OPTICAL TRANSITIONS ON $Zn_{0.8}Mn_{0.2}Se$

P. Quintero, A. B. Vincent and J. M. Martín

Centro de Estudios Avanzados en Optica, Universidad de Los Andes, Mérida. Venezuela

Abstract

Optical absorption, photoluminescence and photoconductivity at 80 K, and at R.T. was carried out on $Zn_{1-x}Mn_xSe$ mixed single crystal grown by chemical transport, with x = 0.2. The results are explained on the basis of the Manganese intra-ionic transitions and on the defect centers. The photoconductivity spectra were well resolved and obtained for the first time. All transition bands could be explained by assuming the Manganese $^6A_1$ level located 0.2 eV below the top of the valence band.
Keywords: Diluted Magnetic Semiconductors. $Zn_{0.8}Mn_{0.2}Se$.

INTRODUCTION

Diluted magnetic semiconductors (DMS) are widely studied for their wide selection of energy gaps [1-4]. One of these families is the Zn/Mn/Se mixed compounds. The Manganese random substitution for the group II element in the alloy, gives rise to specific optical properties coming from the splitting of the lowest excited state of the $3d^5$ level of the Mn^{2+} ion in the presence of a tetrahedral crystal field [5]. In this work we have, therefore, investigated the photoconductivity (PhC), photoluminescence single crystal, in order to compare the different transitions that may arise on the corresponding spectra.

EXPERIMENTAL

The crystals were obtained by chemical transport growth with iodine [6]. The samples were prepared from small pieces of 2 to 6 mm sizes, polished and etched. For PhC measurements, electrical contacts were carried out by melting Indium pellets in an Argon atmosphere, presenting ohmic behaviour up to at least 6 Vdc.

The PL, PhC and OA measurements were performed on PC controlled equipments with the samples placed on the cold-finger of a metallic cryostat. Light detection was carried out with a GaAs PMT while the PhC measurements are explained elsewhere [7].

RESULTS AND DISCUSSION

Figure 1 shows the optical absorption of a $Zn_{0.8}Mn_{0.2}Se$ crystal at 290 K (a) and at 80 K (b). In both, the band edge is clearly identified with values of the energy gap at 2.63 and 2.79 eV respectively. On curve (b), four peaks are observed, located at 2.13 eV (A), 2.34 eV (B), 2.49 eV (C) and 2.66 eV (D). Peaks B and C are exactly reproduced in (a), indicative of temperature independence, confirming they correspond to transition of the split $3d^5$ level of the Mn^{2+} ion in the crystal field. According to the literature [5, 6, 8-10], the separations of the first three levels are 2.36 eV ($^6A_1$--->$^4T_1$), 2.42 eV (--->$^4T_2$) and 2.61 eV (--->^4E, $^4A_1$); hence peaks B, C and D of Fig. 1 may be associated to transitions of the Mn^{2+} ion within the crystal.

Figure 2 shows the emission spectra at both temperatures. Two well-resolved bands appear in these curves, 2.28 eV (E) and 2.10 eV (F) at 80 K and 2.34 (E) and 2.13 (F) at 290 K. As has been reported [11], narrow emission bands are more likely to correspond to Mn transitions than to the self-activated emission usually present in ZnSe. Since peak E is almost temperature independent, it is originated from the Mn $^4T_1$--->$^6A_1$ intra-ionic luminescence transition. It can also be seen from this figure that there exists a shoulder near 630 nm (band G), which probably arises from the presence of self-activated centers [11].

Figure 3 shows the corresponding photoconductivity spectra recorded at 290 K (a) and at 80 K (b). Fig. 3-b shows one peak J along

with two slow structures, which are located at 2.16 eV (I) and 1.87 eV (H). Because of this slow photoresponse, the origin of these two bands must be due to some kind of traps or impurity centers. Earlier reported PL studies [11] showed defect centers near 1.9 eV and 2.2 eV below the conduction band (C.B.) attributed to self-activated centers associated to Zinc vacancies or low energy Copper states. We can then conclude that peaks H and I are due to these types of native defects.

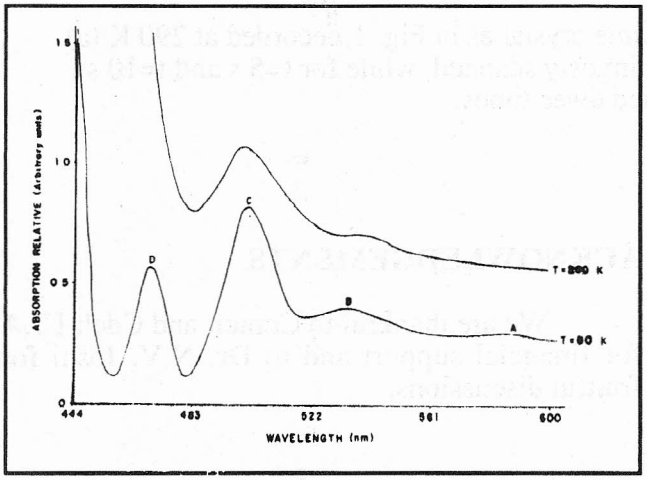

Figure 1. Optical Absorption spectra of a $Zn_{0.8}Mn_{0.2}Se$ single crystal, recorded at 290 K (a) and at 80 K (b).

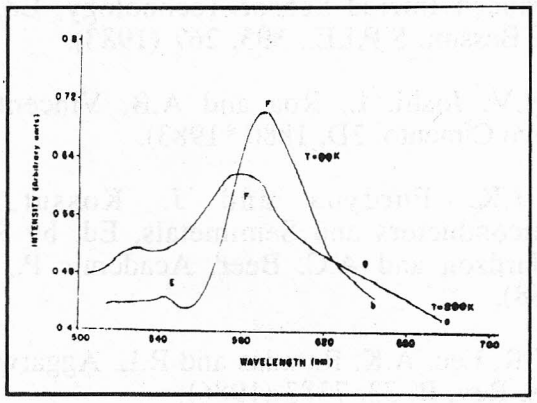

Figure 2. Photoluminescence spectra of same crystal and same temperatures as Fig. 1.

Peak J (2.96 eV), with a value larger than the band gap, is attributed to a transition from a level below the top of the valence band (V.B.) to the bottom of the C.B.. If we consider the $^6A_1$ level of the Manganese ion to lye at 0.2 eV below the top of the V.B. as inferred by López et al [10], then peak J may be explained as a transition from that level to the C.B. since the difference of 2.96 eV with the band gap value at 80 K of 2.79 eV nearly corresponds to the proposed 0.2 eV. Moreover, the origin for bands A and F of figures 1 and 2 respectively, is now well explained. Since the $^6A_1$--->$^4T_1$ transition value is 2.28 eV, this means that the $^4T_1$ level would be at 2.08 eV above the top of the V.B., giving rise to band A in the OA spectrum and to band F in the PL spectrum. This PL transition is probably more favoured as the density of final states is much higher at the top of the V.B. than at the $^6A_1$ level. Because of the interaction of the $^6A_1$ states of the Manganese ion with the upper part of the V.B., the normal density of states would be perturbed and this is consequently reflected in the form of the PhC peak J, and the uncertainty of its measured location. Peak J could not be observed in the absorption studies since the samples were too thin to be securely handled.

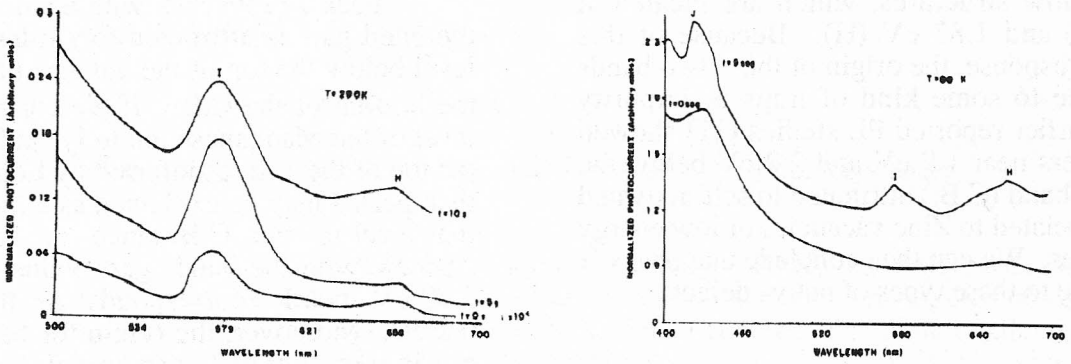

Figure 3. Normalized photoconductivity spectra of same crystal as in Fig. 1, recorded at 290 K (a) and at 80 K (b). Curves at t=0 s were continuosly scanned, while for t=5 s and t=10 s were recorded step by step with the indicated dwee times.

CONCLUSIONS

Figure 4 gives a schematic diagram indicating the relative positions of the relevant Manganese levels within the crystal field, with respect to the V.B. and C.B.. The diagram summarizes the different optical transitions observed in this work.

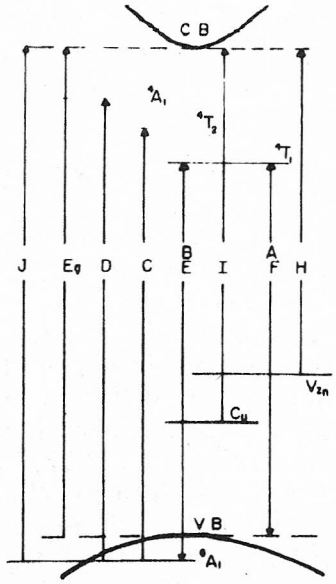

Figure 4.

ACKNOWLEDGEMENTS

We are thankful to Conicit and Cdch-ULA for financial support and to Dr. N.V. Joshi for fruitful discussions.

REFERENCES

1. N.V. Joshi, J.M. Martín and P. Quintero, Appl. Phys. Lett., 39, 70 (1981).

2. J.M. Martín, N.V. Joshi and A.B. Vincent, in Advanced Infrred Sensor Technology, Ed. by Jean Besson, S.P.I.E., 395, 267 (1983).

3. N.V. Joshi, L. Roa and A.B. Vincent, II Nuovo Cimento, 2D, 1880 *1983).

4. J.K. Furdyna and J. Kossut, in Semiconductors and Semimetals, Ed. by R.K. Willardson and A.C. Beer, Academic P., 25, (1988).

5. Y.R. Lee, A.K. Ramdas and R.L. Aggarwald, Phys. Rev. B, 33, 7383 (1986).

6. W. Giriat, Phys. Stat. Sol. (b), 132 K131 (1985).

7. D. Barreto, J. Luengo, Yovaninna DeVita and N.V. Joshi, Appl. Optics, 26, 5280 (1987).

8. A. Fazzio, M.J. Caldas and A. Zunger, Phys. Rev. B, 30, 3430 (1984).

9. J.K. Furdyna, J. Appl. Phys., 64, R29 (1988).

10. S.A. López-Rivera, L. Martínez, W. Giriat, F.D. Medina, H. Wang, H.L. Yuan and C. Parkanyi, this Conference.

11. G. Jones and J. Woods, J. Phys. D, 6, 1640 (1973).