

Photoinduced Defects in Chalcogenide Glasses

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Prolonged exposure to strongly absorbed light induces a large density of metastable defects in chalcogenide glasses. Observed properties of the new defects include light-induced ESR, extrinsic absorption below the band-gap energy and nonradiative recombination. The defect creation apparently underlies the well-known reversible photostructural change, and our data support a recent model of optically induced defect pairs.

Bishop, Strom, and Taylor¹ report that in chalcogenide glasses at low temperatures light irradiation results in an electron spin density which saturates at $\sim 10^{17}$ cm⁻³. Their explanation is that photoexcited electrons and holes are trapped at native centers. The ESR is accompanied by a broad induced absorption band and by the fatiguing of photoluminescence. These experimental data have been used to support a model of defects with a negative effective correlation energy.² In contrast, Molloy, Cernogora, and Benoît à la Guillaume³ assert that the spin density does not saturate at $\sim 10^{17}$ cm⁻³. Instead densities above 10^{20} cm⁻³ are reported after long exposures to highly absorbed light. This Letter describes new studies of induced ESR in chalcogenides which resolve these conflicting results and give the first direct evidence that the reversible photostructural changes are associated with defect creation.⁴

The data described here refer to glassy As₂S₃. Qualitatively identical results are obtained from Ge₂₀Se₈₀, and some data on that material are presented. Preliminary ESR results show that the same effects occur in Se, As₂Se₃, and other glasses in the As_xSe_{1-x} and Ge_xSe_{1-x} systems. Thus the effects described are widespread in chalcogenide glasses. Figure 1(a) shows the ESR spin density of As₂S₃ plotted versus illumination time. Figure 1(b) shows corresponding data for induced optical absorption. Optically thin samples were prepared by squeezing As₂S₃ at its softening temperature to a thickness of ~ 50 μ m. Illumination at 30 K by long exposures of absorbed light results in a spin density [Fig. 1(a)] and induced absorption [Fig. 1(b)] which increases steadily, and even after two hours has not reached complete saturation. The spin density (calculated assuming a homogeneous spin distribution) is nearly two orders of magnitude larger than that reported by Bishop, Strom, and Taylor.¹

Subsequently the spins (and the induced absorption) are bleached, either by sub-band-gap illumination or by annealing to 150 K. When the light

exposure is repeated under the same experimental conditions, ESR is again induced, but at a rate an order of magnitude faster than in the initial experiment. Provided the sample is not annealed substantially above 150 K, the bleaching and fast inducing experiments can be cycled repeatedly. However, prolonged annealing at room temperature or above restores the initial state of the material, and the complete illumination cycle is fully reversible. The different inducing rates cannot be explained by the changing absorption coefficient because of photodarkening. In fact, the reduced penetration means that the difference between the real inducing rates before and after bleaching may be substantially underes-

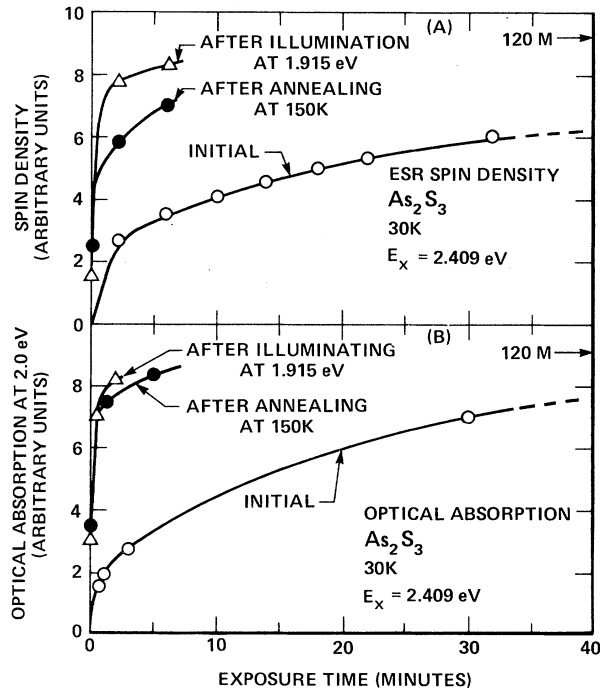


FIG. 1. (a) Induced ESR spin density vs exposure time. The arrow shows the result of a two-hour exposure. Data show that the initial inducing rate is different from the rate after bleaching. (b) Similar data for optical absorption measured at 2.0 eV.

timated and is at least as large as that shown in Fig. 1. Experiments confirm that the induced spin density depends on the total exposure (intensity \times time) independent of the actual intensity.

The data of Fig. 1 clearly show two distinct inducing mechanisms, corresponding to the fast and slow rates. The spin density N_S is the product of N_T , the density of centers, and f , the fraction which are singly occupied. Our interpretation of the fast rate is exactly that of Bishop, Strom, and Taylor,¹ namely, that photoexcited carriers are trapped at existing defects. Thus N_T is constant while f increases, reaching equilibrium in a short time. Again, as in Ref. 1, we interpret the bleaching as optical or thermal detrapping of the centers. Since f reaches saturation in a short time, the slow increase of spin density in the initial experiment must be interpreted as a light-induced increase in the defect density N_T . We therefore conclude that prolonged illumination causes structural damage which introduces specific defects into the glass.

Other experiments confirm this result. Figure 2 shows the induced ESR line shape for As_2S_3 and $Ge_{20}Se_{80}$. Here we use thick samples (~ 5 mm) and low-intensity, weakly absorbed light to reproduce the experimental conditions of Ref. 1. After annealing, we then use the same sample

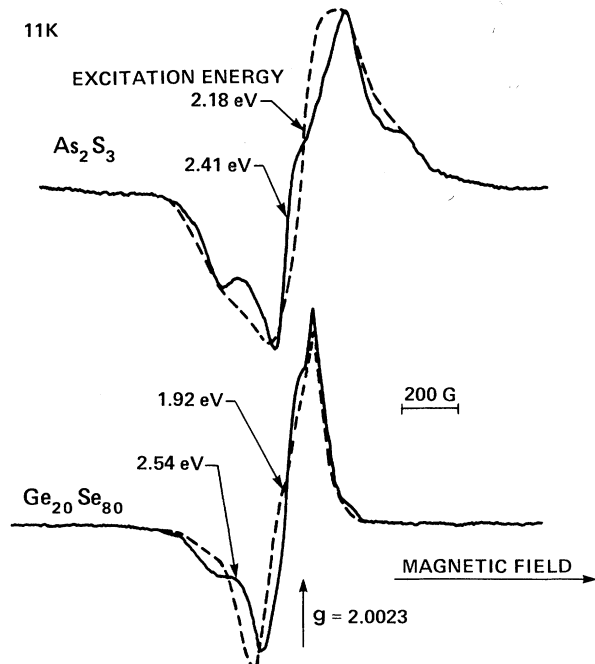


FIG. 2. ESR spectra of photoinduced defects (solid line) and native centers (dashed line).

and the excitation conditions of Fig. 1. The detailed shapes of the two resonances show conclusively that different ESR centers are involved in the two experiments. However, the general similarity of the g values and the overall linewidths suggests that the defects are generically related.

Figure 3 shows induced optical absorption data of As_2Si_3 . Two hours illumination with the same experimental conditions as in Fig. 1, broadens the absorption edge. Bleaching decreases the broadening, but the edge remains shifted to lower energy by ~ 0.2 eV. This shift is the well-known photodarkening effect⁵ which is reversed by annealing above room temperature. The extrinsic absorption is further confirmation of a large density of defect states in the gap. Comparison of Figs. 1(a) and 1(b) shows that the extrinsic absorption band is only associated with the singly occupied photoinduced defects. Figure 3 also shows the related absorption band of native defects observed in Ref. 1. Apart from the larger absorption strength, due to the higher density of photoinduced defects, the two absorption spectra have different shapes, clearly indicating different defects.

Figure 3 also shows published data of induced

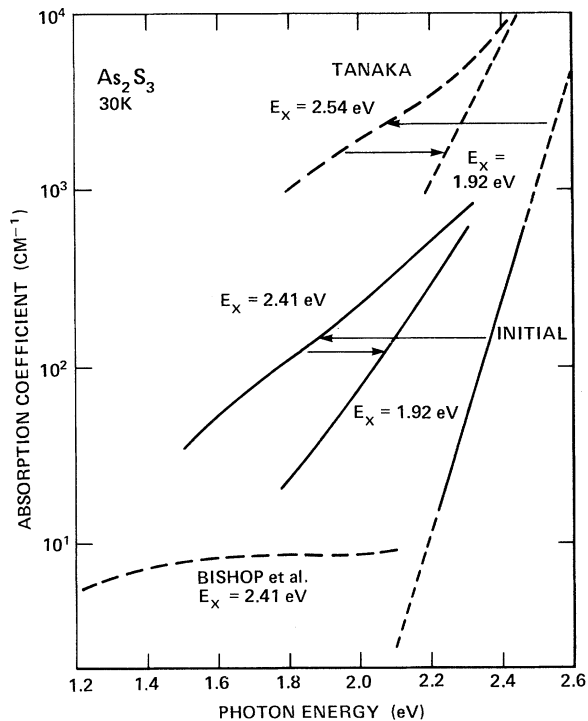


FIG. 3. Optical absorption data showing the initial absorption edge, the result of light exposure, and of subsequent bleaching.

absorption on evaporated and annealed As_2S_3 with higher energy illumination.⁵ The same absorption features are present. However, the extrinsic band has order-of-magnitude larger absorption coefficients, indicating a much larger density of photoinduced defects. Molloy, Cernogora, and Benoît à la Guillaume³ also report that the induced ESR spin density increases very rapidly with energy.

The following is a summary of the properties of the photoinduced defects:

(1) The photoinduced defect density is typically in the range 10^{18} – 10^{20} cm^{-3} , depending on the material, the illumination energy, and the total exposure.

(2) The photoinduced defect has an ESR spectrum, and therefore also an atomic structure, which is different from that of the native centers.

(3) In thermal equilibrium, the photoinduced defects contain only paired electrons (corresponding to the bleached condition). Metastable, singly occupied centers result from band-gap illumination. This behavior is identical to that for the native centers.

(4) The defects give localized electronic states in the gap. Evidence for this result is the extrinsic absorption and the metastability of the singly occupied defect. The threshold of extrinsic appears to be at higher energy than that of the native centers, indicating shallower electronic states. It is difficult to estimate the binding energy accurately because of probable distortion effects; however, the data suggest the range 0.2–0.5 eV.

(5) The photoinduced defects act as nonradiative recombination centers. Our evidence is the luminescence fatigue data shown in Fig. 4. After short light exposures, the fatigued luminescence can be restored almost to its initial value by annealing to 150 K. However, as the exposure is increased, and more photoinduced defects are created, the luminescence intensity decreases, and can no longer be restored by annealing to 150 K. Evidently a competing nonradiative process has been introduced. However, the initial state is recovered by annealing at room temperature.

(6) The photoinduced defects are a manifestation of the same physical mechanism that gives other reversible photostructural effects. Evidence for this assertion is that in each case similar light exposures are involved; the effects anneal in the same temperature range; and the photoinduced defects are always accompanied by photodarkening.

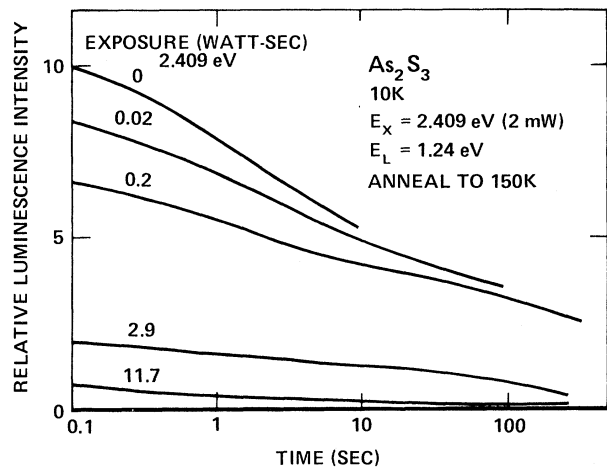


FIG. 4. Luminescence fatigue data, showing the effects of increasing exposures to absorbed light.

Our discussion of the microscopic origin of the photoinduced defects is based on its association with other photostructural effects, for which two models have been proposed. One model suggests that light irradiation modifies the structure without bond breaking,⁵ but this model cannot readily explain the presence of deep defect states. Alternative models are based on bond breaking.⁶ A specific model proposes that a bond is transferred from one chalcogenide atom to another, resulting in a defect comprising a singly coordinated and a neighboring triply coordinated chalcogen.⁴ The creation of such defect pairs was thought to be predominantly a transient process, corresponding to the nonradiative deexcitation of a self-trapped exciton. However, occasionally the defect is metastable, possibly because the pair diffuses apart a small distance, and this was thought to explain the photostructural effects. The defects are close pairs of the D^+ and D^- (C_3^+ and C_1^-) centers that are believed to be the native defects in chalcogenides. D^+D^- pairs have been analyzed in some detail.^{4,7-9}

We now demonstrate that the observed electrical and optical properties of the photoinduced defects agree well with the D^+D^- pair model. From the assumption of a negative correlation energy,^{2,7} the spinless D^+D^- configuration is the ground state of the defect, in agreement with the observation of no ESR in the bleached state. Optical excitation of an electron-hole pair at a D^+D^- pair

may cause one of three possible transitions:

$$D^+D^- \xrightarrow{h\nu} D^+D^0 + \text{free electron}, \quad (1)$$

$$D^+D^- \xrightarrow{h\nu} D^0D^- + \text{free hole}, \quad (2)$$

$$D^+D^- \xrightarrow{h\nu} D^0D^0 \rightarrow D^+D^-. \quad (3)$$

Escape of the free carrier in process (1) and (2) leaves two possible singly occupied defects resulting in induced ESR. Process (3) is expected to result in a rapid nonradiative transition to the ground state as described elsewhere.⁹

The metastable singly occupied defects of transitions (1) and (2) can be bleached either optically [Eq. (4)] or by thermal excitation [Eq. (5)]:

$$D^+D^0 (D^0D^-) \xrightarrow{h\nu} D^+D^- + \text{hole (electron)}, \quad (4)$$

$$D^+D^0 + D^0D^- \xrightarrow{\text{phonons}} 2D^+D^-. \quad (5)$$

Essentially identical processes explain the similar bleaching properties of the native defects.⁹ Process (4) also accounts for the extrinsic optical absorption. Lattice distortion effects associated with negative correlation energy centers ensures that the reverse optical transitions (1)–(3) have thresholds at higher energies, as for the isolated D^+ and D^- ,² and in agreement with the present observations of Fig. 3. It seems plausible that transitions (1)–(3) are responsible for photo-darkening, but we do not yet have confirmation of this.

The pairing of defects modifies the electronic energy levels. Vanderbilt and Joannopoulos⁸ find that the electron-trap and hole-trap states are shallower than the corresponding states of the isolated defects. The same result is obtained by considering only the effects of the Coulomb interaction of the defect pair.¹⁰ Thus our conclusion that the singly occupied photoinduced defect has a smaller binding energy than the native defects is consistent with the D^+D^- model. Furthermore,

the additional structure in the ESR spectra is at least qualitatively consistent with a splitting of the D^0 resonance, since from charge neutrality we expect equal densities of D^+D^0 and D^0D^- .

However, the ESR data are complicated in alloy glasses, because several different atomic configurations for the D^+D^- defect are possible.¹¹

In summary, we have observed new defect states in chalcogenide glasses and have described their basic properties. The defects are induced by long exposures to absorbed light and have properties fully consistent with the model of D^+D^- pairs.

¹S. G. Bishop, U. Strom, and P. C. Taylor, Phys. Rev. Lett. **34**, 1346 (1975), and Phys. Rev. B **15**, 2278 (1977), and references therein.

²R. A. Street and N. F. Mott, Phys. Rev. Lett. **35**, 1293 (1975).

³F. Mollot, J. Cernogora, and C. Benoît à la Guillaume, in Proceedings of the Eighth International Conference on Amorphous and Liquid Semiconductors, Cambridge, Massachusetts, 27–31 August 1979, edited by W. Paul (to be published).

⁴R. A. Street, Solid State Commun. **24**, 363 (1977).

⁵K. Tanaka, in *Structure and Excitation of Amorphous Solids*, edited by G. Lucovsky and F. L. Galeener, AIP Conference Proceedings No. 31 (American Institute of Physics, New York, 1976), p. 148.

⁶J. P. deNeufville, in *Optical Properties of Solids, New Developments*, edited by B. O. Seraphin (North-Holland, Amsterdam, 1976), Chap. 9.

⁷M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. **37**, 1504 (1976).

⁸D. Vanderbilt and J. Joannopoulos, Phys. Rev. Lett. **42**, 1012 (1979).

⁹R. A. Street, Phys. Rev. B **17**, 3984 (1978).

¹⁰R. A. Street, in *Physics of Semiconductors*, edited by B. L. H. Wilson, The Institute of Physics Conference Series No. 43 (The Institute of Physics, Bristol and London, 1979), p. 1291.

¹¹M. Kastner and H. Fritzsche, Philos. Mag. **37B**, 199 (1978).