(1974)].
[3]S. M. Girvin and G. D. Mahan, Phys. Rev. B 20, 4896 (1979).
[4]Y. Inaba, J. Phys. Soc. Jpn. 50, 2473 (1981), and the references cited therein.
[5]E. A. Novikov, Zh. Eksp. Teor. Fiz. 47, 1919 (1964) [Sov. Phys. JETP 20, 1990 (1965)].
[6]C. Zener, Proc. Roy. Soc. London 145, 523 (1934).
[7]R. Benguria and M. Kac, Phys. Rev. Lett. 46, 1 (1981).

Exciton and Pair Recombination at Intimate Valence-Alternation Pairs in a-As_2S_3

S. P. Depinna and B. C. Cavenett
Physics Department, The University of Hull, Hull HU6 7RX, United Kingdom

(Received 14 July 1981)

Optically detected magnetic resonance in a-As_2S_3 has shown that the emission consists of a high-energy triplet exciton recombination overlapping a low-energy pair process. The results are consistent with recombination at axial defects such as (D^+, D^-) intimate valence-alternation pairs.

PACS numbers: 71.35.+z, 71.55.Jv, 76.70.Hb, 78.55.Ds

The observation of light-induced EPR signals in a-As_2S_3 by Bishop, Strom, and Taylor[1,2] was an important step forward to the understanding of the defects which occur in this and related materials since the measurements were consistent with the Mott-Davis-Street model[3] which postulated the existence of D^+ and D^- diamagnetic centers in the dark. The EPR results showed that if a hole is localized near a sulphur atom, then a narrow EPR signal is observed, whereas an electron localized at an arsenic atom is characterized by a much broader resonance due to the arsenic nuclear spin ($I=\frac{3}{2}$). These signals were assigned to the isolated defects D^+ and D^- capturing holes and electrons, respectively, and it has been generally assumed that these centers are the native defects in a-As_2S_3. More recently Biegelsen and Street[4] reexamined the photoinduced EPR in the light of measurements by Mollot, Cernogora, and Benoît à la Guillaume[5] on Ge_xSe_{1-x} glasses and showed that spin densities of $\sim 10^{20}$ cm^{-3} can be induced by light in As_2S_3. These new measurements suggested that there are two sets of defects, the isolated "native" defects and the photoinduced defects, which Biegelsen and Street[4] suggested were due to (D^+, D^-) pairs that can capture either an electron or a hole, inducing paramagnetism and midgap absorption. Luminescence in a-As_2S_3 was first reported by Kolomiets, Mamontova, and Babaev[6] and the generally accepted recombination model proposed by Street[7] suggests that the luminescence observed at ~ 1.2 eV involves hole capture at a D^- center followed by electron-hole recombination involving a tail-state electron, i.e. $(D^0, e^-) \rightarrow D^-$. However, recent time-resolved spectroscopy (TRS) measurements by Street,[8] Bosch and Shah,[9] and Higashi and Kastner[10] are far from agreement. The only consistent pattern in these studies is that at longer delay times there is a shift of the emission to lower energies. In fact, Bosch and Shah[9] have observed two emission components, one at high energy, with short lifetime, and a second longer-lived band at lower energy. In analogy with recent TRS[11] and optically detected magnetic resonance[12] measurements in amorphous phosphorus (a-P), this suggests that the high-energy emission is excitonic, and that the low-energy emission is a pair process (contrary to a-P, where triplet exciton recombination occurs at low energies). We have explored the link between the luminescence and the identity of the defects by optically detected magnetic resonance, and report in this paper triplet and pair optically detected magnetic resonance signals which confirm that the luminescence in a-As_2S_3 is due to exciton and pair recombination, where the high-energy region is principally exciton emission. We propose that the magnetic and optical properties of a-As_2S_3 can be attributed to (D^+, D^-) pairs alone.

The photoluminescence (PL) at 2 K induced by excitation above the band gap is a broad, featureless band centered at ~ 1.2 eV, and we show a typical PL spectrum, measured with a Ge detector, in Fig. 1(a). The effect of exciting below

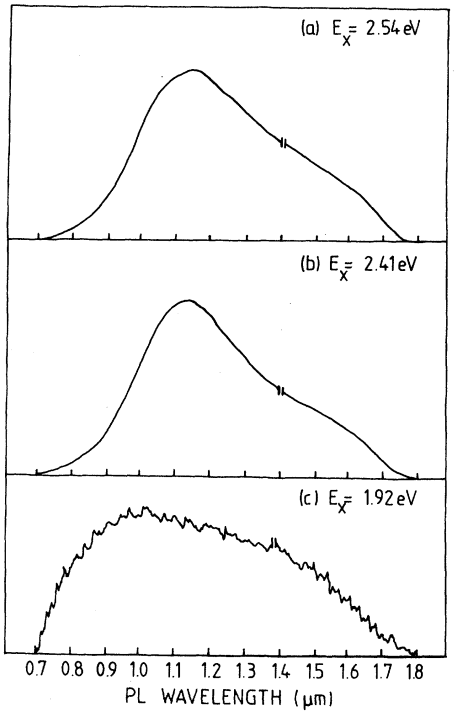

FIG. 1. Uncorrected photoluminescence spectra of a-As_2S_3 at 2 K, with use of a germanium detector, for excitation energies (E_x) above and below the optical gap. (a) E_x = 2.54 eV, (b) E_x = 2.41 eV, and (c) E_x = 1.92 eV.

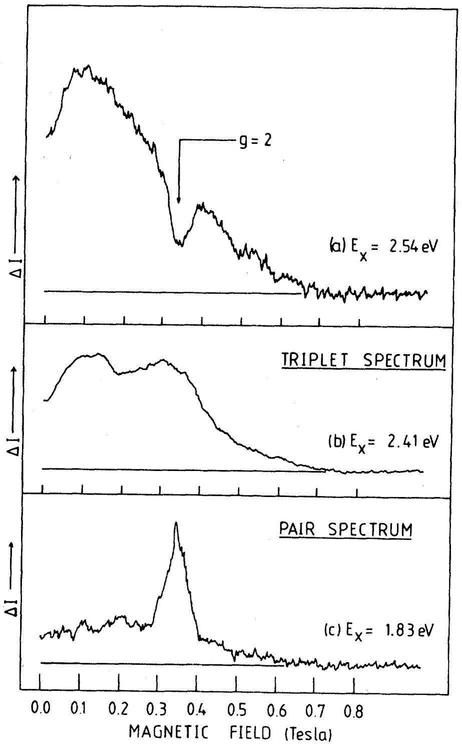

FIG. 2. X-band (9 GHz) optically detected magnetic resonance signals in a-As_2S_3 for various excitation energies (E_x): (a) E_x = 2.54 eV, (b) E_x = 2.41 eV, and (c) E_x = 1.83 eV.

the optical gap is shown in Fig. 1(c), for $E_x = 1.92$ eV. The PL spectrum is observed to broaden significantly, particularly towards higher energy, suggesting that selective excitation is enhancing a weak PL feature which normally underlies the main 1.2 eV band. The optically detected magnetic resonance measurements (see Cavenett[13] for a review) were carried out at 9 GHz, using the Ge detector, and observing total PL, and Fig. 2(a) shows the optically detected magnetic resonance spectrum for excitation above band gap ($E_x = 2.54$ eV). The spectrum is composed of two components—a broad line, characteristic of an $S = 1$ triplet, which is a resonant increase in PL intensity, and a narrower ($\Delta H_{\mathrm{FWHM}} \sim 60$ mT) resonant decrease in I_{PL}, near $g = 2$. Exciting with laser radiation at successively lower energies [2.41 eV, Fig. 2(b); 1.83 eV, Fig. 2(c)] results in a gradual disappearance of the triplet optically detected magnetic resonance spectrum, while the narrow $g = 2$ line changes sign and eventually becomes the dominant feature. A detailed discussion of the origin of the triplet spectrum can be found elsewhere.[12] Essentially, an electron-hole pair with $S = 1$, localized at an axial defect, has the energy scheme in a magnetic field shown in the inset of Fig. 3. If the triplet is unthermalized, the population differences between the levels are determined by the different PL decay rates, $R1$, R_0, and R_{-1}. Three resonances can occur, for a given triplet orientation: two $\Delta m_s = \pm 1$ and one $\Delta m_s = \pm 2$, as indicated in the figure. The latter has a resonant field position which is only weakly dependent on the zero-field splitting D, in this simple model. Therefore, when one considers a distribution of all orientations of the defect axis with respect to the magnetic field axis, the anisotropic $\Delta m_s = \pm 1$ transitions sum to a broad signal centered around $g_\parallel \sim g_\perp = 2$, and the $\Delta m_s = \pm 2$ transitions give a characteristic low-field resonance, near an effective $g = 4$. Thus, the signal in Fig. 2(b) is consistent with radiative electron-hole (exciton) recombination. We note that Murayama, Suzuki, and Ninomiya[14] have previously reported a broad, featureless optically detected magnetic resonance near $g = 2$ in a-As_2S_3, but could provide no identification of the mechanism involved.

The optically detected magnetic resonance results of Fig. 2 suggest that at least two distinct components are responsible for the steady PL, one of which is related to exciton emission, and another which is related to pair emission, and gives the $g=2$ optically detected magnetic resonance doublet, consistent with the general observation that enhancing ($\Delta I>0$) optically detected magnetic resonance signals are observed for an unthermalized pair process.[13] Excitonic recombination is preferentially excited by above-band-gap illumination, while the pair emission can be selectively excited by below-gap irradiation as in Fig. 2(c). The comparison with our previous study of a-P[12] is indeed striking, as precisely analogous results have been observed for both materials—the only important difference in terms of observing the signals is that in a-As_2S_3 the spectral regions relating to the pair and exciton resonances are more overlapping, and cannot be separated as clearly as in a-P. For a-As_2S_3, the results suggest that the high density of excitation associated with above-gap illumination is responsible for the increased probability of exciton formation for $E_x \gtrsim 2$ eV. For below-gap excitation, the low free carrier density should result in a predominance of distant-pair emission, also in agreement with the optically detected magnetic resonance results. The observation of a quenching pair resonance on the exciton optically detected magnetic resonance spectrum [Fig. 2(a)] suggests that a strong linking between these emissions exists, such as would be expected where both pair and exciton emissions take place at the same intrinsic defects. Thus, after capture of a single carrier at a defect, recombination can take place either through pair interaction with a carrier trapped at a second distant defect, or through trapping of a second carrier at the same defect, resulting in the formation of a bound exciton. Increasing the pair emission rate through resonance at either defect will therefore reduce the probability of exciton formation, explaining the negative pair resonance superimposed on the exciton optically detected magnetic resonance spectrum. However, exciton resonance only increases the exciton emission rate, and does not directly influence the pair rate.

These considerations suggest that the defects responsible for the luminescence must be capable of involvement in either a pair or exciton emission. The isolated defects D^+ and D^- seem unlikely candidates in this case, since Street[15] suggests that excitons will not be formed at isolated D^- centers as it is expected that the capture of the second carrier will be radiative, as discussed above. Although at this stage of the investigation one cannot rule out exciton recombination at isolated defects, it is clear that the intimate valence-alternation pair (IVAP) centers[16] consisting of nearest-neighbor (D^+, D^-) pairs are ideal candidates for binding either one or two carriers as required. The recombination processes are these:

Pairs

Capture	$(D^+,D^-)+e^-\rightarrow(D^0,D^-)$;
	$(D^+,D^-)+h^+\rightarrow(D^+,D^0)$
Recombination	$(D^+,D^0)+(D^0,D^-)\rightarrow 2(D^+,D^-)+h\nu_{\text{pair}}$

Exciton

Capture	$(D^+,D^-)+e^-\rightarrow(D^0,D^-)$;
	$(D^0,D^-)+h^+\rightarrow(D^+,D^-)^{\text{exc}}$
Recombination	$(D^+,D^-)^{\text{exc}}\rightarrow(D^+,D^-)+h\nu_{\text{exciton}}$

By analogy with crystalline materials, the localization of an exciton at the isoelectronic (D^+, D^-) center is highly probable, and the model is consistent with the observed optically detected magnetic resonance results.

An interesting difference is expected between binary materials, such as a-As_2S_3, and unary materials such as a-P, since in the former case, two inequivalent (D^+, D^-) defects are possible, while in the latter case, only one kind of IVAP can be formed. In fact, whereas in a-P the optically detected magnetic resonance triplet spectrum can be well fitted by a simple model involving a single $S=1$ center,[12] our attempts to produce a similar fit assuming a single axial center for the spectrum in Fig. 2(b) have been unsuccessful. However, the results are consistent with the proposal that at least two varieties of triplets may be involved, both with g value near 2 and $D \sim 0.1$ cm^{-1}, corresponding to excitons bound at (As^+, S^-) and (S^+, As^-) centers, respectively.

In general, when PL emission occurs from a triplet ($S=1$) state, a nonresonant increase in the emission intensity is expected in a magnetic field, when the $m_s=0$ Zeeman level crosses either the $m_s=+1$ or the -1 level (see the inset in Fig. 3). The "level crossing" experiment is thus a sensitive indicator of the presence of triplet emission.[13] In As_2S_3, the details of the magnetic field dependence of the luminescence intensity are complicated and the results depend on the

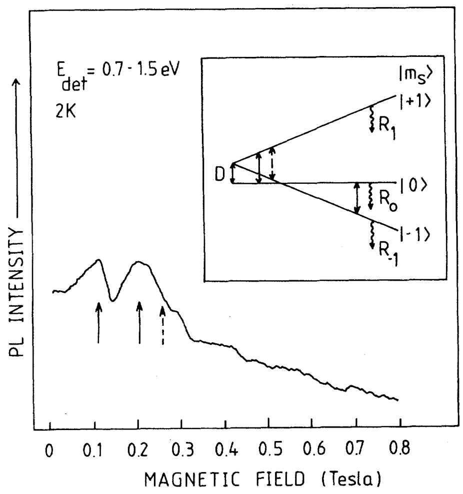

FIG. 3. "Level-crossing" increases in luminescence intensity observed in a magnetic field (without microwave excitation) for a-As_2S_3. The positions of the level crossings are indicated by arrows. Inset: Energy levels of a triplet exciton ($S = 1$) bound at an axial defect for magnetic field parallel to the defect axis.

sample illumination history. However, we have observed two resolved "level crossings," occuring near 0.12 and 0.2 T, in confirmation of the suggestion that more than one triplet exciton is present in a-As_2S_3. An example of the level crossings is shown in Fig. 3.

In order to test the conclusions from the optically detected magnetic resonance results, we should make a comparison with the TRS measurements. In particular, the pair emission peak for recombination at distant IVAP's should shift slightly to higher energy with increasing delay, if the Coulombic interaction is sufficiently strong, while no time shift at all would be expected for recombination involving one IVAP and one isolated D^+ or D^- (or one IVAP and one VAP). As discussed above, there is general agreement with the lifetime measurements from the published TRS studies,[8-10] but, for a detailed comparison, these results must be analyzed taking into account the existence of several distinct emission processes.

In conclusion, the optically detected magnetic resonance results have shown that the recombination processes in chalcogenide glasses must be reconsidered. The observation of triplet and pair resonance shows that the exciton and pair recombination involving two related defects accounts for the emission in As_2S_3. The results are consistent with recombination at near-neighbor (D^+, D^-) pairs: At this stage the role of the isolated defect is unclear. In fact, since the photoinduced structural changes have been attributed to the formation of (D^+, D^-) pairs, and now the luminescence can be assigned to similar pairs, with the possibility of metastable triplet states,[2] we are drawn to the conclusion that the IVAP is the fundamental recombination defect in pnictide glasses.

We are grateful to Professor E. A. Davis and Dr. G. Fasol for discussing their TRS measurements before publication, and to Dr. Austin and Dr. Searle for providing the samples on which the measurements were performed. One of us (S.P.D.) is grateful to Science Research Council for a research assistantship, and we are grateful to Science Research Council for financial support of this program.

---

[1] S. G. Bishop, U. Strom, and P. C. Taylor, Phys. Rev. Lett. 34, 1346 (1975).

[2] S. G. Bishop, U. Strom, and P. C. Taylor, Phys. Rev. B 15, 2278 (1977).

[3] N. F. Mott, E. A. Davis, and R. A. Street, Philos. Mag. 32, 961 (1975).

[4] D. K. Biegelsen and R. A. Street, Phys. Rev. Lett. 44, 803 (1980).

[5] F. Mollot, J. Cernogora, and C. Benoît à la Guillaume, J. Non-Cryst. Solids 35-36, 939 (1980).

[6] B. T. Kolomiets, T. N. Mamontova, and A. A. Babaev, J. Non-Cryst. Solids 4, 289 (1970).

[7] R. A. Street, Adv. Phys. 25, 397 (1976).

[8] R. A. Street, Solid State Commun. 34, 157 (1980).

[9] M. A. Bosch and J. Shah, Phys. Rev. Lett. 42, 118 (1979).

[10] G. S. Higashi and M. Kastner, J. Non-Cryst. Solids 35-36, 921 (1980).

[11] G. Fasol and E. A. Davis, to be published.

[12] S. P. Depinna and B. C. Cavenett, to be published.

[13] B. C. Cavenett, to be published.

[14] K. Murayama, H. Suzuki, and T. Ninomiya, J. Non-Cryst. Solids 35-36, 915 (1980).

[15] R. A. Street, Phys. Rev. B 17, 3984 (1978).

[16] M. Kastner, D. Adler, and H. Fritzche, Phys. Rev. Lett. 37, 1504 (1976).