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STUDY OF DONOR SPECIES IN ZnSe AND ZnTe WITH A NEW PHOTOLUMINESCENCE TECHNIQUE

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'Two-electron' satellites of donor bound exciton (DBE) luminescence lines become very narrow under selective excitation with a narrow laser line, so inhomogeneous broadening is dominant. Precise information about properties of the host semiconductor and the donor species may be obtained, when line-widths are appreciably broadened by back-doping, particularly since the energy resonance with the excitation simplifies magnetic splittings. New information is obtained about excited DBE states associated with the n=2 free exciton and the excitation channels for different classes of DBE.

I. Introduction

Direct gap semiconductors ZnSe and ZnTe have electron to hole effective mass ratios $\sigma = m_e^*/m_h^*$ sufficiently small to allow exciton binding at ionised donors (the I_3 or D^+X lines), in addition to binding at neutral donors (the I_2 or D^0X lines), which occurs for all σ [1]. The transition energy of the I_2 lines measured below the free exciton (FE) energy gap E_{GX}, gives the exciton localisation energy E_{BX}. Donor species are best differentiated through the 'two-electron' luminescence satellites, whose displacement energy below the parent I_2 no-phonon line is the internal excitation energy to the excited state in which the donor is left following BE recombination [2]. Unfortunately, the linewidth ΔE of BE luminescence lines is typically $\gtrsim$0.1meV, comparable with the chemical shifts ΔE_D between adjacent DBE or even the entire span of DBE energies for extreme cases such as GaAs, and also with the line splittings at modest magnetic fields. The majority of this linewidth arises from inhomogeneous broadening processes, obviated by selective excitation with a narrow laser line as we describe.

II. Experimental

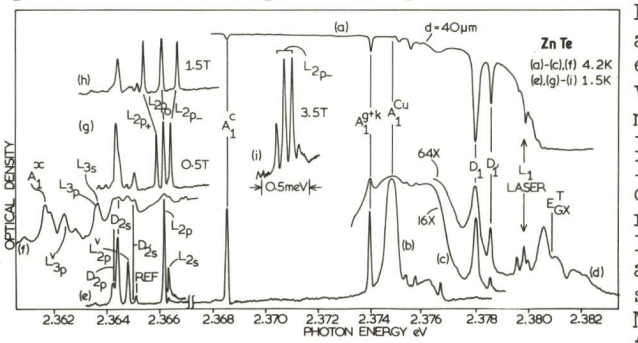
The lightly compensated p-type ZnTe single crystals were grown from a Te-rich melt by B Schaub of LETI, Grenoble. Most of the ZnSe single crystals were grown by B J Fitzpatrick of North American Philips Laboratories, using liquid phase epitaxy from Zn or Bi solutions in a covered multi-well graphite boat. Others were prepared by K Nassau of Bell Laboratories by vapour transport [3].

Excitation was by a variety of fixed wavelength lines from He-Cd or Kr^+ lasers. Blue light from stilbene III dye in a tuneable dye laser was used for many ZnSe spectra.

III. Results and Discussion

(a) Zinc Telluride

The coincidence of the 520.8nm line of the Kr^+ laser line L_1 with the third excited state DBE line is evident from the photographic spectra to the right in Fig.1. A set of ultrasharp replicas such as L_{2p}, L_{2s} shown at the left appear strongly, but not for excitation above the transverse FE E_{GX}^T. The displacement energies L_1-$L_{2p,2s}$~ 13.5meV, are consistent with 1s-2p,2s excitations of donors in ZnTe, as noted for resonant excitation into the lowest energy DBE lines [4], and into a variety of DBE states by Romestain and Magnea [5] (RM). We exploit the narrow Kr line, ΔE~ 0.01meV compared with ~0.2meV of RM, and a high resolution spectrograph to emphasise the line narrowing from spatially selective excitation within the inhomogeneously broadened DBE lines. The L_{2p} satellite has a linewidth of only ~0.02_5meV at zero magnetic field in the best crystals, compared with ~0.08_5meV for the non-resonantly excited ground state satellite D_{2s}. L_{2p} is identified by the easily resolved splittings from orbital magnetism (large triplet splitting in Fig.1i). The width of a single spin subcomponent reduces towards 0.01_5meV at 3.5T, close to the instrumental limit and the homogeneous limit of ~10^{-2}meV imposed by the likely lifetime of ~0.1nsec for transitions from this very shallow DBE excited state, E_{BX}=1.1meV. Transitions to 2s excited states show only the spin splitting, whereas orbital splittings also appear clearly in transitions to the 3p donor excited state. The 2p-3p energy separation provides an accurate effective mass binding energy E_D^{EM} 17.78±0.2$_5$meV and ΔE_D = +0.3$_4$meV. The orbital magnetic splittings yield m_e^*=0.128+0.004, and a static dielectric constant ϵ_o=9.9±0.2 from E_D^{EM}. The spin splittings give an electron g value g_e=0.40±0.03, in good agreement with an optically detected magnetic resonance (ODMR) result [6].



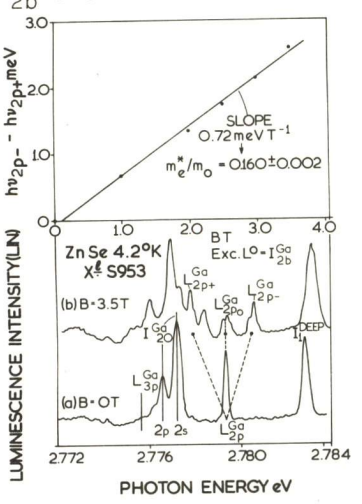
The advantage of narrow linewidth persists in much more heavily doped samples. For example, L_{2p} shows ΔE still only ~0.06meV for ZnTe:P with N_A-N_D~$4x10^{16}cm^{-3}$, when the acceptor A BE linewidth has increased to ~3.5meV due to Anderson-type delocalisation of the A BE! [7]. All the structure in Fig.1 can be interpreted by a single donor species. Crystals doped with P, Al, Li, Cu, Ag, Au and Al have failed to show a second species.

The intensity ratio L_{2p}/L_{2s} is ~20 in Fig.1, remarkably large compared with ~0.2 for D_{2p}/D_{2s}. We describe the D BE excited states with H_2 molecule-like wave functions, the relatively heavy hole representing one 'nucleus'. We conclude, in agreement with RM, that the hole is in a p-like orbital state relative to the donor core, keeping the electron of the FE in a similar configuration, and that the hole recombines with the electron around the donor for the $L_{2s,2p}$ replicas. This contrasts strongly with the D BE ground state, where all electronic particles are in s-like orbital configurations with the two electrons paired off. The simplicity of the Zeeman splittings of $L_{2s,2p}$ compared with those of $D_{2s,2p}$ results from the necessity to preserve exact resonance with the laser line in the

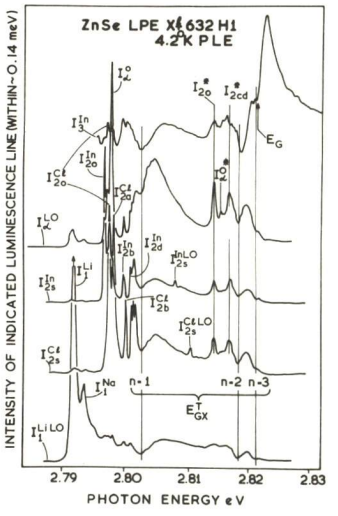
D BE excited state, so the hole magnetic substate remains unchanged during the transition. Electron spin-flip transitions are allowed in the 'two-electron' satellites, unlike a direct 1s-2p photo-excitation process.

(b) Zinc Selenide

The linewidth ΔE of the 'two-electron' satellite of the Ga D BE in ZnSe for resonant excitation into the second D BE excited state, I^{Ga}_{2b} [3] is limited to ~0.09meV by the dye laser (Fig.2). It is still narrower than the satellites of the lowest D BE, ΔE~0.4meV. The excited D BE states cover an energy range of ~4.4meV in ZnSe, twice as great as in ZnTe, and the energy dispersion between chemical species is also much larger. Thus, all the advantages of the resonance excitation technique discussed for ZnTe can be reproduced even with this larger excitation linewidth. The splittings of the transitions to 2p donor states yield m^*_e= 0.160±0.002 (Fig.2) with ε_o=9.14±0.1 for E^{EM}_D= 26.06meV. The values of ΔE_D range between -0.42meV for Al donors and +2.74meV for F donors, both ±0.16meV. The spin splittings, poorly reproduced in Fig.2, give g_e=1.06±0.05 compared with +1.13$_2$ from ODMR [9]. We find that the decrease of intensity of the 'two-electron' replicas at large magnetic fields arises from a diamagnetic shift in the D BE transition energy. Resonant 'two-electron' satellites have been observed from the complete set of D BE excited states [3]. The intensity ratio L_{2p}/L_{2s} is ≫1 and largest for resonance with I_{2b}, leading to conclusions similar to Section 3a about the orbital character of these excited D BE states.



Two strong peaks I^*_{2o} and I^*_{2cd} appear in the PLE spectra of D BE luminescence, just below the n=2 FE (Fig.3). These peaks, particularly I^*_{2cd}, show a large diamagnetic shift rate, approaching that of the n=2 FE, ~5.6×10^{-2}meV T^{-2}. A similar observation in ZnTe [4] suggested a BE derived from the n=2 FE state. The involvement of these components with D BE is proved by resonantly sharpened 'two-electron' satellites, which shift as the narrow laser line is tuned within the large, inhomogeneously broadened ~0.45meV linewidth of I^*_{2o} and I^*_{2cd}. Excited D BE states from different donor species contribute to different degrees across this linewidth. These D BE states involve excitations of the electron relative to the hole in the nearly FE, in contrast to the excitations of the whole FE relative to the neutral donor responsible for the lower D BE excited states (Section 3a). Resonant excitation into I^*_{2cd} gives a very small intensity ratio L_{2p},L_{2s}, ~0.05 for the In donor, so we conclude that this quasi-FE state has s-like envelope character. Resonant excitation into I^*_{2o} suggests the opposite.



The strong response above the free particle band gap E_G near 2.8215eV in the PLE spectra of I_3 D BE (Fig.3) suggests that in these samples these BE states are formed predominantly by sequential capture of electrons and holes at ionised donors. Apart from surface recombination effects, which contribute minima at the intense sharp FE absorption features in optically thick (at the FE) crystals used here, the contrasting form of the PLE for I_2 D BE features shows that FE creation provides a much more significant channel for the formation of these BE states.

References

1) J.J. Hopfield: Proc.Int.Conf.Phys.Semicond. Paris (Dunod, Paris, 1964) p 725.
2) P.J. Dean, J.D. Cuthbert, D.G. Thomas and R.T. Lynch: Phys. Rev.Lett. 18 (1967) 122.
3) J.L. Merz, H. Kukimoto, K. Nassau and J.W. Shiever: Phys. Rev. B 6 (1972) 545.
4) H. Venghaus and P.J. Dean: Phys.Rev. B 21 (1980) 1596.
5) R. Romestain and N. Magnea: Solid State Commun. 32 (1979) 1201.
6) N. Killoran, B.C. Cavenett and P.J. Dean: to be published.
7) P.J. Dean and A.M. White: Solid State Electron. 21 (1978) 1351.
8) D.J. Dunstan, J.E. Nicholls, B.C. Cavenett, J.J. Davies and K.V. Reddy: Solid State Commun. 24 (1977) 677.

Figure Captions

Fig.1 a) Transmission, b)-d) BE luminescence for above gap excitation and e)-i) satellite luminescence spectra for resonant Kr^+ laser excitation at L_1 for undoped ZnTe, with and without a magnetic field

Fig.2 Lower: satellite luminescence spectra for dye laser excitation at D BE excited state L_{2a}^{Ga} in vapour grown ZnSe with and without a magnetic field

Upper: splitting of indicated satellite subcomponents in magnetic field

Fig.3 Photoluminescence excitation (PLE) spectra in solution grown ZnSe for the detected luminescence components indicated at the left. I_α is an unidentified BE just above the D BE

Conclusions

This technique should be applicable to the wide range of direct gap semiconductors for which resolution of contributions from different donors to the near gap luminescence presents difficulties for conventional spectroscopy. Narrow gap materials such as GaAs and InP present the greatest problems. A thin intra-cavity etalon is required to narrow the linewidth of the tuneable dye laser suitably towards 0.01 meV, ~10% of the complete range of ΔE_D in such materials.