Single Crystal Electron Paramagnetic Resonance (EPR) Study of Mn^{2+} Ions in $CuGaS_2$

P.Prabukanthan[1*] and G. Harichandran[2]
[1]Department of Chemistry, Muthurangam Government Arts College, Vellore – 632002, India.
[2]Department of Polymer Science, University of Madras, Guindy Campus,
Chennai – 600025, India.
e-mail:pprabukanthan76@hotmail.com

Abstract— **Single crystals of one mole % Mn doped $CuGaS_2$ (CGS) compound semiconductor were grown by a chemical vapor transport (CVT) technique in a closed system using iodine as a transporting agent. The electron paramagnetic resonance (EPR) of the Mn^{2+} ions in a CGS single crystal has been studied with an X-band spectrometer recorded at 80 K. The spectroscopic splitting tensor (g), hyperfine constant (A) and zero field splitting (D) parameters were determined using the effective spin Hamiltonian. It turns out that the Mn^{2+} ions substitute for Ga^{3+} ion in the sulphur tetrahedron without nearby charge compensation.**

Keywords- single crystal; semiconductor; EPR; hyperfine constant

I. INTRODUCTION

Chalcopyrite compounds of I-III-VI_2 are ternary analogs of binary II-VI compounds. The structure of chalcopyrite is derived from their binary by ordered substitution of two kinds of cations along the c-axis. I-III-VI_2 compounds can be used in photovoltaic solar cells, light-emitting diodes, infrared detectors and in various non linear optical devices [1-2]. There are two tetragonal (D_{2d}) cationic sites, I-group ions and III-group ions sites in this type of semiconductor [2]. $CuGaS_2$ (CGS) has a direct band gap of 2.49 eV in the green region [3] and has been considered to be a promising material for visible and ultraviolet (UV) light emitting device [4]. When a transition metal ($3d^n$) impurity ion enters these crystals the determination of the substitutional site of impurity is difficult because of the similarity of the first anionic shells in I-group and III-group cationic sites. However for technical applications, its is necessary to understand the nature and the substitutional site of impurity incorporated in these semiconductors because the impurity centers have great influence on the electric, magnetic and optical properties of semiconductors. Electron paramagnetic resonance (EPR) gives information on the site location, the local site symmetry the ground state energy levels and the structure of point defects as well as on the impurity ions in the host materials. So many EPR spectra were made for $3d^n$ ions in I-III-VI_2 semiconductor [5-8]. In CGS semiconductor, the impurities (Mn) tend to enter substitutionally on the metal sublattice. This is partly due to flexibility in structure and the fact that two different cation sites exit in this crystal. The energy for Mn substitution in Ga (0.43 eV/Mn) is lower than that for Cu site (0.80 eV/Mn) [9]. This implies that Mn substitutes into the Ga site rather than the Cu site [9-10].

In this paper, the rotation patterns of the resonance fields of Mn^{2+} ions in CGS single crystal have been obtained in the crystallographic (001), (100) and (010) planes. The electron paramagnetic resonance (EPR) spectra of Mn^{2+} were analyzed using an effective spin Hamiltonian with the effective spin $S=5/2$. The spectroscopic splitting tensor g, hyperfine constant (A) and zero filed splitting (D) parameters for Mn^{2+} ions in CGS were determined from the observed experimental resonance spectra. The local site symmetry and the site location of the Mn^{2+} ions in the host crystal are also discussed.

II. EXPERIMENTAL

A. Growth of Mn doped $CuGaS_2$ single crystal

Single crystals of one mole % Mn doped $CuGaS_2$ (CGS) were grown by the chemical vapor transport method using iodine as the transporting agent. The purity of the elements used for the present experiments was 4N. A mixture of elements Cu, Ga, one mole % Mn and S has been taken in a quartz ampoule of length 18 cm and a diameter of 1 cm along with iodine concentration of 10 mg/cm^3. The ampoule cooled by ice, was evacuated to around $2x10^{-6}$ Torr and sealed off. The ampoule was placed into the double-zone horizontal furnace controlled by temperature controllers having accuracy of ± 0.1 K. A reverse temperature profile was developed across the ampoule over several hours to get cleaning effects on the quartz walls of the growth zone. The duration is 20 hours. After this, the temperatures of source zone and growth zone have been maintained at 1173 K and 1023 K respectively. The duration of the growth was 7 days and then the furnace was slowly cooled at a rate of about 10 K per hour upto 873 K after reaching this temperature it was cooled rapidly at rate of 60 K per hour. Several growth runs were made to optimize the growth conditions. Obtained single crystal is green in colour with dimension of 2.5x3x4 mm^3. The growth and characterization of as-grown pure CGC and Mn doped CGC single crystals have been reported earlier [11-12].

B. Characterization

Single crystal X-ray diffraction analysis was carried out using an Bruker X8 kappa diffractometer with MoK_α (λ = 0.177 Å) radiation to identify the structure, space group, volume of unit cell and to estimate the lattice parameter values. Electron paramagnetic resonance (EPR) spectra were recorded at 80 K on a Varian E-112 EPR spectrometer operating at X–band frequencies having a 100 kHz field modulation and phase sensitive detection to obtain the first derivative EPR signal. DPPH with a g value of 2.0036 was used as an internal field marker for g factor calculations.

C. Crystal Structure of Mn doped $CuGaS_2$

The single crystal X-ray diffraction analysis shows that one mole % Mn doped $CuGaS_2$ (CGS) single crystal is tetragonal (chalcopyrite) system. The point group is D_{2d} with unit cell parameters a = 5.2504 Å and c = 10.4502 Å. The volume of the unit cell is 300.2 $Å^3$ and contains four molecules per unit cell. The resulting c/a ratio is 1.9904, which indicates that there is a significant compression of the lattice alone the c-axis. Each Cu^+ and Ga^{3+} ions are surrounded by four sulphur atoms, which belong to tetrahedron. The interatomic distance of Cu-S and Ga-S are 2.3128 ± 0.0012 Å and 2.3102 ± 0.0018 Å in the case of pure $CuGaS_2$ single crystal interatomic distance of Cu-S and Ga-S are 2.3128 ± 0.0018 Å and 2.921 ± 0.0014 Å

The anion parameter (u) has a room-temperature value of 0.275 in pure CGS [13] and one mole % doped Mn doped CGS: u = 0.283. It is a measure (when capered to ¼) of the relative rotations of the sulfur tetrahedral about the copper and gallium sites. The unique axis in CGS is labeled the [001] direction (or c-axis) and the two equivalent axes in basal plane are labeled the [100] and [010] directions (or a-axes). Thus it is assumed, that Mn is really built in the chalcopyrite structure. Moreover no hints for the existence of Mn precipitates or other Mn alloys as well as Mn oxides can be found. In the regular CGS lattice, the “twist” angle that describes these small and opposite, rotations of the two GaS_4 units about the [001] axis is 3.2°. This shifting in positions of the sulfur ions occurs because the copper and gallium ions have different covalent radii and thus, different bond lengths with the neighboring sulfur ions (i.e., the Cu-S separation is greater than the Ga-S separation). These clockwise and counterclockwise rotations of the sulfur ions about the cations result in two crystallographically equivalent, but magnetically inequivalent, sites for the Mn^{2+} ions that replace Ga^{3+}.

III. RESULTS AND DISCUSSION

Electron paramagnetic resonance (EPR) is a sensitive tool to detect the paramagnetic impurities even when they are in very small concentration. The embedding of Mn inside the matrix is also interred from EPR measurements. Because the hyperfine splitting constants depends on the environments of Mn ions, the bonding characteristic between Mn ions and the host lattice can be explained by EPR analysis. The Mn^{+2} charge state has a half filled d shell ($3d^5$) with angular momentum L = 0 and spin S = 5/2. The distinctive feature of EPR of Mn is its hyperfine splitting arising from the ^{55}Mn nucleus (I = 5/2). We analyze the experimental data according to the standard spin Hamiltonian [12-13] can be written as $H_S = g\mu_B HS + ASI + D [S_z^2 – 1/3 S (S+1)] + a/6 [S_x^4 + S_y^4 + S_z^4 – (1/5)S(S+1)(3S^2 +3S +1)]$. Here, the first tern is the Zeeman interaction, μ_B is the Bohr magnetron and g is the g factor. S and I are spin operators for the electronic and the nuclear spin, respectively. The second term corresponds to the hyperfine structure (HFS) coupling that is assumed to be isotropic. A is the hyperfine constant. The third and fourth terms describe the fine structure (FS) structure, corresponding to axial and cubic symmetries of the crystal field, respectively. The hyperfine coupling of the electronic spin S with nuclear spins of neighbouring ions is not consideration because this super-hyper-fine interaction does not affect the positions of the resolved EPR lines but leads to line broadening only.

No EPR signal was detected in the spectra of pure $CuGaS_2$ (CGS) single crystals indicating that free from paramagnetic impurities. In the EPR spectrum of applied field (H) parallel to a-axis and b-axis allowed hyperfine transitions lines are same spectrum observed in Mn doped CGS single crystal. Figure 1 (a-c) and Figure 2 (a-c) shows the EPR spectrum of Mn^{2+} ions in CGS single crystals for H parallel to the bc and ab axis recorded at 80 K. For an arbitrary orientation, the EPR spectrum consists of a number of lines corresponding to allowed ($\Delta M = \pm 1$ and $\Delta m = 0$) transitions. There are five sets of six lines in each spectrum (indicate by the “stick” diagrams above the data), as expected for an S=5/2 electron spin interacting with the 100 % abundant I=5/2 nuclear spin of the ^{55}Mn nucleus. Figure 1 (a-c) corresponds to the angle, when the D term nearly vanishes. A close look at the spectrum indicates more than twenty lines are observed. This indicates the presence of a second site. However, Figure 1c and 2c contains six and above lines, further confirming the previous hypothesis of two sites. In the EPR spectrum of H parallel to bc-axis and ac-axis allowed hyperfine transitions lines are same spectrum observed due to tetragonal system for Mn doped CGS single crystal.

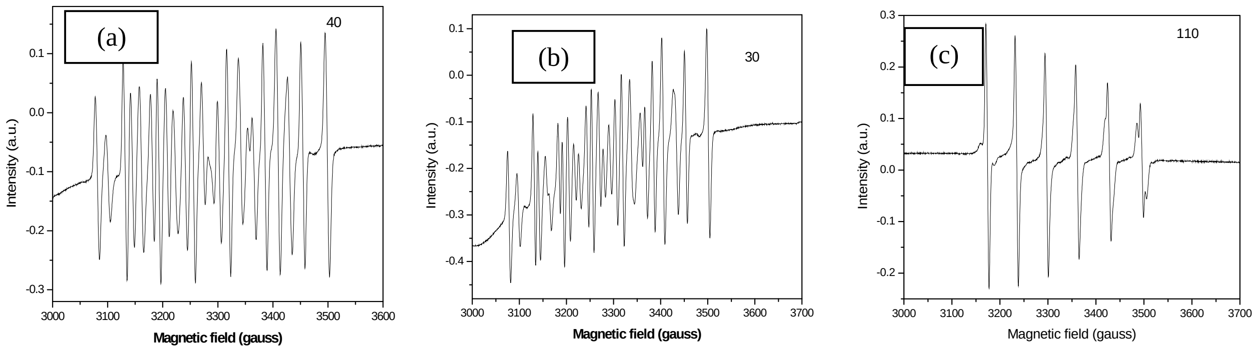

Figure 1 (a-c) Single crystal EPR spectra of Mn doped $CuGaS_2$ at three orientations in bc plane recorded at 80 K temperature (a) 40 degree rotation (b) 30 degree rotation (c) 110 degree rotation.

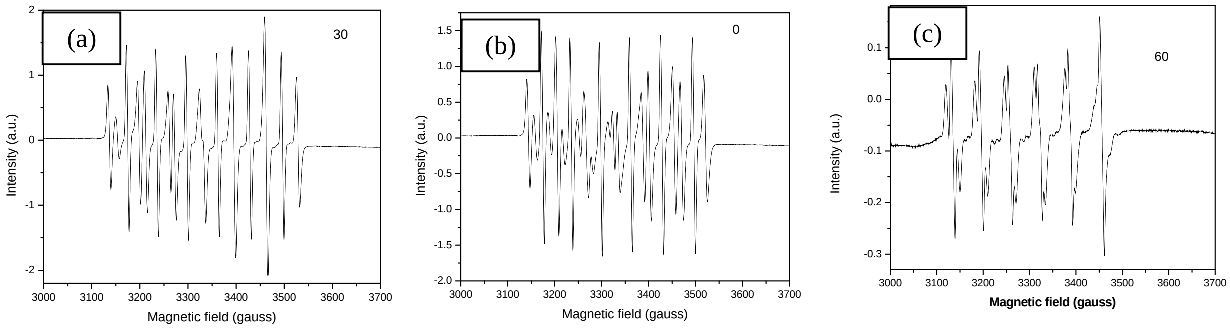

Figure 2 (a-c) Single crystal EPR spectra of Mn doped $CuGaS_2$ at three orientations in ab plane recorded at 80K temperature (a) 30 degree rotation (b) 0 degree rotation (c) 60 degree rotation.

The positions of 30 spectral lines, corresponding to six orientations of the nuclear spin (I), (M_I = -5/2,…..,5/2) and to five different spin-flip transitions $M_S \leftrightarrow M_S + 1$ between six energy levels labeled by M_S (M_S = -5/2,….,3/2) were calculated according to spin Hamiltonian. To evaluate the spin Hamiltonian parameters we took the best fit of all spectra measured for various field orientations. From the single crystal rotation data at 80 K, isofrequency plots (001), (100) and (010) planes have been plotted and shown in Figure 3 & 4, respectively. However as mentioned earlier, the variation of resonance lines and followed only for the strong resonance lines. This road map clearly follows the expected pattern [14]. The data points in the (001) plane are symmetric about the B/0° or 90° direction. The data points in the (010) plane also show symmetric angular dependences about the B/0° direction, as well as the B/90° direction (100). These show that the local site symmetry around the Mn^{2+} ions is orthorhombic.

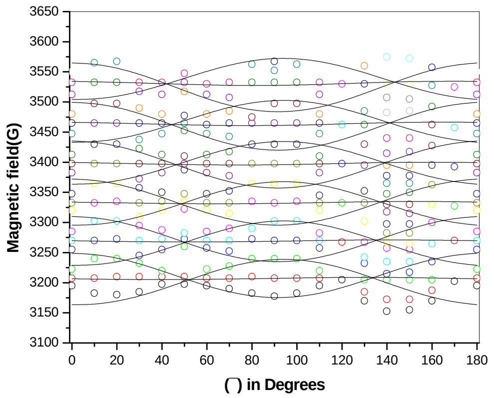

Figure 3 Iso-frequency plot for Mn doped $CuGaS_2$ at 80 K temperature in bc plane of rotation.

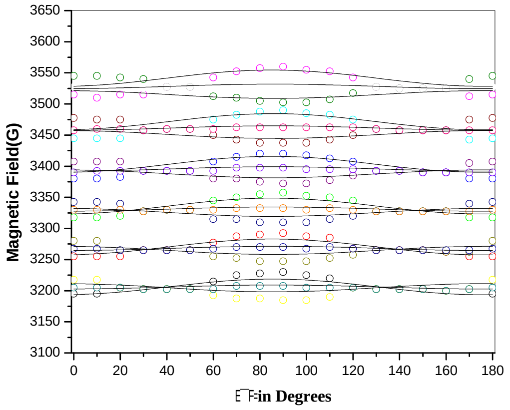

Figure 4 Iso-frequency plot for Mn doped $CuGaS_2$ at 80 K temperature in ab plane of rotation.

Definitely, the anisotropy does not originate from magnetic-dipole interactions. Such a shape-related anisotropy should be by an order of magnitude smaller and the easy axis would have to lie in plane. So it is obvious that the anisotropy, in particular, the axial component of the anisotropy, is caused by mechanical strain that occurs in the crystal lattice. The Mn^{2+} ion to be a substitutional defect at a Ga site in CGS compounds, actually there are two non equivalent Ga sites in the chalcopyrite structure of CGS single crystals which differ by the sense of rotation of their nearest-neighbour sulphur tetrahedrons [15] but substitute Mn in CGS single crystals, it is clear from Figure 1c (applied the H to bc-axis) and Figure 2c (applied the H to ab-axis) that there magnetically equivalent and chemically identical Mn^{+2} sites. When they become equivalent along crystal rotation, only one-site (i.e) only one-hyperfine sextet lines were observed. This may be due to the overlap of second site of Mn^{2+}, which has very low zero filed splitting value. In CGS, where cation substituted Mn^{2+} ion is tetragonally distorted with tetrahedral crystal field of the chalcopyrite structure. The above observation due to chalcopyrite structure of CGS single crystals is the two cations Cu and Ga alternately occupy the cation sites in the stack forming CuGaCuGaCuGa… sequence with an interval c/2 parallel to c axis, while CuCuCuCu... and GaGaGaGa…sequences are parallel to the a axis [16]. The computer program [17] employed here sets up the spin Hamiltonian matrices and determines their eign values by using exact diagonalization.

The set of input parameters is optimized using a non-linear least-squares fit so as to minimize the deviations between the observed and the calculated transition frequencies, as well as resonance lines due to the fine structure of Mn^{2+} in CGS recorded in the crystallographic planes are used for fitting the g and zero field splitting (D), hyperfine constants (A) parameters. The final best fit components of g_{ii}, A_{ii}, and D_{ii} obtained with the computer program are listed in Table 1.

TABLE - PRINCIPAL VALUES AND DIRECTION COSINES OF THE D, g AND A TENSOR FOR Mn DOPED $CuGaS_2$ SINGLE CRYSTAL AT 80 K TEMPERATURE AND DIRECTION COSINES

Principal values	**Matrix D (symmetric) for spin # 1 (electronic), in units of G**		
3.5794021774	-0.4675346020 0.3341458995	-1.0711251507 0.3957935634	1.2000000000 0.0000000000
-0.5184224913		2.8791907278 0.3271314215	-1.2147936387 0.3884163071
-3.0609796861			-2.4116561258 0.3407047031
	Matrix g (symmetric) for spin # 1 (electronic), no unit		
1.9918984257	1.9914450246 0.0012416464	-0.0011395739 0.0011351904	0.0001000000 0.0000000000
1.9889470110		1.9887463296 0.0010759885	0.0016738598 0.0014101348
1.9841936429			1.9848477254 0.0015589875
	Matrix A (symmetric) coupling spin # 1 (electronic) with spin # 2 (nuclear), in units of G		
67.5011221638	62.6241040737 1.2205068053	0.1612504695 1.0934178298	-0.5700000000 0.0000000000
62.6287003821		63.8252579161 1.0552958678	-2.4896349780 1.3766766063
62.0397204225			65.7201809786 1.5190601391

It is clear from the Table-1 that g and A are no longer isotropic, but show orthorhombicity. One generally expects a g value of close to 2.0023 for Mn^{2+} ions, since the excited states are too far to deviate g value from this. However, the range of deviation from 2.0023 is 0.0182 to 0.0087. Such a large difference may be due to a slight spin transfer from Mn^{2+} ions to ligands [18-20] or the presence of some excited states, which interacted with the ground state. However, slightly lower hyperfine values noticed indicate the former suggestion. Here, in order to confirm the location of the paramagnetic impurity in the host lattice.

To identify the substitutional site location of the Mn^{2+} ion in CGS single crystal, considered several point. First, the ionic radii of Mn^{2+} ions are 0.66 Å for a 4 coordination number and 0.83 Å for a 6 coordination number. Mn^{2+} ion can substitute for the Ga^{3+} ion (0.62 Å) or for Cu^{+} ion (0.74 Å) in the sulphur (4 coordination number) in sulphur tetrahedron (4-coordiantion number) in CGS. Their local site symmetry is tetragonal, having only an axial zero field splitting parameter D. If the Mn^{2+} ion occupies the Cu^{+} site in the sulphur tetrahedron, then the local site symmetry of the Mn^{2+} ion will be distorted tetrahedron. However, the local site symmetry of Mn^{2+} ion turns out to be orthorhombic, having both an axial zero field splitting parameter (D). These show that the Mn^{2+} ion in a CGS single crystal substitutes not for the Cu^{+} ion in the sulphur tetrahedron but for the Ga^{3+} ion in the sulphur tetrahedron. We could not find any evidence that Mn^{2+} is locally charge compensated. Thus, it is reasonable to conclude that the Mn^{2+} ion occupies the Ga^{3+} ion site, instead of the Cu^{+} ion site, without nearby charge compensation.

In summary, the magnetic resonance spectra of Mn^{2+} ion in CGS single crystals are obtained in the crystallographic planes by using an electron paramagnetic resonance (EPR) spectrometer at 80 K. The spectroscopic splitting tensor g, A and D are determined with an orthorhombic spin Hamiltonian. From the rotation patterns and the zero field splitting parameter of the Mn^{2+} ion is orthorhombic even though that of the crystal structure is tetragonal. In turns out that the Mn^{2+} ions in the CGS crystal substitute, without nearby charge compensation, for the Ga^{3+} ions in the sulphur tetrahedron. The room temperature to liquid nitrogen temperature study of powder spectra indicates the absence of any phase transitions in one mole % Mn doped CGS compound.

REFERENCES

[1] J.L. Shay, J.W. Wernick, Ternary Chalcopyrite Semiconductors: Growth, Electronic Structure and Applications; Pergamon Press, New York, 1975.

[2] J.E. Jaffe, A. Zunger, Phys. Rev. B Vol. 29, 1984, pp. 1882-1890.

[3] J. Eberhardt, H. Metzner, T. Hahan, V. Reislohner, J. Cieslak, U. Grossner, R. Goldahn, F. Hudert, G. Gobsch W. Witthuhu, J. Phys. Chem. Solids Vol. 64, 2003, pp. 1781-1786.

[4] K. Oishi, S. Kobayashi, S.I. Ohta, N. Tsuboi, F. Kaneko, J. Crystal Growth Vol. 177, 1997, pp. 88-92.

[5] K. Sato, I. Aksenov, N. Nishikawa, Jpn. J. Appl. Phys. Vol. 32 (suppl.), 1993, pp. 841-845.

[6] N. Nishikawa, I. Aksenov, T. Shinzato, T. Sakamoto, K. Sato, Jpn. J. Appl. Phys.Vol. 34, 1995, pp. L975-L977.

[7] K. Stevens, N.Y. Garces, L. Bai, N.C. Giles, L.E. Halliburton, S.D. Setzier, P.G. Schunemann, T.M. Pollak, R.K. Route, R.S. Feigelson, J. Phys.: Condens. Matter. Vol. 16, 2004, pp. 2593-2596.

[8] U. Kaufmann, A. Rauber, J. Schneider, Solid State Commun. Vol. 15, 1974, pp. 1881-1886.

[9] S. Picozzi, Yn-Jun Zhao, A.J. Freeman, B. Delley, Phys. Rev. B Vol.66, 2002, pp.205206-12.

[10] Yn-Jun Zhao, A. Zunger, Phy. Rev. B Vol. 69, 2004, pp. 104422-8.

[11] P. Prabukanthan, R. Dhanasekaran, Crystal Growth & Design, Vol. 7, 200), pp. 618-623.

[12] P. Prabukanthan, R. Dhanasekaran, J. Phys. D: Appl. Phys. Vol. 41, 2008, pp. 115102 (6 pages).

[13] J.E. Jaffe and Alex Zunger, Phys. Rev. B Vol. 28, 1983, pp. 5822-5827.

[14] B. Blearey, D. Ingram, J. E. Proc. R. Soc. (London) Ser. A Vol. 205, 1951, pp. 336-339

[15] B.R. McGarvey, Transition Metal Chemistry (Marcel Dekker Inc.) Vol.3, 1966, pp. 189-194

[16] A. Abragam, B. Bleaney, Electron Paramagnetic Resonance of Transitions Ion, Clarendon press, Oxford, 1970.

[17] H.J. Von Bardeleben, A. Goltzene, C. Schwab, R.S. Feifelson, Phys. Rev. B Vol. 21, 1980, pp. 1757-1760.

[18] G. Eilens, M. Matsui, Jap. J. Phys. Soc. Vol. 65, 1996, pp. 2227-2231.

[19] F. Clark, R.S. Dickson, D.B. Fulton, J. Isoya, A. Lent, D.G. McGavin, M.J. Mombourquette, R.H.D. Nuttall, P.S. Rao, H. Rinneberg, W.C. Tennact, J.A. Weil, Operating Instruction for Computer Program EPR-NMR, Version 6, University of Saskatchewan, Saskatoon, Canada, 1995.

[20] M.Vithal, R. Jagannathan, J. Chem. Soc. Dalton Trans. (1988), pp. 983-987.