

Comment on "Gravitationally Induced Density Gradients near the Liquid-Liquid Solution Point"

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(Received 21 July 1975)

Dickinson, Knobler, Schumaker, and Scott have incorrectly interpreted the experimental results of Hildebrand, Alder, Beams, and Dixon. The latter work is shown to be untroubled by turbulence and to remain consistent with a density-fluctuation interpretation.

Dickinson, Knobler, Schumaker, and Scott¹ report a mathematical analysis of the rate of concentration-gradient formation in liquid mixtures near the critical solution point. They predict that a density inversion can occur a few degrees above T_c at high gravitational fields; they also note that turbulence associated with the inversion would give the appearance of a phase separation. They conclude that Alder, Hildebrand, Beams, and Dixon² observed this turbulence phenomena and not a true phase separation.

The purpose of the Comment is to show that the observations of Alder *et al.* were not related to turbulence and to reassert that interpretation in terms of density fluctuations is valid. The validity of the mathematical approach used by Dickinson *et al.* will not be considered.

Alder *et al.* used a turbulence-sensitive Philpot-Svensson-Schlieren optical system for their measurements. Turbulence was observed when

the rotor (centrifuge) speed was increased but it ceased when the rotor speed was held constant for a few minutes. Thus, there is no reason to believe that a turbulence-caused "phase separation" was observed rather than a true phase separation.

Hildebrand and Lamoreaux³ presented further evidence supporting a density fluctuation model. In view of this, there is no reason, at this time, to suspect that the density-fluctuation interpretation given by Alder *et al.* needs modification.

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Optically Induced Localized Paramagnetic States in Amorphous Semiconductors

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(Received 20 November 1975)

In addition to the previously reported paramagnetic hole center localized on the chalcogen, a conjugate optically induced electron center localized on an As atom is observed in glassy As_2S_3 and As_2Se_3 . The chalcogen center is further identified as a hole localized in a nonbonding p orbital. These optically induced centers are unique to the amorphous phase, and their density saturates at or below 10^{17} spins/cm³.

Recently we reported the first observation of optically induced localized paramagnetic states in the forbidden gap of chalcogenide glasses¹ and amorphous arsenic (α -As).² It was found that low-temperature irradiation of chalcogenide glasses such as As_2S_3 , As_2Se_3 , and Se with photon energies corresponding to the Urbach tail in the absorption edge (absorption coefficient ≈ 100 cm⁻¹)

produces an electron spin resonance (ESR) which is not present in the cold dark. An associated induced midgap optical absorption demonstrates that the paramagnetic states are located in the forbidden gap of these glasses. Analysis of the ESR spectra led to the conclusion that the paramagnetic centers in the chalcogenide glasses are holes localized on chalcogens.

In this Comment we present the results of further optically induced ESR studies of arsenic chalcogenide glasses which provide a more detailed description of the hole center on the chalcogen and reveal a previously unobserved optically induced paramagnetic electron center localized on the As atoms. In addition, we report that these optically induced ESR centers are not observed in crystalline chalcogenides (As_2S_3 and As_2Se_3) and that there is a saturated density of stable paramagnetic centers which can be optically induced in the glasses regardless of light intensity. Finally, specific models³ for the optically induced, localized ESR centers in As_2Se_3 , As_2S_3 , Se, and As are discussed in terms of supporting evidence from both ESR and photoluminescence (PL) experiments.

In Ref. 1 the paramagnetic centers were assumed to be localized and were identified as holes on the basis of the measured g values. The observed linewidths of the resonances in As_2Se_3 and As_2S_3 were shown to be too small to be consistent with a hole localized on an As atom and led to the conclusion that the holes were localized on chalcogens. In Ref. 2, all of the optically induced effects reported for chalcogenide glasses were reported for a -As. As expected, the optically induced ESR spectrum in a -As is much broader (see Fig. 1) than those observed in the chalcogenide glasses. Analysis of the ESR line shape in a -As indicated that the center is highly localized, probably on a single As atom, and that the unpaired spin exists predominantly (95%) in a p orbital with $\sim 5\%$ admixture of s orbital spin density.

We have repeated the optically induced ESR experiments on glassy As_2S_3 , As_2Se_3 , and Se with an improved, variable-temperature experimental system and obtained the spectra shown in Fig. 1. Our present results demonstrate that the optically induced ESR spectra are stable and can be induced and bleached at temperatures as high as 80 K. The experimental procedures, inducing wavelengths, etc., are identical to those discussed in Refs. 1 and 2. All three chalcogenide-glass spectra in Fig. 1 exhibit the relatively narrow resonances originally presented in Ref. 1, but in addition the As_2S_3 and As_2Se_3 spectra show a second broader resonance which is not present in the Se spectrum (Fig. 1). Comparison of the As_2S_3 and As_2Se_3 spectra with that for a -As indicates that the second broader resonance is attributable to paramagnetic centers localized on As atoms. In the As_2S_3 spectrum, the central peaks

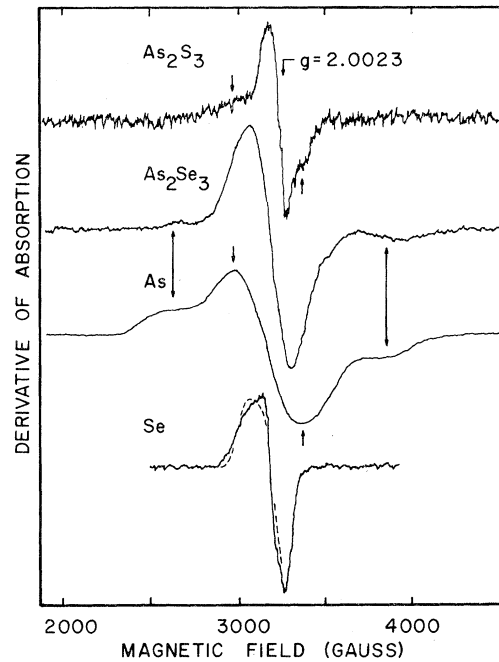


FIG. 1. Optically induced ESR spectra in chalcogenide glasses and a -As. Dashed line superimposed on Se curve is a computer simulation.

of the As-center spectrum near 3000 and 3400 G (see arrows) are clearly resolved as shoulders on the narrower sulfur-hole-center resonance; the ESR signal in the As_2S_3 glass was not sufficient to reveal the low- and high-field shoulders of the As-center spectrum which occur near 2500 and 4000 G, respectively. In the case of glassy As_2Se_3 , the shoulders near 2500 and 4000 G (arrows) are clearly visible. In fact, the As_2Se_3 spectrum can be approximated closely by a properly weighted sum of the a -As spectrum and the glassy Se spectrum.

Since the glassy Se ESR spectrum contains no broad, underlying resonance, one can reliably extract the principal components of the g tensor for the hole center by standard powder-pattern techniques.⁴ A computer-simulated fit, indicated by the dashed line in Fig. 1, yields values for the principal components of the g tensor ($g_1 = 2.00$, $g_2 = 2.03$, $g_3 = 2.14$ with an error of ± 0.02). Although the underlying As-center resonance complicates similar measurements for the chalcogen center in As_2Se_3 glass, principal values of the g tensor identical to those determined for Se are consistent with the experimentally observed line shape. In As_2S_3 glass the corresponding g values are estimated to be 2.00, 2.02, and 2.07 (± 0.02).

The optically induced localized paramagnetic

states are not observable in either synthetic crystals of As_2Se_3 or natural crystals of As_2S_3 (orpiment). Experiments carried out under conditions for which $\sim 10^{17}$ spins/cm³ were observed in glassy As_2Se_3 and As_2S_3 set a limit of $\leq 10^{16}$ spins/cm³ for the highly pure As_2Se_3 crystals and a limit of $\leq 5 \times 10^{16}$ spins/cm³ for the rather impure orpiment crystals. There is clearly some structural characteristic or property *unique to the disordered phase* which is responsible for both the optically induced localized paramagnetic states and the fatigue of the PL⁵⁻⁷ (PL fatigue is also not observed in synthetic crystals of As_2Se_3 and $\text{As}_2\text{Se}_{3-x}\text{S}_x$).⁸

In Ref. 1 we mentioned the apparent saturation of the density of stable, optically induced ESR centers which could be generated with 1 mW/cm² of illumination intensity at a wavelength whose penetration depth is ≈ 100 μm . Subsequent measurements on glassy Se using ~ 5 W/cm² of deeply penetrating (~ 1 mm) light ($\lambda = 6328$ \AA) confirm this saturation behavior. Although the high-intensity, deeply penetrating light yields a much stronger ESR signal since it excites a much larger sample volume, the optically induced spin density for Se is $\sim 10^{16}$ spins/cm³ in both measurements. Similar saturation behavior was observed in As_2Se_3 using only 1 mW/cm² of illumination intensity, but the saturated value was $\sim 10^{17}$ spins/cm³ for this material. The occurrence of saturation implies that there is some concentration of "defects" or other structural features which determines the saturated density of optically induced paramagnetic centers.

The observed deviations Δg_i of the three principal values of the hole-center g tensor from the free-electron value g_0 ($\Delta g_i = g_i - g_0$) were found¹ to scale with the S and Se spin-orbit coupling constants, λ . This would be expected under equivalent bonding configurations for a paramagnetic center located on the chalcogen in the sulfide and selenide glasses. The following extension of these arguments (concerning Δg_1 scaling with λ) to oxide glasses allows us to conclude that the hole center on the chalcogen is localized in a nonbonding (lone pair) p orbital.

The Δg_i are proportional to $\lambda \sum_j \Delta E_{ij}^{-1}$, where the ΔE_{ij} are energy differences between the ground state of the paramagnetic hole and those excited states which are admixed by the spin-orbit interaction. If the ground state of the hole is known, the excited states which are admixed can, in principle, be determined from photoemission data. The photoemission data indicate that the

valence-band densities of states for O in SiO_2 ,⁹ S in As_2S_3 , and Se in Se and As_2Se_3 ¹⁰ are quite similar in the following respects: (1) The highest-lying level is a nonbonding p orbital (lone pair); (2) the entire upper portion of the valence band is p -like with essentially no s admixture; (3) the energy differences between resolved valence-band peaks are comparable (within a factor of 2). In borate and silicate glasses, where γ - and x-ray induced paramagnetic centers have been studied extensively, an oxygen hole center has been observed with spin-Hamiltonian parameters similar to those of the optically induced hole centers on S and Se in the chalcogenide glasses. This center has been identified as a hole localized on a nonbonding (lone pair) oxygen p orbital.¹¹ If the hole centers observed in the oxides and chalcogenides are indeed located in the same type of orbital on the O, S, and Se atoms, then the photoemission data indicate that the sums over excited states $\sum_j \Delta E_{ij}^{-1}$ should be comparable to first order for all three elements (i.e., the local bonding configurations are essentially equivalent), and the Δg_i should scale with λ in all three cases. The comparative sizes of λ for Se (~ 1700) and O (~ 150)¹² predict values of Δg_i for an equivalent hole center in an oxide glass roughly one order of magnitude less than those observed in Se glass. The radiation-induced paramagnetic hole centers in borate and silicate glasses exhibit a maximum Δg_i of 0.02 ± 0.01 ,¹¹ which is very nearly the predicted factor of 10 less than the value 0.14 observed for the optically induced hole center in Se.

Since the values of Δg_i for the hole centers in oxide, sulfide, and selenide glasses meet the rather severe test of scaling with λ for variations of an order of magnitude, it is concluded that the most plausible description of the optically induced paramagnetic hole center in the chalcogenide glasses is an electron missing from a nonbonding chalcogen p orbital.

Our knowledge of the conjugate localized hole and electron centers in the chalcogenide glasses is now sufficient to allow us to categorize those simple models which will explain the data. All such models must incorporate the restriction that there be essentially no overlap between the wave functions of the paramagnetic hole and the As atoms. The simplest model assumes an "ideal" glass structure with no dangling bonds or homo-bonds (for example S-S) (ideal-glass model). In this picture the hole center is formed by optically removing an electron from the normally

filled nonbonding chalcogen orbital, and the electron center in As_2Se_3 and As_2S_3 is formed by adding an electron to a fourth nonbonding As orbital.

A second simple interpretation allows for the existence of dangling bonds but no homo-bonds (dangling-bond model). In this model the dangling bonds are either doubly occupied or unoccupied in the cold dark in order to be consistent with the observed diamagnetism of the glasses.^{3,13} This model has the property of incorporating charged centers in the cold dark. The most likely optically induced ESR centers (consistent with the data) are then holes on chalcogen dangling-bond orbitals and electrons on As dangling bonds. Here one must make the logical assumption that the singly occupied dangling-bond orbital, which is normally bonding, is similar to a nonbonding orbital in order for the g -tensor scaling arguments described above to remain valid. One cannot rule out the possibility that, while dangling bonds may be essential for the optical production of paramagnetic centers, one or both of the centers described in the ideal-glass model might still represent the correct interpretation of the observed ESR spectra.

Although the obvious simplicity of the ideal-glass model is attractive, the apparent requirement of charged centers in the cold dark to explain the luminescence data⁵ lends support to the dangling-bond model. Street, Searle, and Austin⁵ have suggested that in arsenic chalcogenide glasses an estimated 10^{17} cm^{-3} dangling As bonds serve as charged radiative recombination centers in the vicinity of which optical absorption is enhanced. Since the estimated densities of recombination and (saturated) ESR centers⁴ are roughly equivalent in As_2Se_3 , and since the growth of the optically induced ESR signal is known to parallel the progressive "fatigue" (decay during continuous excitation)⁵⁻⁷ of the PL, the obvious suggestion first stated in Ref. 1 is that the radiative recombination centers which become inactive in the PL fatiguing process are closely associated with the growing ESR intensity^{1,2} and midgap optical absorption.^{1,2,6} For example, during optical excitation a negatively charged diamagnetic recombination center can be neutralized and rendered paramagnetic by the capture of a hole. If the nearby electron tunnels away instead of recombining radiatively with the trapped hole, the center is left in a metastable paramagnetic state which, since it is now neutral, no longer enhances absorption and is removed from the radiative recombination channel (i.e., it is fatigued).

This mechanism is precluded in the crystalline phase because of the higher electron and hole mobilities.

Street and Mott³ have recently proposed a more detailed model of localized gap states in chalcogenide glasses based on specific dangling-bond configurations. A positively charged recombination center consists of an unoccupied dangling bond (D^+) which interacts with the nonbonding lone pair of a neighboring fully bonded chalcogen; the negatively charged center consists of a doubly occupied dangling bond (D^-) which forms a valence-band-like lone pair. The optically induced, metastable ESR centers (D^0) are explained by these authors as the trapping of free electrons or holes by these charged centers. This model considers only one specific type of defect which can be unoccupied (D^+), singly occupied (D^0), or doubly occupied (D^-), while it is now obvious that the observed ESR spectra in As_2Se_3 and As_3S_3 require two rather specific types of D^0 , a hole on a chalcogen and an electron on an As atom. It is also unclear how the model relates to amorphous As where there is no conclusive evidence for the existence of nonbonding p -type lone-pair wave functions.

We conclude on the basis of the ESR spectra that the most probable description of the optically induced paramagnetic hole center in the chalcogenide glasses is an electron missing from a nonbonding chalcogen p orbital. In the arsenic chalcogenides, the ESR spectra also provide evidence for a conjugate electron center predominantly localized on an As p orbital. The observed saturation of the density of optically induced paramagnetic centers implies that there is some concentration of structural features or defects in the glass which determines an upper limit on the density of these centers. While these features may be related to the dangling As bonds proposed as radiative recombination centers in both glassy and crystalline arsenic chalcogenides, the structural or electronic characteristic which is essential to the *production* of the optically induced localized paramagnetic states is apparently unique to the amorphous phase.

The authors gratefully acknowledge valuable experimental contributions by E. J. Friebele and many helpful discussions with D. L. Mitchell.

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