PROC, 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN **49** (1980) SUPPL. A p. 611–618

OPTICAL DETECTION OF EXCITON RESONANCES IN SEMICONDUCTORS

B.C. Cavenett

Department of Physics
University of Hull
Hull
England

This paper outlines the general principles on which the technique of optically detected magnetic resonance is based in the case of semiconductors where both the electron and hole spins must be considered in a recombination process. The advantages of the method are illustrated by examples from studies of triplet excitons in layered semiconductors such as GaSe and GaS.

I Introduction

The realization that electron spin can be important in electron-hole recombination, carrier trapping processes and electron scattering has opened many new areas of investigation of the optical and electrical properties of semiconductors. The possibility of different cross sections for singlet and triplet processes is a very simple idea but fundamental to the understanding of spin effects in solids and Solomon [1], Lampel [2] and Zacharchenya [3] were the first to explore these ideas in studies of spin dependent transport and optical pumping in semiconductors. These effects have been further exploited in optical resonance studies which have recently been reviewed by Cavenett [4].

II Spin Dependent Recombination in Semiconductors

In order to appreciate the importance of spin in electron-hole recombination consider donor-acceptor recombination shown in Figure (1). In (a) an electron is excited to the conduction band leaving a hole or unpaired spin in the valence band. The electrons and holes can be localized at donors and acceptors, respectively, and if the donors and acceptors can be considered as weakly coupled pairs, the situation shown in (b) corresponds to the triplet situation where the electron and hole spins are parallel. The Pauli principle excludes recombination in this case. Figure (1) shows the other possibility, namely,

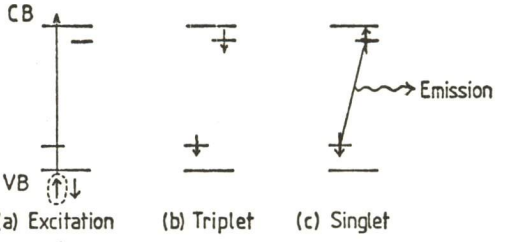


Figure (1) Spin-dependent D-A recombination

the singlet pair state corresponding to antiparallel spins. In this case, recombination is allowed and shown to be radiative in the diagram. Clearly in the case of (b) the triplet non-radiation state can be converted to case (c) by a spin flip of either the donor or acceptor spins and if this occurs

emission from the singlet states will increase in intensity. If we now consider a magnetic field present there are two possible models, one where the D-A pair is unthermalized and the other where the pair is thermalized. The D-A pair recombination involving deep acceptors described by S = $\frac{1}{2}$ rather than by the spin of the valence band holes is generally observed to be unthermalized and the population differences between the states shown in Figure (2a) are determined by the relative decay rates from levels. Thus for long relaxation rates the strongly emitting singlet states shown have populations below the triplet states and at resonance the total emission intensity increases as illustrated for the donor resonance. In contrast figure (2b) shows the case of D-A pair recombination in CdS and for B// c-axis the emission along this axis is circularly polarized. Resonance in the donor states is shown and it can be seen that at resonance $I_{\sigma-}$ increases in intensity and $I_{\sigma+}$ decreases. Clearly in this case and in the examples of exciton resonances discussed later one must take into account selection rules for the allowed transitions which may be more complicated than expressed by the simple spin conserving model of Figure (1). These examples illustrate the basic mechanisms which allow the optical detection of magnetic resonance and, in fact, it is interesting to compare the consequence of having two particles (electron and hole) both with spin with examples of optical resonance studies involving transition metal ions in insulators where the magnetic ion is either in one state (eg the excited state) or another (the ground state, say). These early studies have been reviewed by Geschwind [5] who was involved with the development of ODMR.

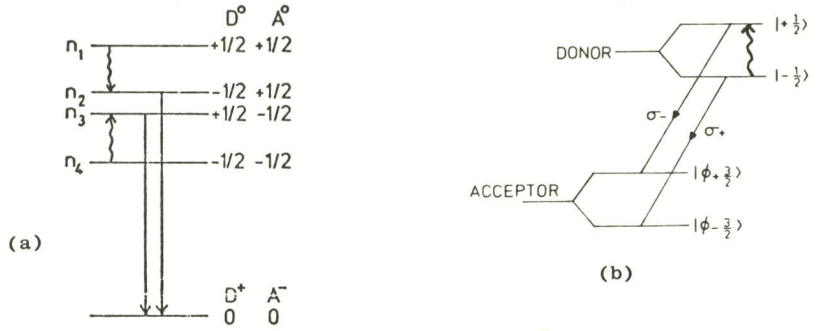
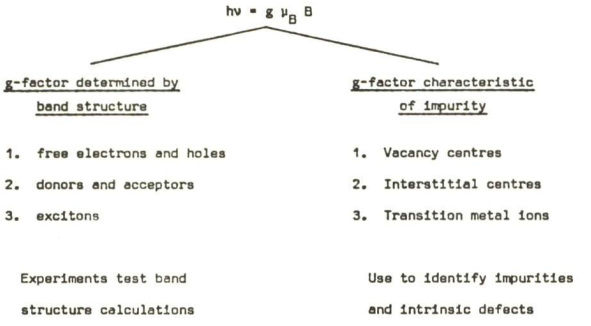


Figure (2) unthermalized (a) and thermalized (b) D-A recombination

The complementary roles of EPR and ODMR for investigating semiconductors were illustrated in the very first ODMR studies of ZnS by James et al 6 where ODMR signals of donors and acceptors were observed by monitoring a blue, so called self-activated emission. The identity of the acceptor was determined by a comparison of the A-centre (a V_{Zn}-donor pair) data obtained from photo-induced ESR measurements by Kasai and Otomo [7]. The ODMR measurements have the advantage that the sensitivity is greater by several orders of magnitude than ESR and in the above example no ESR signals from the A-centre were observed but very strong ODMR signals were recorded. Equally important to sensitivity is the fact that the ODMR measurements allow the resonances to be directly related to an emission line or band by a spectral dependence measurement. This is carried out by monitoring the luminescence through a spectrometer and recording the strength of the microwave induced signals as a function of wavelength and in the above example a band at 450nm was assigned to donor - A centre recombination. Sometimes, however the ODMR signal appears on more than one emission band and so models involving coupling of centres or cross-feeding must be considered [4].

There are two types of problems which can be explored as shown in Figure (3). Excitons, electrons and holes have magnetic parameters determined by the band structure of the material whereas defect centres such as vacancies and transition metal ions are localized and the ODMR signals are representative of the local enviroment (symmetry, nuclear interactions). Since excitons are usually short lived excited states of a crystal, the ODMR technique can be used to study the electronic structure of these systems. Attempts both in Paris and at Hull to observe free and bound triplet excitons in III-V compound semiconductors have been unsuccessful and this has been disappointing since the knowledge gained about excitons in these materials from Zeeman measurements would be supplemented by detailed spectroscopic information (ODMR resolution to $\sim \pm 0.005\ cm^{-1}$). However exciton resonances have been observed in the layered semiconductors GaSe and GaS and examples from these studies will be discussed.

Figure (3) CLASSIFICATION ACCORDING TO g-FACTOR



III Excitons in GaSe

GaSe and GaS are III-VI semiconductors with layered structures characterized by Ga-Ga bonds. The crystals are formed by stacking of 4-fold planar layers where the layers are held together by weak Van der Waals forces and the stacking is one of at least three polytypes, β, ε and γ. In the case of GaSe, there has been some controversy over the origin of the emission processes which give a spectrum such as shown in Figure (4). The sharp line at the

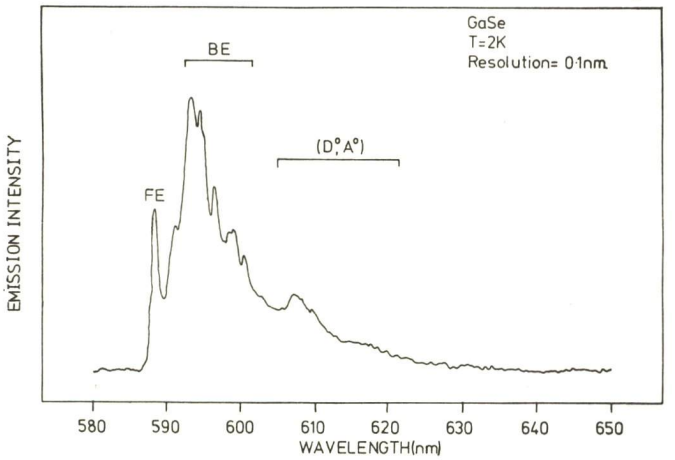


Figure (4) GaSe type I emission

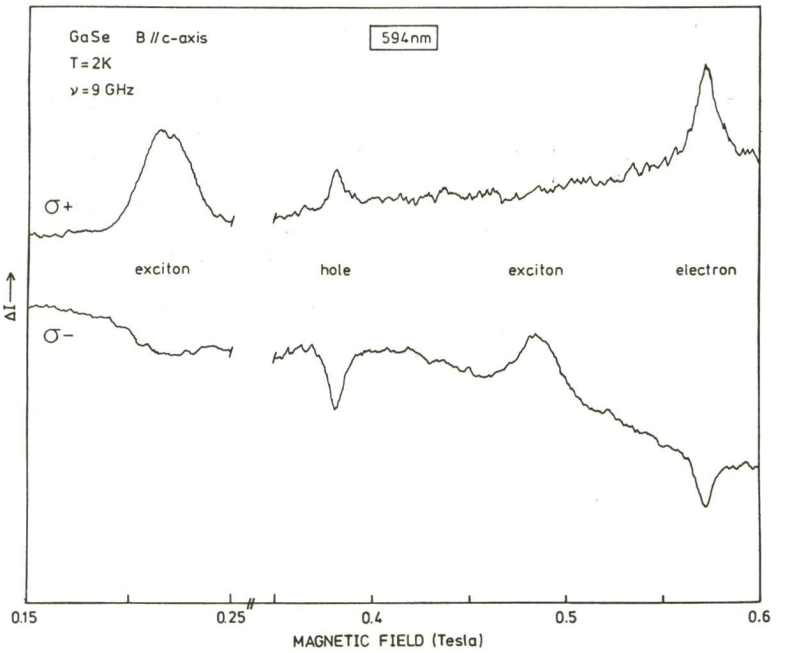


Figure (5) ODMR in GaSe type I showing exciton, electron and hole resonances

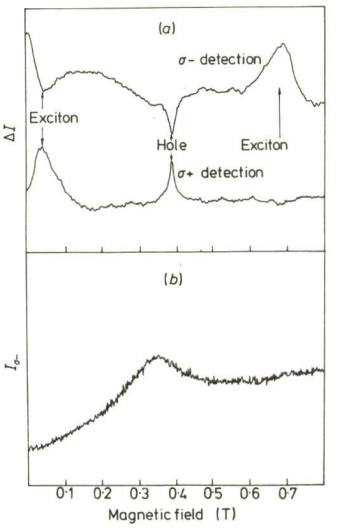


Figure (6) ODMR (a) and level crossing in type II GaSe

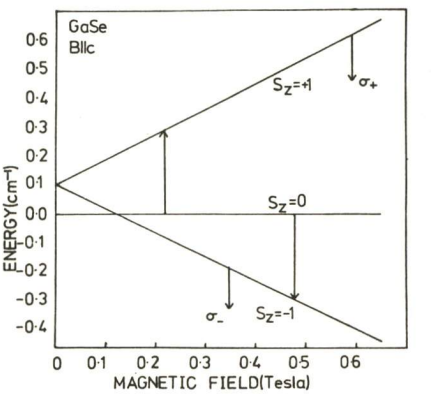


Figure (7) Energy level scheme for type I excitons

highest energy has been attributed to free direct exciton whereas the many lines at lower energy were assigned to donor-acceptor transitions by the Lausanne workers [8] but to bound excitons by the Sendai group [9]. Optical resonance studies have been carried out at Hull on crystals from both groups and the results show that the sharp lines are due to bound excitons as labelled in Figure (4). Voitchovsky and Mercier [7] had already observed differences in the emission spectra from GaSe crystals and these differences were shown to be related to different bound excitons by Morigaki et al [10] and Cavenett et al [11]. The ODMR spectra corresponding to the emission shown in Figure (4) is shown in figure (5) whereas in materials with very weak free exciton emission the resonances shown in Figure (6) were recorded. In both cases the resonances are characteristic of triplet (S=1) excitons with $g_{ex//} = 1.85 \pm 0.03$ and $D_I = +0.110 \pm 0.004$ cm^{-1} (Figure (5)) and $D_{II} = +0.288 \pm 0.002$ cm^{-1}. The energy level scheme for type I is shown in Figure (7) and the increases in the σ+ and σ- emissions at resonance are characteristic of an unthermalized system where the emission from the $M_s = \pm 1$ states causes the populations of these states to drop below that of the $M_s = 0$ state. This is only so for B//c-axis and for B away from this axis no resonances were observed. The observation of the two resonance spectra with the same g-values was possibly due to different stacking

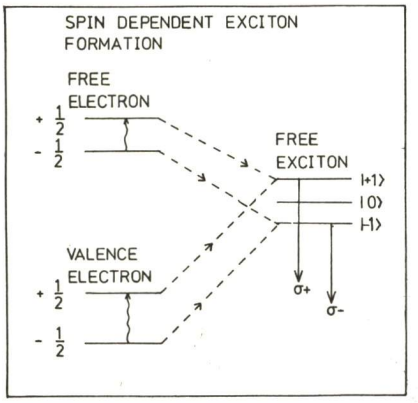


Figure (8) Spin dependent exciton formation

of the layers in the two types of crystals since the γ and ε polytypes are most common. The understanding of these results has been further complicated by recent measurements by Dawson et al [12] who have observed a third triplet resonance in GaSe:Cu material. In fact all three triplets are present and a sharp $\Delta M_j = 2$ transition common to all three systems with the same g-value is observed. For this new triplet $D = +0.217 \pm 0.004$ cm^{-1}. In all cases the triplet nature of the excitons was confirmed by level crossing experiments and in Figure (6b) the level crossing is shown for the type II exciton. Figure (5) also shows electron and hole resonances which are characteristic of thermalized systems since the sign of the signals depends on which emission polarization is monitored. Morigaki et al [10] attributed the observation of these signals to the spin-dependent formation of free excitons from thermalized electrons and holes as shown in Figure (8) since these resonances are observed on both free and bound exciton lines. The electron and hole resonances shown in the figure increase the exciton σ+ emission and correspondingly decrease the σ- emission. No free exciton resonances were observed however. In summary, detailed information of triplet excitons has been obtained by ODMR in GaSe but the nature of the localization of the excitons has still not been clarified.

IV Excitons in GaS

In the case of GaS five triplet exciton resonances have been reported by Dawson et al [13] as shown in figure (9) where the $\sigma-$ emission was monitored at various regions throughout the emission spectrum. All excitons have $g^{ex}_{//} = 2.006 \pm 0.003$ and the zero field splittings are $D^{I} = +0.013 \pm 0.001\ cm^{-1}$ $D^{II} = +0.024 \pm 0.001\ cm^{-1}$, $D^{III} = +0.025 \pm 0.001\ cm^{-1}$, $D^{IV} = +0.975 \pm 0.005\ cm^{-1}$

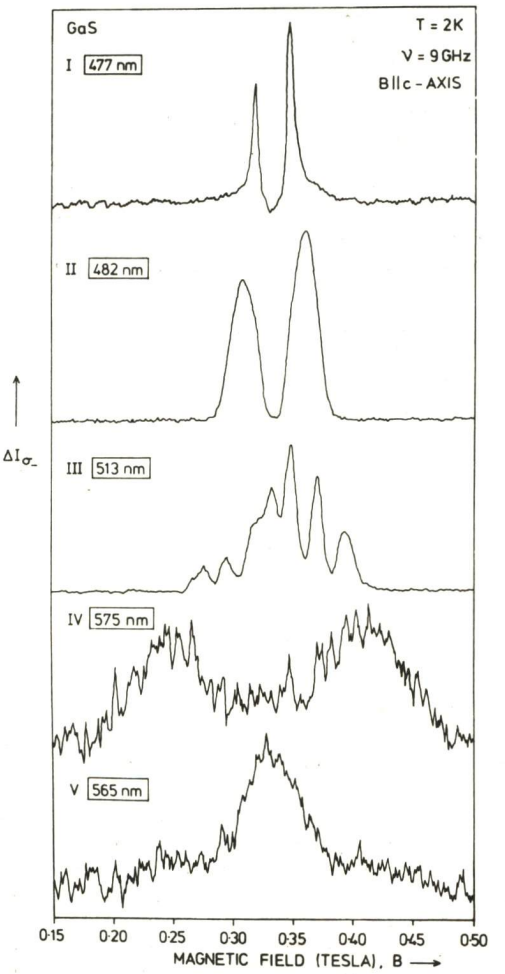


Figure (9) Triplet exciton ODMR in GaS

The type III resonance shows resolved hyperfine interaction and so a nuclear hyperfine term describing the interaction with one Ga nucleus must be considered. So far angular dependence studies have been carried out in detail only on the type I spectra as shown in figure (10); analysis gives $g_{\perp} = 1.87 \pm 0.06$. Since the five excitons all have the same $g^{ex}_{//}$ it is assumed that the same indirect excitons are recombining under different enviromental conditions. In particular type I resonances which are remarkably narrow for ODMR signals have been attri-

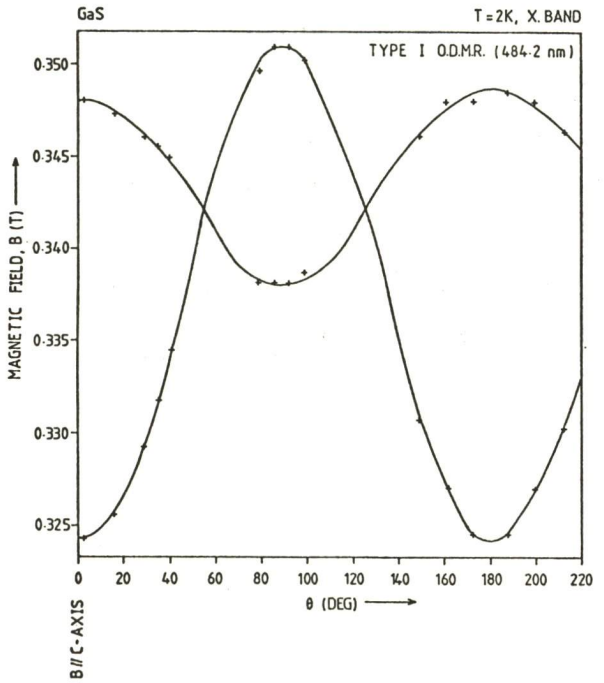


Figure (10) Angular dependence of type I ODMR in GaS

buted to free indirect excitons where the line width is motionally narrowed. The nature of the electronic states which give the almost equal signal strength for both low and high field resonances is not understood and clearly a considerable amount of work is necessary to clarify the nature of localization in these layered materials.

Acknowledgements

Many people have been involved in these investigations and to them I am grateful. In particular I wish to thank Dr. K. Morigaki with whom the GaSe work was started at Hull and to Drs Nishina and Levy for supplying crystals. I am grateful to the Science Research Council for generous financial support.

References

1) Solomon: Proc. Warsaw Semiconductor Conference. Elsevier, Amsterdam (1972) p27.

2) G. Lampel: Proc. Stuttgart Semiconductor Conference, Ed. M.H. Pilkuhn, Teubner, Stuttgart (1974) p748.

3) B.P. Zacharchenya: Proc. Edinburgh Semiconductor Conference Ed. B.L.H. Wilson, Institute of Physics, London (1979) p31.

4) B.C. Cavenett: Advances in Physics, to be published.

5) S. Geschwind: Chapter 5 "Electron Paramagnetic Resonance" Plenum, New York, (1972).

6) J.R. James, J.E. Nicholls., B.C. Cavenett., J.J. Davies and D.J. Dunstan: S.S. Comm. 17 (1975) 969.

7) P.H. Kasai and Y. Otomo: J. Chem. Phys. 37 (1962) 1263

8) J.P. Voitchovsky and A. Mercier: Nuovo Comento 22 B (1974) 273.

9) N. Kusoda, and Y. Nishina: Phys. Stat. Sol. (b) 72 (1975) 81.

10) K. Morigaki., P. Dawson and B.C. Cavenett: S.S. Comm. 28 (1978) 829.

11) B.C. Cavenett., P. Dawson and K. Morigaki: J. Phys. C. 12 (1979)L197.

12) P. Dawson., B.C. Cavenett., K. Morigaki and F. Levy, to be published.

13) P. Dawson., N. Killoran and B.C. Cavenett: S.S. Comm. 32 (1979) 1133.