AD-A127 686 OPTICAL DETECTION OF ELECTRON SPIN RESONANCE IN COMPOUND SEMICONDUCTORS(U) TRINITY COLL DUBLIN (IRELAND) PHYSICAL LAB B HENDERSON 31 MAR 82 1/1

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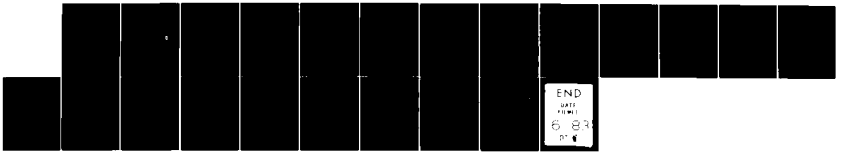

yet been identified. However the results are decisive since they imply that isolated, substitutional Cr ions cannot be involved. The [111] defect system seems likely to be a Cr^{2+} - vacancy pair.

ii) Recombination luminescence in GaAs:An

Laser excitation leads to recombination luminescence with band peaks near 1.45-1.51 eV: of the three bands the one near 1.51 eV seems to be due to band-to-band transitions. There are two broad ODMR lines at g = 1.81 and g = 0.6: the former is observed on each of the luminescence bands at 1.447 eV, 1.487 eV and 1.510 eV. This resonance is identified as an electron combining at a shallow acceptor; whereas the high field line (g = 0.6) is associated with a free electron resonance.

5. Triplet excitons in $GaSe_xS_{1-x}$

Luminescence of pure GaSe excited with 488 nm from an Ar^+ laser is shown in Fig. 7: there are at least four bands in the range 588-607 nm. These bands shift linearly with sulphur concentration to shorter wavelengths such that in Ga they fall in the range 510-532 nm. Fig. 8 shows the ODMR spectrum observed when detecting this emission from GaSe. There are two recognisable features: the triplet state resonance centred on g=1.88 and a free electron resonance at g = 1.113. The spectral dependences of these resonances show that the free electron resonance is associated with the 589 nm and 607 nm emission bands. The triplet exciton resonance is associated with bands at 593 nm, 596 nm and 600 nm. There is a closely linear variation in the g-value behaviour with increasing sulphur content (towards g = 2.00) and in the zero-field splitting (D), which decreases with increasing sulphur content.

6. Magnetic resonance of thermally oxidised Si.

The defect structure of bulk Si and SiO_2 has been characterised in terms of electrons trapped at broken bonds. An important technological problem in MOST devices is the nature of the fixed charge associated with the interface states in Si/SiO_2 junction. Since broken bonds on either side of the interface are likely to contribute to the fixed charge then it is obvious that highly sensitive spectroscopic methods might be applied to their study. The most significant studies of this type have been carried out by Poindexter and Caplan in the U.S. Army laboratories at Fort Monmouth, N.J. Our initial studies were orientated towards reproducing their results.

For the most part we used thermally oxidised, low resistivity Si, the interface being mainly a [100] face. We carried out ESR and SSP measurements on samples having oxide thicknesses of 50-100 nm and the conductivities ranged between 2.5 Ωcm and 5.0 Ωcm at room temperature. These samples created very considerable difficulty in obtaining good lineshapes and signal/noise ratios, although signal averaging techniques were used. There was no doubt that in the single (111) faced sample used that the major ESR signal was that due to the P_b centre i.e. the interface analogue of the isolated Si vacancy in bulk material. This signal is present in all samples, but with varying concentration (i.e. intensities). In the presence of band gap light from a Kr^+ ion laser one observes a substantial improvement in signal intensity for some samples. The light is directed onto the sample through the transparent SiO_2 layer in this case. Since visible region light is absorbed within a very short distance of the Si surface, this signal enhancement is due to processes originating within the oxide layer or at the interface. For example trapped holes might be released which on being trapped at a doubly occupied Si dangling bond adds to the concentration of P_b centres. These measurements have been extended by

using a tunable dye laser as excitation source. As can be seen in Figure 9 the enhancement of the signal is confined to the visible spectrum. Band gap and infra-red light from an F_2^+ centre laser directed through the bulk Si has no effect upon the strength of the P_b signal. We emphasise that these effects are strongly sample dependent; in some case visible light has no effect on the ESR signal. At the moment we have not had a sufficiently wide ranging batch of samples to establish trends that would account for this variability.

In some samples showing the P_b spectrum we have implanted the interface region with H^+ ions. The ion energy was varied between 0.4-2.0 MeV depending upon the oxide depth. Subsequent ESR spectra showed a much weaked P_b signal, in some cases reduced to zero. Concomitantly there was a large E_2^1 signal due to the formation of these centres in the amorphous oxide region by the ion damage. In contrast to the ESR spectra, the SSP spectrum on some samples showed the P_b centre resonance and the E_2^1 centre resonance also albeit rather weakly in the case of the E_2^1 centre. This spectrum had the lineshape appropriate the polycrystalline quartz. Both signals are eliminated by H^+ implantation. Hence it is concluded that the P_b and E_2^1 centres must aggregate with implanted H^+ and form diamagnetic species. The $E2^1$ centres formed in the bulk do not contribute to the SSP signal since they are not smaples by electrons moving in the conduction band of the silicon slice.

7. Concluding Remarks

We have been modestly successful with all the topice originally envisaged in the original application. The triplet exciton study in GaSe-GaS alloys is now being prepared for publication, although a theoretical calcuation needs to be completed. Similarly the SSP studies in CdTe and GaAs:Cr can be taken no further, and should form the basis of a short publication. We still have much

to do in the area of $Si:SiO_2$ largely by combining the three techniques of ODMR, SSP and photosensitive ESR. This will be the subject of a further application to the ERO for a continuation grant.

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Key

A	20 dB attenuator
F	Filter
I	10 dB isolator
K	600 mW Klystron
L	lens
La	laser
M_1	¼ m, monochromator
M_2	1 m monochromator
O	oscillator
P	pin diode
Ph	phototube
P_o	polariser
R	X-Y recorder
S	superconductive magnet
T	travelling wave tube
X	Xenon lamp

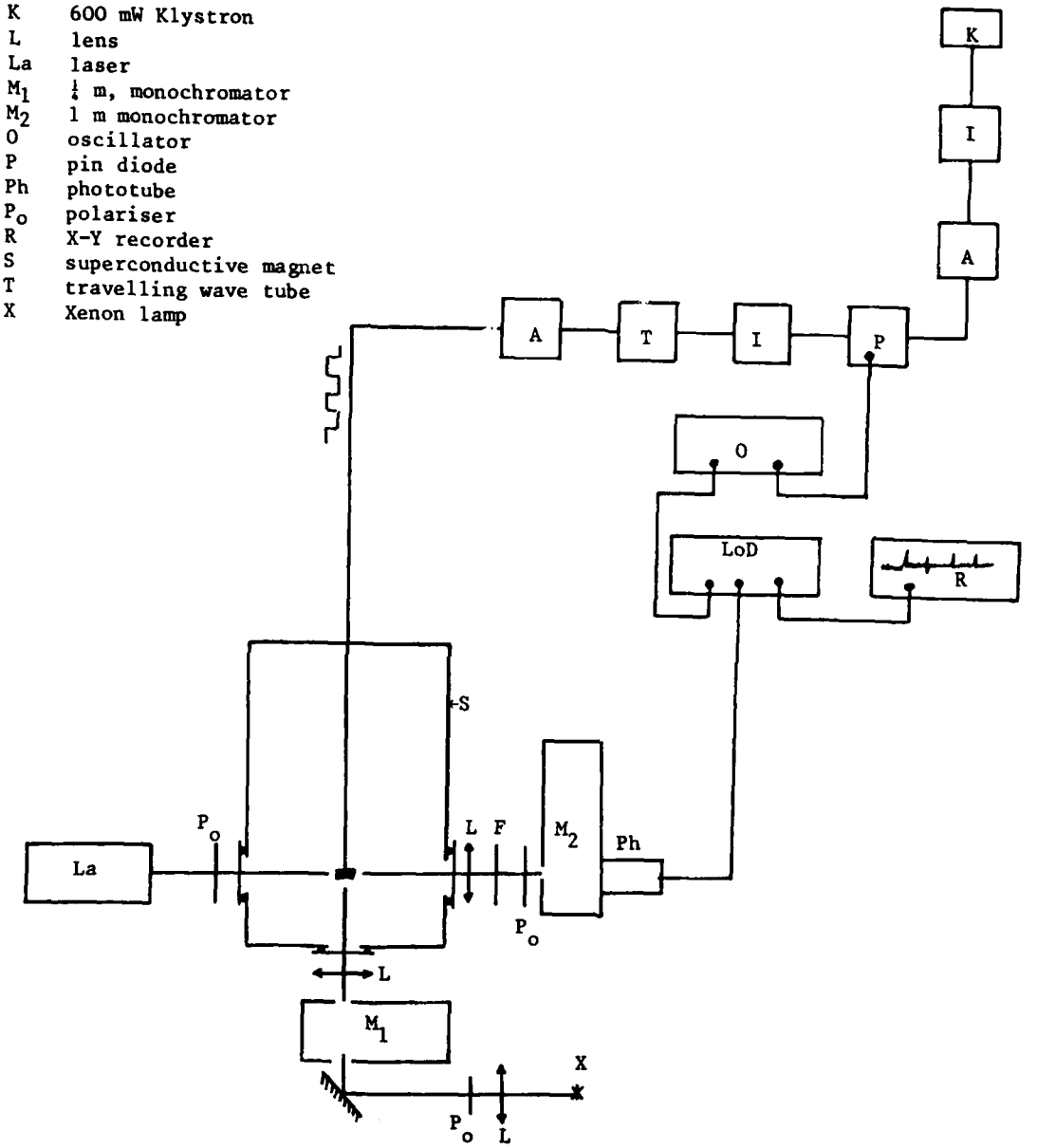
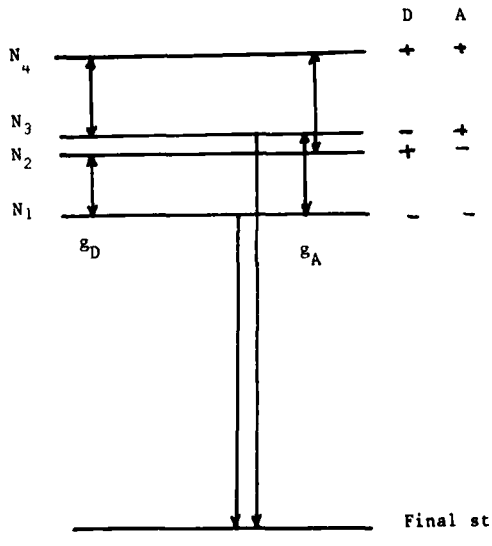


FIGURE 1

Block diagram of ODMR spectrometer



$$E = \pm\tfrac{1}{2}(g_A \pm g_D)\ \mu_B B$$

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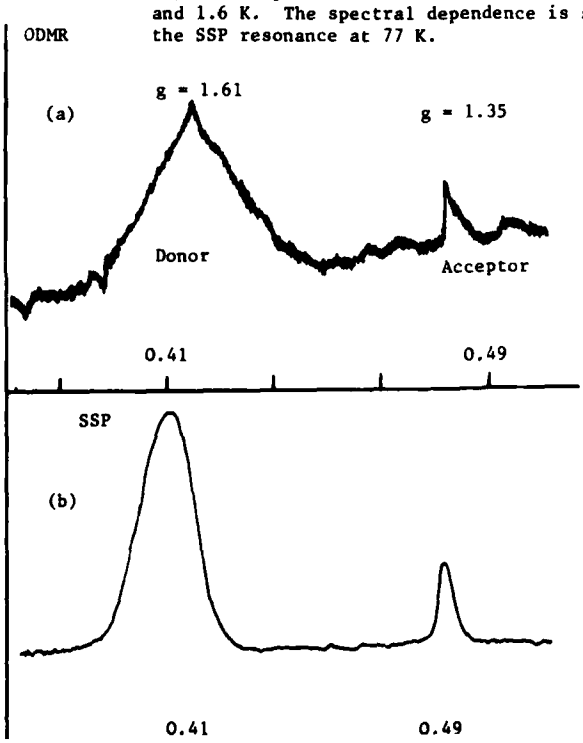
FIGURE 3

(a) ODMR spectrum of D-A recombination centres in CdTe at X-band and 1.6 K. The spectral dependence is shown in (c) whereas (b) portrays the SSP resonance at 77 K.



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The electronic structures of defects and impurities in GaSe-S alloys, GaAs:Cr, GaAs: Zn, ColTe and Si/SiO_2 have been investigated using the techniques of optically detected magnetic resonance (ODMR) and spin sensitive photoconductivity (SSP). In GaSe-S the ODMR has been used to study a wide range of triplet states. The photoluminescence bands associated with triplet state deexcitation change linearly with composition. The g-values of the triplet state ODMR as well as the crystal field splitting parameter also change linearly with alloy composition. Similar work on GaAs: Cr shows that the ODMR

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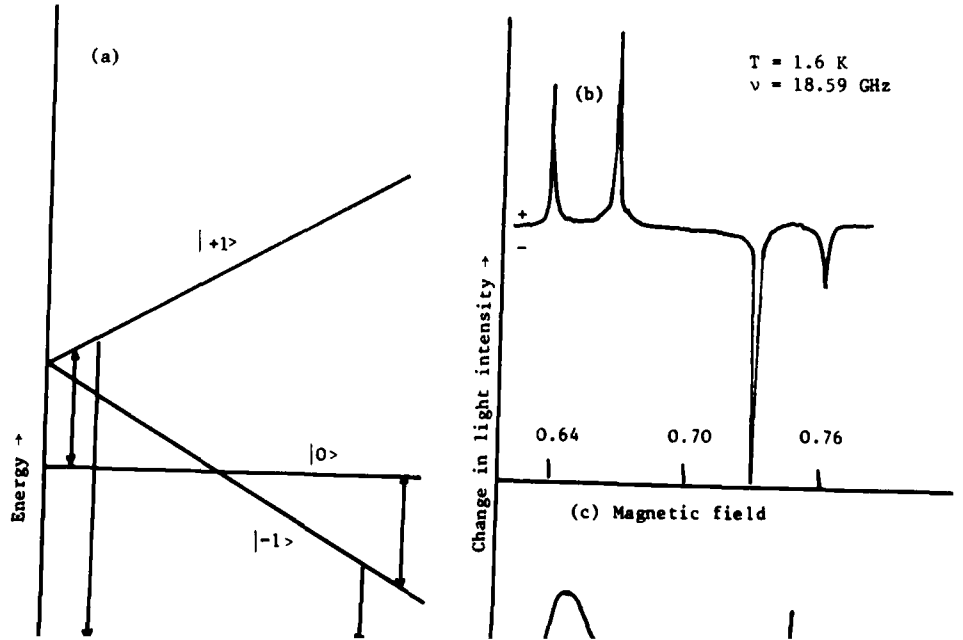
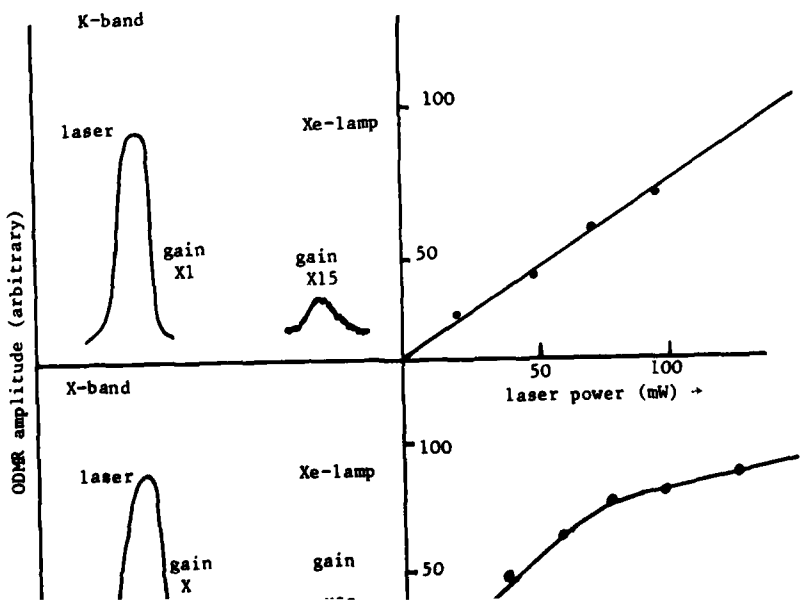
Principles of triplet state ODMR





and SSP spectra are not associated with internal [illegible]

of the Cr^{2+} ion in GaAs. At least two spin triplet state resonances are observed due to electron-hole recombination at Cr^{2+} ions in distorted Ga^{3+} sites. The ODMR results for GaAs:Zn are interpreted as recombination luminescence at substitutional Zn^{2+} impurity ions with a distortion axis along a [111] axis. In CdTe resonances observed with g-values of 1.61 and 1.35 have been identified as due to electrons recombining at neutral acceptors (or donors) and holes recombining at neutron donors respectively.

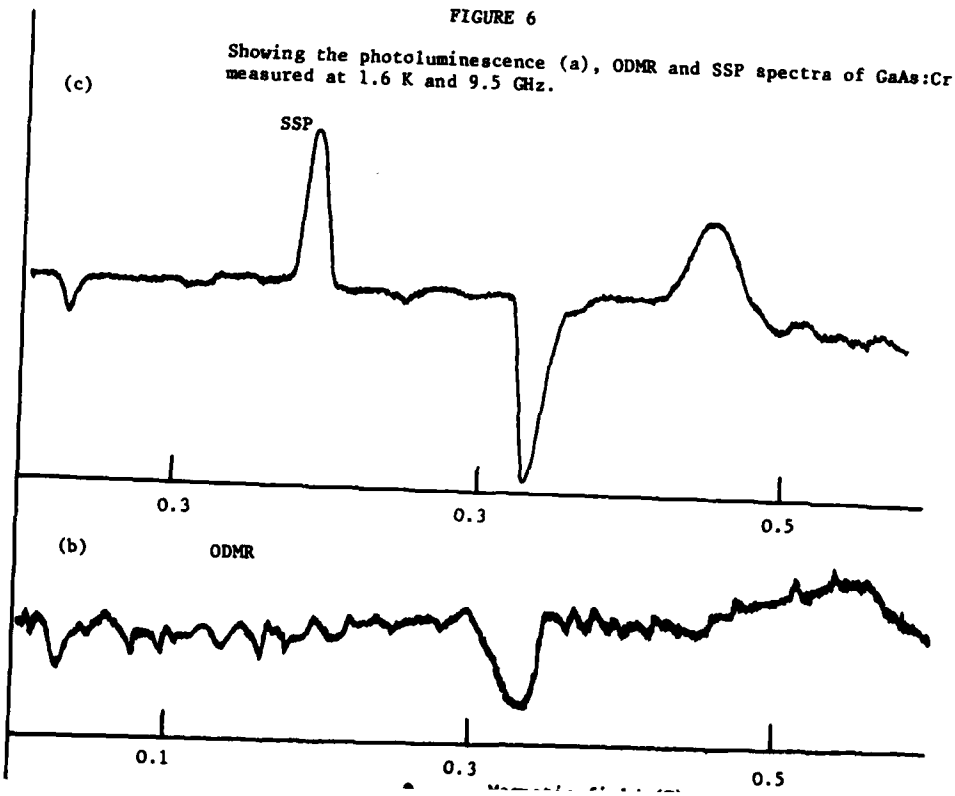
During the last eight months of the project a pilot study was initiated in MOS materials, to identify the defect states at the interface. The preliminary results show that SSP is a valuable means of examining defect structure at the interface, where the greatly enhanced sensitivity enables one to observe additional spectra.

1. General Objectives

The applications of electron spin resonance to the elucidation of electronic structure of donors and acceptors in semiconductors is well documented. However many uses of semiconductor involves optically active

FIGURE 6

Showing the photoluminescence (a), ODMR and SSP spectra of GaAs:Cr measured at 1.6 K and 9.5 GHz.



O'Connell. Two graduate research students carried out some of the experimental programme: they were Dr C.M. McDonagh and Mr J.M. Bolton. Secretarial assistance was provided by Mrs N.M. Kelso.

2. Experimental details

(i) ODMR Spectrometer

The spectrometer operated at one of two microwave frequencies; either X-band ($\nu \sim 9.5$ GHz) or Q-band ($\nu \sim 35$ GHe). The microwave source was either a klystrom or a Gunn diode capable of modest power levels (60 - 500 mW). The instrumentation is shown in Fig. 1, here I indicates a 40 dB isolator, P is a PIN diode modulator for 100% amplitude modulation of the microwave power, A is a 40 dB variable attenuator and T is a travelling wave amplifier giving amplification up to 10W. The magnet is a 6.5 T superconductive solenoid, within which the sample is enclosed in a resonant microwave cavity.

For maximum flexibility optical excitation is carried out using a broad band lamp (500 W Xe lamp) coupled to a 3/4 metre monochromator to select the excitation wavelength. Otherwise a 6 W Ar^+ laser is used. The emitted light is detected in a direction perpendicular to the exciting radiation using a 1 metre grating monochromator, GaAs phototube and lock-in amplifier.

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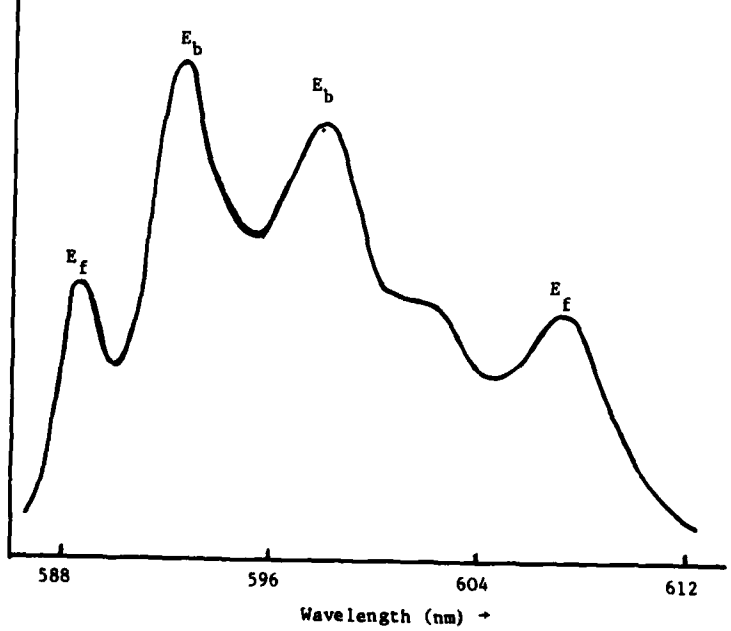
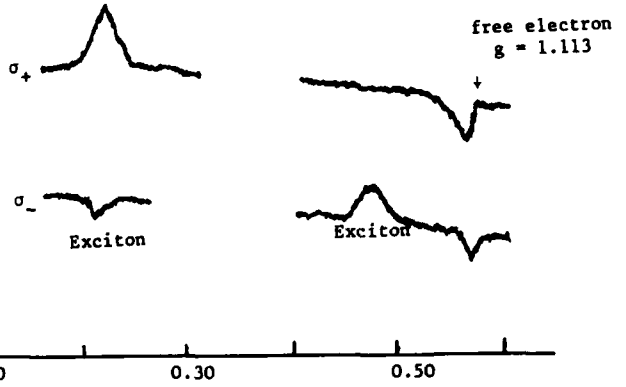


subsequently the electron is trapped on a shallow donor and the hole at an acceptor site. In the presence of weak spin-spin coupling the electron-hole excited state is fourfold degenerate (Fig. 2). For radiative decay to the ground state the allowed transitions conserve total spin i.e. $\Delta S = 0$. In a magnetic field the energy levels are

$$E = \pm^1/_2(g_A \pm g_D)\mu_B B$$

where g_A and g_D are the g-values of acceptor and donor respectively. If $\tau_R < T_1$ then the populations n_{++} and n_{--} build up at the expense of the emitting levels n_{+-} and n_{-+}. Hence in the presence of a resonant microwave magnetic field inducing spin flip transitions (e.g. $|-->\rightarrow|+->$ and $|-+>\rightarrow|++>$), there is an increase in the recombination luminescence intensity, for both donor and acceptor resonances. However, if $T_1 < \tau_R$ thermal equilibrium exists within the spin multiplet, and relatively small changes in total intensity are observed for donor and acceptor resonances.

Note however, that these changes in population at resonance also are detected in the photocurrent. Electrons and holes contribute to the photoconductivity signal only when they are in the conduction and valence bands respectively. Once trapped they no longer give a photocurrent. Since the EPR

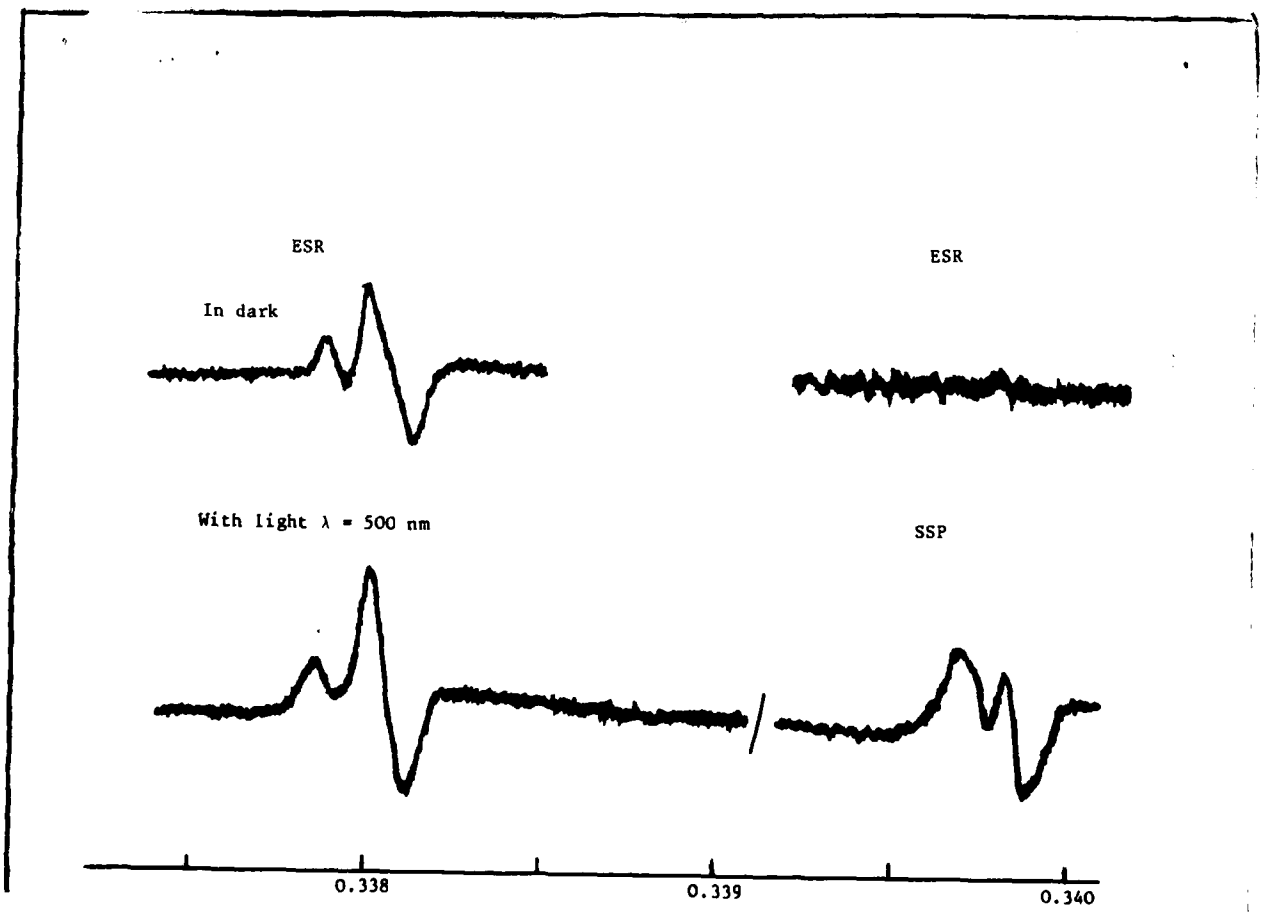


luminescence lines give an identical ODMR signal. On the basis of photoluminescence measurements these lines had previously been assigned to excitons recombining at neutral acceptors (A-x) or neutral donors (D°-x) or holes recombining at a neutral donor (D°-h). The g_A = 1.35 resonance appears only on the A°-x luminescence line.

Similar resonances are observed in the SSP spectrum even at 77 K. The change in photocurrent is 1.5% at the resonance field corresponding to g = 1.62(Fig. 3c). Comparison of the ODMR and SSP signals (Figs. 3a and 3c) shows how for the same sample, signal/noise ratio for SSP is greatly enhanced relative to the ODMR case.

ii) Triplet state ODMR

Fig. 4a shows the energy level of an S=1 state as a function of magnetic field, B. In observations parallel to the magnetic field the π-polarised transition is forbidden and only the $\sigma_\pm$ polarised transitions are observed. Such phenomena are anticipated to apply to triplet excitons in semiconductors. If the triplet states are in thermal equilibrium ($T_1 < \tau_R$) microwave transitions $|0\rangle \rightarrow |1+1\rangle$ lead to an increase in σ_- intensity whereas $|0\rangle \rightarrow |1-1\rangle$ transitions



where α is the fractional population change in the total population, [illegible] triplet levels at resonance. The coefficient α represents the fractional population change at resonance : it is determined by the microwave pumping action. Hence α depends upon frequency and the microwave power. The geometrical factor $\eta \sim 10^{-1}$ for laser excitation and 10^{-3} for a broad band lamp. This dependence upon experimental variables for our spectrometer is shown if Fig. 5, from which the clear advantage of using laser excitation is evident.

4. Experimental Results for GaAs

(i) Semi insulating GaAs:Cr

The luminescence of GaAs:Cr measured at 1.6 K and excited using 100 mW of power in the 799 nm line from a Kr^+ laser is shwon in Fig. 6. OIMR associated with the line at 147.15 nm is shown in Fig. 6b : the signal : to noise ratio is only about 3:1 for the most intense OIMR line at 0.32 T. The change in sensitivity for the SSP signal is clearly evident in Fig. 6c. These resonance lines are strongly dependent upon the relative orientation of magnetic field and crystal axes. Orientation dependence suggests that at least one S = 1 system with a [111] axis of symmetry is involved. Other resonances have not