OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 9, No. 11-12, Nov. – Dec. 2015, p. 1425 - 1428

EPR and magnetic properties of vapour phase grown $Cd_{1-x}Fe_xTe$ single crystals

J. SUBRAMANYAM[a,*], B. K. REDDY[b], N. MADHUSUDHANA RAO[c], G. KRISHNAIAH[d]
[a]*Department of Physics, NBKR Arts and Science College, Vidyanagar-524413, India*
[b]*Department of Physics, S.V. University, Tirupati-517 502, India*
[c]*School of Advanced Sciences, VIT University, Vellore-632 014, TamilNadu, India*
[d]*Department of Physics, Govt. Degree College, Puttur – 517 583, India*

EPR spectra were carried out at room temperature for vapour phase grown $Cd_{1-x}Fe_xTe$ ($0\leq x\leq 0.003$) diluted magnetic semiconducting single crystals in the frequency range 8.8-9.6 GHz. The results confirm the presence of uncoupled Fe^{3+} in the samples of all compositions with characteristic g-value around 2.002 ± 0.001, giving rise to the associated paramagnetic behaviour. The line width (ΔH) decreased as composition of 'Fe' increased due to dipole-dipole interaction between Fe^{3+} ions and the number of spins also decreased linearly with increasing Fe content. The magnetic studies on $Cd_{1-x}Fe_xTe$ samples of all compositions revealed the Van Vleck type of paramagnetism of crystals.

(Received March 21, 2013; accepted October 28, 2015)

Keywords: II-VI Diluted Magnetic Semiconductors, Vapour growth technique, Electron paramagnetic, Resonance, $Cd_{1-x}Fe_xTe$ Single crystals

1. Introduction

Diluted magnetic semiconductors (DMS) or semimagnetic semiconductors (SMSC) are classical II–VI, IV–VI and III–V semiconducting compounds in which a fraction of non-magnetic cations has been substituted by magnetic transition metal or rare earth metal ions such as Mn, Fe, Co, Cr, Ni, Sm, Er, Dy, Gd. DMS attracted the scientific community because of their exciting Properties.[1] Among all the members of II-VI semiconductor family, CdTe is good candidate with largest range of potential device applications. A great interest has been devoted to the DMS where Fe^{+2} ions are incorporated in II-VI semiconductors. One of the reasons is that Fe^{+2} is a Van-Vleck ion, so that the physical properties of such materials [2, 3] are dramatically different from those met in classical semimagnetic semiconductors where other transition ions carry a localized spin. Due to the d^6 electron configuration of the Fe^{+2} ions, the magnetic properties exhibited by Fe based DMS differ significantly from those of the Mn based DMS [4]. In the present work EPR and magnetization have been carried out on vapour phase grown CdFeTe single crystals. The results of these investigations with relevant discussions are presented in this paper.

2. Experimental

Single crystals of $Cd_{1-x}Fe_xTe$ with x=0.00, 0.01, 0.015, 0.02, 0.025 and 0.03 were grown by modified vapor phase growth technique [5]. Appropriate quantities of CdTe (99.99% M/s Sigma Aldrich) and FeTe prepared freshly from Fe and Te (99.99% M/s Sigma Aldrich) by solid state reaction method, were weighed, mixed and ground thoroughly in an agate mortar with an agate pestle to ensure homogeneity. The powder was packed tightly in the growth tube with the help of a clean quartz rod and was placed in the furnace such that the material was in the uniform temperature region. The mixture was sintered at 750^0C for about 48 h. Then the temperature was slowly brought down to room temperature in about 6 hours. The sintered material was used as the charge for crystal growth. The charge was loaded in the well cleaned growth tube and the opening end is drawn into a fine capillary of 20 cm length leaving a space of 5-6 cm for growth. The growth tube was carefully introduced in well cleaned protective quartz tube, evacuated to $2x10^{-6}$ Torr, and it is placed in a furnace such that the charge is at the highest temperature region of the furnace. The temperature of the furnace was slowly raised to 980°C in a period of about 24 hours. The crystal pullers were connected to protective tubes and were pulled at the rate of 0.6 mm/hour for about 6-7 days. Good quality $Cd_{1-x}Fe_xTe$ crystals were grown after a great deal of trail and error procedure. EPR spectra were recorded for samples of all $Cd_{1-x}Fe_xTe$ crystals using JEOL FE 1X spectrometer operating at X- band microwave frequency (8.8 to 9.6 GHz) at room temperature. Magnetization of $Cd_{1-x}Fe_xTe$ crystals of all compositions was studied at room temperature in the range of magnetic field 0-8KG using vibrating sample magnetometer (PAR, 155 EG & G, Princeton).

3. Results and discussion

Fig. 1 shows the first derivative electron spin resonance spectra of $Cd_{1-x}Fe_xTe$ samples with x = 0.00, 0.01, 0.015, 0.02, 0.025 and 0.03. The central peak corresponds to a 'g' value of 2.001 and is attributed to M = -½ →½ transition [6, 7]. It is well established that at room temperature while Fe^{2+} does not give EPR signal, Fe^{3+} gives resonance signals as reported by others [8-10]. The fact that EPR signals are observed for the present samples at room temperature (300 K) obviously indicates that in the present samples some 'Fe' ions exist in Fe^{3+} state.

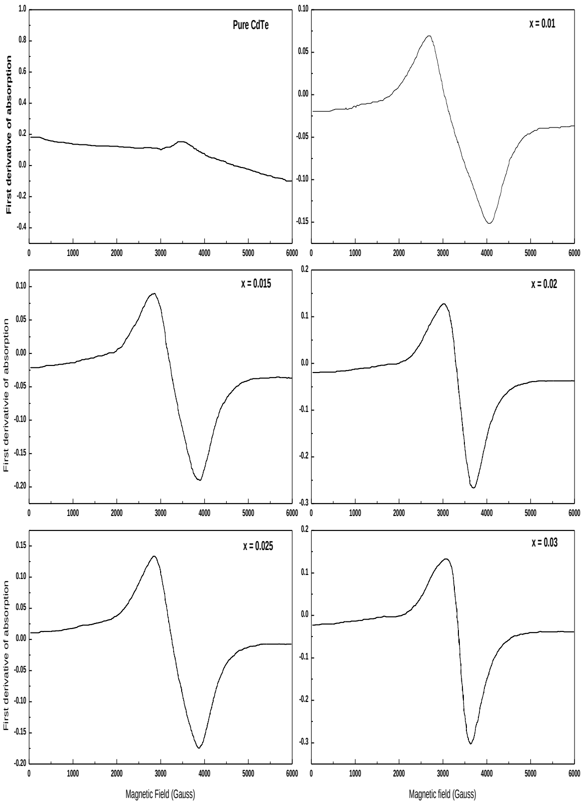

Fig. 1. EPR Spectra of $Cd_{1-x}Fe_xTe$ single crystals

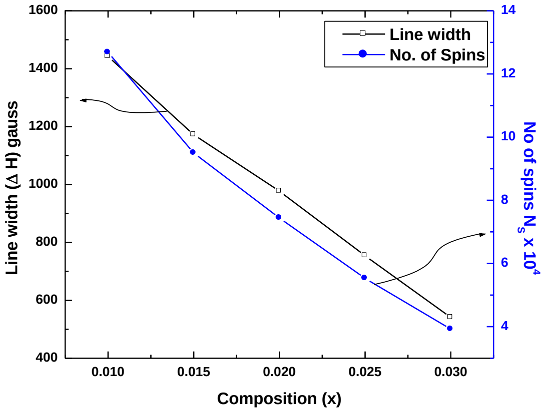

Fig. 2. Variation of line width (ΔH) and No. of spins with composition (x)

Table 1. Lande 'g' Factor, line width (ΔH) and number of spins (Ns) of $Cd_{1-x}Fe_xTe$ samples

Composition (x)	g-value	Line width (ΔH) Gauss	No of spins (N_S) x 10^4
0.01	2.002	1442	12.68
0.015	2.001	1172	9.50
0.02	1.998	977	7.44
0.025	2.001	754	5.53
0.03	1.998	541	3.92

The line width (ΔH), the number of spins (N_S), and the values of 'g' for samples of all the compositions were calculated using Rubbins and Bleanny relation [11, 12] and are given in Table 1. Fig. 2 shows the variations of line width (ΔH) and the No. of spins with Fe concentration (x) for the present $Cd_{1-x}Fe_xTe$ samples. The observed decrease in line width (ΔH) as the concentration of Fe increases is attributed to the dipole-dipole interaction between Fe ions and also due to inhomegenities in the internal field due to random distribution of Fe ions. From Fig. 2 it is evident that the number of spins decreases linearly with increasing 'x'. As 'x' increases the resonance signal becomes sharper and ΔH decreases and hence the number of spins decreases. Usually, if Fe is present in the substitutional site in CdTe lattice in tetrahedral symmetry, the valence state of Fe is expected to be 2+. However, the present EPR results confirm the presence of uncoupled Fe^{3+} within the samples, giving rise to the associated paramagnetic behaviour. The various possibilities for the presence of iron in both the valence states of Fe doped CdTe lattices are discussed here. The uncoupled Fe^{3+} ions may be due to the presence of nearest neighbour cationic vacancies and thus effectively doping holes in the system. In other words if cationic vacancies (Cd for the present case) are present in the nearest neighbour hood of Fe^{2+} in the substitutional cationic site, to neutralize the charge imbalance, the valance state of Fe can be converted to 3+. A cation vacancy near Fe, can promote Fe^{2+} into Fe^{3+} and also mediate the Fe^{2+} - Fe^{2+} exchange interaction. Since the transition metal (Fe) doping percentage is slightly on the higher side towards cationic percolation thresholds, Fe^{2+} - Fe^{3+} exchange, although being less in number compared to Fe^{2+} - Fe^{2+} interaction, may also be possible resulting in paramagnetic nature with g=2.002 and there is a possibility that EPR spectra may not resolve the signals for Fe^{3+} from the tetrahedral and octahedral sites [13]. In the Fe-doped CdTe system, Fe ions may be present in tetrahedral site, if due to the pressure of cation vacancy, the valence state changes to 3+, the crystal field no longer possesses tetrahedral symmetry. Hence, from the analysis of EPR signals of samples of all compositions having an average value of 'g' around 2.001±0.001 at room temperature with existing literature, it is inferred that 'Fe' most likely corresponds to isolated Fe^{3+} with cubic symmetry. EPR studies by Lischka et al, Brunthaler et al [9] and several others [10-16] also showed the presence of iron impurity in the Fe^{3+} state in CdTe and other II-VI host lattices

Magnetization as a function of magnetic field for all the samples was shown in Fig. 3. All the curves are almost straight lines passing through the origin and do not saturate up to the highest fields used. This is in striking contrast to the Brillouin – function behaviour and constitutes a strong signature of the Van vleck paramagnetism unique to Fe based DMS [17-22]. The observed magnetization behaviour in the present $Cd_{1-x}Fe_XTe$ may be understood as follows. The $3d^6$ electronic-configuration of Fe^{2+} ions possess both orbital and spin angular momenta (L=2, S=2). In tetrahedral symmetry, the ^5D configuration of free Fe ion is split by the crystal field into an orbital doublet ^5E and triplet $^5\Gamma_2$ (separated by Δ) lying at higher energy. Further, the spin-orbit interaction splits ^5E ground state into 5 nearly equidistant sub levels (Γ_1, Γ_4, Γ_3, Γ_5, Γ_2) separated by about $6\lambda^2/\Delta$ with λ being spin- orbit interaction parameter. The $^5\Gamma_2$ level is split into six levels with $^5\Gamma_2$ as the lowest energy level. The ground state Γ_1 is a magnetically inactive singlet resulting in Van Vleck type paramagnetism.

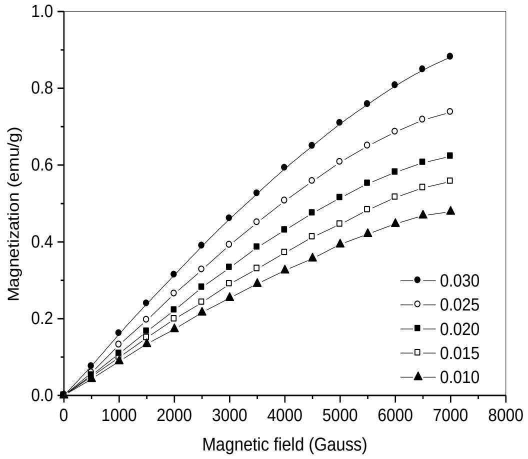

Fig. 3. Variation of magnetization with magnetic field

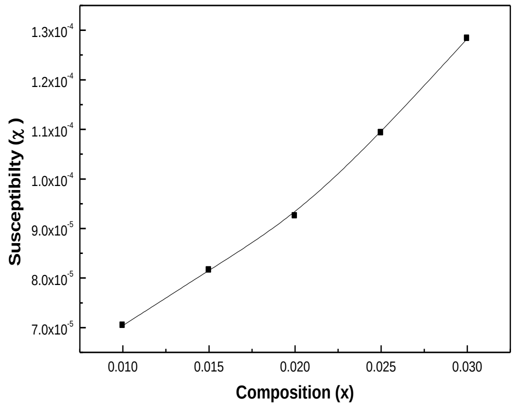

Fig. 4. Variation of susceptibility with composition (x)

The room temperature molecular susceptibility (χ_m) of the present $Cd_{1-x}Fe_xTe$ samples as a function of concentration (x) is shown in Fig. 4. The susceptibility increases with increase in Fe concentration. This is expected because as Fe concentration increases the magnetization increases and hence the magnetic susceptibility increases with ‘x ‘. For lower concentrations of Fe (x~0.02) the slope of the curve is smaller compared to the slope (rate of increase) at higher concentrations (x>0.02).

4. Conclusions

Single crystals of $Cd_{1-x}Fe_xTe$ were grown successfully by vapour phase growth technique for nominal concentrations $0 \le x \le 0.03$. The room temperature EPR studies confirmed the presence of uncoupled Fe^{3+} in the samples of all compositions with characteristic g-value around 2.002±0.001, giving rise to the associated paramagnetic behaviour. The magnetic studies on $Cd_{1-x}Fe_xTe$ samples of all compositions revealed the Van vleck type of paramagnetism of the crystals.

References

[1] J. K. Furdyna, J. Kossut, **25**, Academic Press, New York, 1988.
[2] A. Mycielski, J. Appl. Phys. **63**, 3279 (1988).
[3] D. Scalbert, J. A. Gaj, A. Mauger, J. Cernogora, C. B. Guillaume, Phys. Rev. Lett. **62**, 2865 (1989).
[4] A. Twardowski, M. Von Ortenberg, M. Demianiuk, J. Cryst. Growth **72**, 401(1985).
[5] P. Chandrasekharm, D. Raja Reddy, B. K. Reddy, J. Cryst. Growth. **63**, 304 (1983).
[6] A. Abragam, B. Bleaney, Electron Paramagnetic Transistion ions, clarendon press, Oxford (1970).
[7] K. Lischka, G. Brunthaler, W. Jantsch, J. Cryst. Growth., **72**, 355 (1985).
[8] K. Lischka, G.Brunthaler, W. Jantsch, J. Cryst. Growth., **72**, 355 (1983).
[9] G. Brunthaler, U. Kaufmann, J. Schneider, J. Apply. Phys. **56**, 2974 (1984).
[10] U. Kaufmann, Phys. Rev. B. **14**, 1848 (1976).
[11] D. Bleanny, R. S. A. Rubbins, Proc. Phys. Soc. JPN, **77**, 103(1961).
[12] J. M. Nedlac, Bouazaoui M. Turrell S Phys. Chem. Glasses., **40**, 264 (1999).
[13] C. B. Azzoni, Solid State Commun., **117**, 511 (2001).
[14] Gordon G. Wepfer, Phys. Rev., **170**, 445 (1968).
[15] Dieleman, J. Phillips. Res. Rept, **20**, 206 (1965).
[16] T. L. Estle, W. C. Holton, Phys. Rev., **150**, 159 (1966).
[17] H. Alawadhi, I. Miotkowski, M. Mc Elfresh, A. R. Ramdas, Phys. Rev. B. **63**, 155201 (2001).
[18] E. Kartheuser, Sergio Rodriguez, Murielle Villeret, Phys. Rev. B. **48**, 14127 (1993).

[19] C. Testelin, C. Rigaux, A. Mauger, D. Scal bert, C. Benoit, Guillaume, A. Mycielski, J. Apply. Phys. **70**, 6383 (1991).
[20] C. Testelin, A. Mauger, C. Rigaux, M. Guillot, A. Mycielski, Solid State Commun., **78**, 659 (1991).
[21] C. Testelin, A. Mauger, C. Rigaux, M. Guillot, A. Mycielski, Solid State Commun., **71**, 923 (1989).
[22] Twardowski, A. Lewicki, M. Dermianiuk, Phys. Rev. B, **38**, 10749 (1988).

---

*Corresponding author: drsubbuphd@gmail.com