delivered to the refrigerator was determined calorimetrically and all excitation photons which passed the screen were assumed to be ultimately absorbed by the sample. At 2.18 eV and low temperatures the absorption coefficient of virginal As_2S_3 is about 1 cm^{-1} so that the sample is uniformly excited throughout its volume.

Electric echo amplitudes generated in a-As_2S_3 by two 200-nsec, 0.61-GHz microwave pulses separated by 3 μsec are shown in Fig. 1(a) as a



(a)

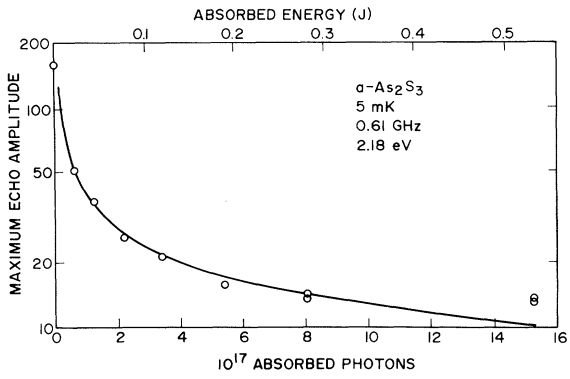


FIG. 1. (a) Pulse area dependence of echo amplitude for a-As_2S_3 after cooling to 5 mK from 300 K in the dark (circles), after exposure to 0.54 J of 2.18-eV band-edge light (squares), and after exposure to 0.51 J of 1.16-eV bleaching light (triangles). The rf pulse width is 200 nsec. (b) Echo amplitude as a function of the dose, n_{ph}, of band-edge light absorbed by the sample. The circles are experimental points; the line is proportional to $n_{ph}^{-1/2}$.

function of excitation amplitude. The echo maxima occur nominally at pulse areas $\theta = 2\pi/3$ and are proportional to $\bar{P}\mu$, where μ is the induced dipole moment.[12] The position of the maximum allows us to estimate an average $\mu = 5.9\times10^{-30}$ C m (1.8 D) for the unirradiated sample. After excitation the dipole moment of the states responsible for the remaining echo is 8.1×10^{-30} C m.

A series of optical irradiations decreases the echo amplitude by a factor of 10 as shown in Fig. 1(b), where the peak echo amplitude is plotted versus n_{ph}, the number of absorbed photons at 2.18 eV. The echo amplitude drops as $n_{ph}^{-0.53}$ until saturating at an integrated dose of $n_{ph} > 2\times10^{18}$ cm^{-3}. Bleaching with 1.16-eV photons partially restores the echo, and restores the original dipole moment. However, in contrast to the optical excitation response, the echo amplitude after bleaching is time dependent, increasing for periods as long as 5×10^5 sec as log$t$. Reirradiation of the bleached state with 2.34-eV photons reduces the echos to slightly smaller amplitude than the 2.18-eV excitation. Finally, annealing the glass at 150 K for about 10 h restores the echoes to about 30% of their initial amplitude. Room-temperature annealing restores the system to its original behavior.

We attribute the large changes in the amplitude to optically induced changes in the tunneling density of states $\bar{P}$ at and near the resonant frequency of 0.6 GHz. Additional evidence for modification of $\bar{P}$ comes from examination of echo dephasing times T_2' on irradiations as shown in Fig. 2. Excitation at 2.18 eV causes T_2' to increase by a factor of 2 whereas bleaching tends to restore T_2' to its original value. In glasses T_2' is believed to be governed by a spectral diffusion process[13-15] whereby resonant tunneling species are dephased by elastic dipolar interactions with thermally excited tunneling systems of energy $\lesssim 2k_BT$. The rate $1/T_2'$ depends on the concentration of centers as $\bar{P}^{1/2}$, for Gaussian decay, or as $\bar{P}$ in other regimes. Since, in practice, the echo decays roughly as t^{-1}, comparison with theory is, at best, qualitative.[16] Nevertheless, the optically modified dephasing rates at 5 mK are in general agreement with a significant reduction of $\bar{P}$ at very low energies ($2k_BT \approx 0.2$ GHz).

In glasses, the dielectric constant ϵ has a logarithmic temperature dependence arising from resonant tunneling processes with slope $d\epsilon/d\ln T \approx \bar{P}\mu^2$ in the regime $\hbar\omega \ll k_BT$, where ω is the measuring frequency.[17] In contrast to the large

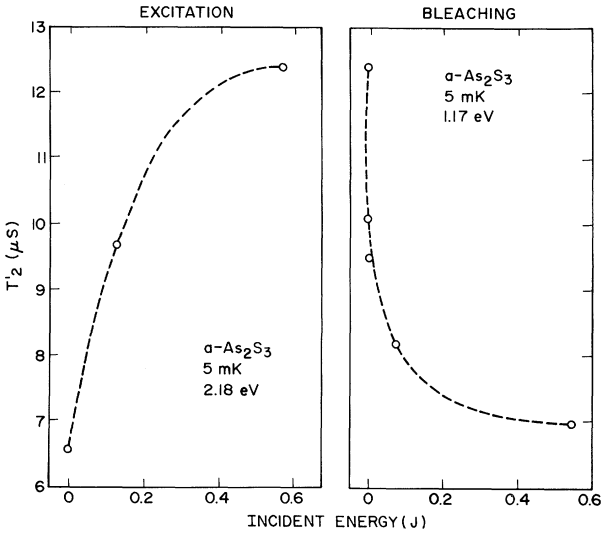


FIG. 2. Dephasing times T_2' of tunneling levels at 0.61 GHz at 5 mK. The dashed lines are guides for the eye. The changes in dephasing time arise from the optical modifications of the low-energy tunneling density of states $\bar{P}$.

change in echo amplitude, there is no apparent change in slope from 60 to 600 mK on irradiation, to within experimental uncertainties of about $\pm 10\%$. These data therefore suggest *no* change in $\bar{P}$.

The apparently contradictory results for the behavior of $\bar{P}$ on optical excitation can be reconciled if it is realized that the tunneling contribution to ϵ arises from states near $2k_BT$ and not at the measurement energy (0.6 GHz corresponds to 30 mK). We have performed a numerical Kramers-Kronig inversion of the tunneling absorption for various densities of tunneling states. The results show that complete removal of all states with energies less than 5 GHz produces small changes in the dielectric constant below 50 mK, where the temperature dependence is very weak, but negligible effect on the logarithmic region.

We propose that band-gap optical excitation of a-As_2S_3 opens a metastable gap in the low-energy portion of the tunneling system density of states. The depleted spectral region extends downward from approximately 5 GHz to possibly the minimum tunneling energies. The gap corresponds to a severe truncation of the upper range of the uniformly distributed tunneling parameter $\lambda = (d/\hbar)(2mV)^{1/2}$, since the minimum tunneling energy E is given by $\hbar\Omega_0\exp(-\lambda_{max})$, where Ω_0 is a zero-point frequency, d a tunneling coordinate, m an

atomic mass, and V the tunneling barrier. The number density of tunneling systems affected can be estimated from the specific-heat density of of states[18] P, resulting in $P(\Delta E) \approx 2\times10^{16}$ cm^{-3}.

An explanation of these results is that the photosensitive tunneling centers are spatially correlated with the metastable electronic centers. Tunneling systems couple strongly to strain and thus the excitation of a nearby defect would change their energy splittings. As many tunneling systems would be shifted into resonance as are shifted out of resonance if they were randomly distributed with respect to the electronic centers.[19] This is clearly not the case. We propose that the low-energy tunneling systems are intimately related to the ground state from which optically induced metastable paramagnetic centers are generated, as a result of (1) close correspondence of number densities 10^{16}–10^{17} cm^{-3}, (2) metastability at low temperature, (3) restoration with midgap radiation (bleaching), and (4) similar thermal annealing behavior.[9]

Photoluminescence studies of chalcogenide glasses have shown a relatively small quantum efficiency[20] ($\approx 10\%$ at low temperature) so that most recombination proceeds by nonradiative channels. Photoluminescence also exhibits fatigue under continuous excitation[21] which can be interpreted as the removal of radiative recombination centers. It has been shown that the fatique parallels the growth of paramagnetism and that efficient luminescence can be restored by bleaching.[22] Thus the metastable paramagnetic centers can be considered a subset of the radiative recombination centers in As_2S_3 although it is also possible that they consist of an admixture of the two types of states. Arguments have been given for believing that these centers consist of close pairs of oppositely charged defects, IVAPS (intimate valence alternation pairs)[4,10] or close D^+, D^- pairs.[3]

It has been suggested that a distribution of small potential barriers at the defect sites with energies $0 < V < k_B T_g$ maximally weighted at small V can control the character of excitation decay.[23,24] The large barriers are associated with restricted atomic relaxation and give rise to radiative processes. The small barriers allow appreciable relaxation and nonradiative decay. If atomic tunneling occurs through these potentials, high-barrier radiative sites should clearly be associated with low-energy tunneling processes with large λ, since $E \sim \exp(-\lambda)$. In this context, it is consistent to associate the low-energy part of the tunneling spectrum with radiative centers. The high-energy tunneling systems, associated with nonradiative recombination centers, do not have the opportunity to be trapped into a metastable state. A prediction of this hypothesis is that the high-energy side of the tunneling gap should be time dependent, moving to lower energy at long times.

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