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RELATION OF MAGNETO-OPTICAL PROPERTIES OF FREE EXCITONS TO SPIN ALIGNMENT OF Mn^{2+} IONS IN $Cd_{1-x}Mn_xTe$

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A direct comparison of the splitting of free exciton states with the magnetic moment of the Mn^{2+} ion system shows excellent agreement with simple exchange interaction model throughout the composition range studied ($0.005 < x < 0.3$) at liquid helium temperature in magnetic field up to 5.6 T. Measurements of magnetic moments up to 15.5 T at 1.5 K show paramagnetic behaviour of samples with low manganese contents. With increasing amount of manganese mile fraction, strong influence of interaction of antiferromagnetic type between Mn^{2+} ions is observed. Comparison of optical and magnetic data yields refined values of exchange integrals of Mn^{2+} ions with conduction and valence electrons: 0.22 and -0.88 eV, respectively.

1. INTRODUCTION

SEMICONDUCTING SYSTEMS with controlled quantity of magnetic elements – as well impurities as components of alloys – have recently received considerable attention. The alignment of a system of magnetic ions produces in these materials strong splittings of electronic energy states. Resulting giant magneto-optical phenomena have been reported in $Hg_{1-x}Mn_xTe$ by Bastard *et al.* [1], in CdTe:Mn and in ZnTe:Mn by Komarov *et al.* [2, 3], as well as in $Cd_{1-x}Mn_xTe$ [4, 5]. In all those cases, the observed effects have been explained by introducing influence of the system of Mn^{2+} ions on exciton or band electron states by means of exchange interaction. This is typically done in the form of an Heisenberg type Hamiltonian which can be written, e.g. for a conduction electron as:

$$\mathcal{H}_{\text{int}} = -\sum_i J(\mathbf{r} - \mathbf{R}_i)\mathbf{S} \cdot \mathbf{S}_i,$$

where $\mathbf{r}$ and $\mathbf{S}$ are, respectively, the position and the spin of the conduction electron and i numbers Mn^{2+} ions of positions $\mathbf{R}_i$ and spins $\mathbf{S}_i$. Within typical approximations, it allows to calculate energy states of conduction and valence electrons by $k.p$ perturbation method. The $k.p$ matrix is augmented by diagonal terms which for the conduction band are equal to [1]:

$$A = \pm \tfrac{1}{2} N_0 \alpha x \langle S_z \rangle, \tag{1}$$

where $\alpha = \langle \Psi | J | \Psi \rangle$ is the exchange integral, parameter of interaction of electrons with Mn^{2+} ions, N_0 is the number of unit cells per unit volume, x is the mole fraction of Mn and $\langle S_z \rangle$ is the thermal average of zth component of Mn^{2+} spin.

In $Cd_{1-x}Mn_xTe$, large value of the energy gap [6, 7] – therefore large effective masses and small "intrinsic"‡ g-factors of band electrons – allows to apply a very simplified approach, neglecting direct influence of the magnetic field on the band electron states [4]. As a result, the calculated splittings of transition energies are simply proportional to expressions of the form of equation (1) and consequently to the magnetization of the Mn^{2+} ion system. In order to check the range of validity of that approach, measurements of magnetization and of magnetoreflectivity were performed on the same samples.

2. MATERIAL

Single crystals of zincblende structure were grown by a modified Bridgman technique at the Institute of Physics of Polish Academy of Sciences (Warsaw). It was verified by chemical analysis that composition of the crystals corresponded exactly to the amount of components used for the growth. Linear dependence of free exciton energy on composition that has been established in this material [7], allows a precise verification of

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‡ "Intrinsic" means here: without taking into account the exchange interaction with Mn^{2+} ions.

Table 1. Numerical results of magnetization and magnetoreflectivity measurements in $Cd_{1-x}Mn_xTe$

Composition		Temperature		Parameters of magnetization function			Exchange constant
Techno-logical x (%)	Corrected x_{opt} (%)	Magnetic exp. T_m (K)	Optical exp. T_{opt} (K)	T_0 (K)	Saturation value S_0	Standard deviation	$N_0(\alpha-\beta)$ (eV)
0.5	0.55	1.49	1.37	0.29	2.11	0.014	1.15
1.	0.88	1.56	1.38	0.68	2.12	0.030	1.17
2.	1.86	1.46	1.39	0.94	1.97	0.012	1.12
5.	4.88	1.44	1.40	2.29	1.54	0.030	1.12
10.	10.	1.46	1.39	3.84	1.08	0.027	1.09
20.	20.	1.47	1.39	7.3	0.71	0.025	1.06
30.	30.	1.53	1.40	14.9	0.52	0.011	1.06

homogeneity of the samples. For optical measurements, where only a small fraction of the crystal is involved, the value of composition assumed for interpretation was corrected using free exciton energy obtained from reflection spectra. For magnetization measurements where experiment integrates over the whole volume of the sample, composition values were merely deducted from the amount of components. All optical measurements were done on cleaved (110) surfaces. Seven materials of different manganese mole fraction x were studied in the range $0.005 \leqslant x \leqslant 0.30$ (see Table 1).

3. MAGNETIZATION MEASUREMENTS

Magnetization was measured by an extraction method [8] at temperature 1.5 K and magnetic fields from 0.2 up to 15.5 T at Service National des Champs Intenses (Grenoble). Assuming that the magnetization of the sample comes entirely from the Mn^{2+} ions, it may be presented in the form of $\langle S_z\rangle$ vs magnetic field. That was done in Fig. 1. For composition x up to 0.02 experimental results can be well described by the Brillouin function for a spin value of $S = \frac{5}{2}$, by adjusting saturation value and introducing an effective temperature $T_{eff} = T + T_0$:

$$\langle S_z\rangle = S_0 B_{5/2}\left(\frac{\frac{5}{2}g\mu B}{kT_{eff}}\right), \tag{2}$$

where $g = 2$ and μ is Bohr magneton. The obtained values of parameters S_0 and T_0 are collected in Table 1. Figure 1 shows as an example the fit for $x = 0.02$. Measurements of magnetization were performed also for 4.2 K showing the same features with T_0 close to that obtained for 1.5 K. Detailed data on temperature dependence will be presented in a future paper.

The obtained saturation values smaller than $\frac{5}{2}$ suggest that a fraction of Mn^{2+} ions form pairs and/or complexes with strong antiferromagnetic ordering, thus, producing no magnetic moment. That fraction understandably increases with the amount of manganese in the sample. The remaining ions align in the magnetic field according to a Brillouin function with T_{eff} greater than the real temperature (positive T_0). It reflects an antiferromagnetic type of interaction also among those ions. That interaction, apparently of a longer range, similarly increases with composition. Results obtained for higher compositions are presented also in Fig. 1.

An approximate description of those results in terms of Brillouin function is still possible (see Table 1). However, the accuracy of fitting is lower; moreover, due to relatively small range of argument $\frac{5}{2}g\mu B/kT_{eff}$ the parameters obtained possess rather qualitative character. The continuing decrease of magnetic moment per ion reflects increasing interaction between the manganese. Possibly formation of a spin glass phase takes place for higher compositions.

4. OPTICAL MEASUREMENTS

Reflection spectra were measured in a standard system with a tungsten iodine lamp, a Jobin–Yvon monochromator and a GaAs photomultiplier. Samples were immersed in liquid helium. Temperature was controlled by the pressure in the cryostat, with a precision of 0.02 K. In accordance with previous reports [5], a splitting of the exciton structure into six components was observed. Ratios of splittings of particular components were also found constant, independently of temperature, composition or magnetic field. To determine (within the used model) splittings of conduction and valence bands in a given magnetic field, it is sufficient to study the four components observable in Faraday configuration. According to [5] their energies are following:

$$E_{1\pm} = E_0 \pm \tfrac{1}{2}(\alpha-\beta)N_0 x\langle S_z\rangle \tag{3a}$$

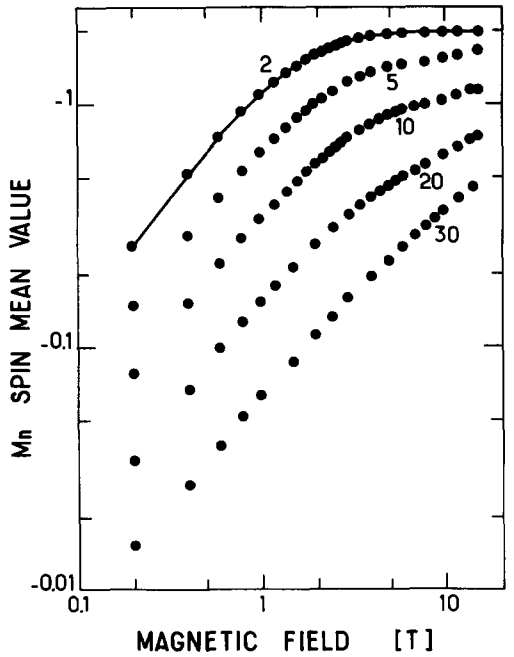

Fig. 1. Mean value of the component of Mn^{2+} spin in $Cd_{1-x}Mn_xTe$ along the magnetic field, obtained from magnetization data at 1.5 K. Composition values indicated in %. Continuous line represents a Brillouin function.

for transitions $|3/2, \mp 3/2\rangle \rightarrow |1/2, \mp 1/2\rangle$ and

$$E_{2\pm} = E_0 \mp \frac{1}{2}\left(\alpha + \frac{\beta}{3}\right)N_0 x\langle S_z\rangle \tag{3b}$$

for transitions $|3/2, \mp 1/2\rangle \rightarrow |1/2, \pm 1/2\rangle$ where α and β are exchange constants for conduction and valence bands respectively.

The components of energies $E_{1\pm}$ are about 3 times stronger than the others and in $Cd_{1-x}Mn_xTe$ they split much stronger. Therefore, for verification of magnetization dependence their splitting ΔE was chosen. From (3a)

$$\Delta E = E_{1-} - E_{1+} = (\beta - \alpha)N_0 x\langle S_z\rangle. \tag{4}$$

Plotting ΔE vs $x\langle S_z\rangle$ one should obtain a straight line with a slope of $N_0(\beta - \alpha)$. That was done in Fig. 2: all experimental data, for various compositions and magnetic fields, fit a single straight line. It means that the same value of exchange itegrals α and β applies to all those results. That procedure was performed more precisely for all compositions studied separately. The results are shown in Table 1. The values of exchange integrals, determined independently for each series of measurements, are very similar. The observed decreasing of exchange integral values with composition appears to be systematic. However, given the uncertainty of the composition (especially for its smallest values) and other sources of experimental error, we choose to

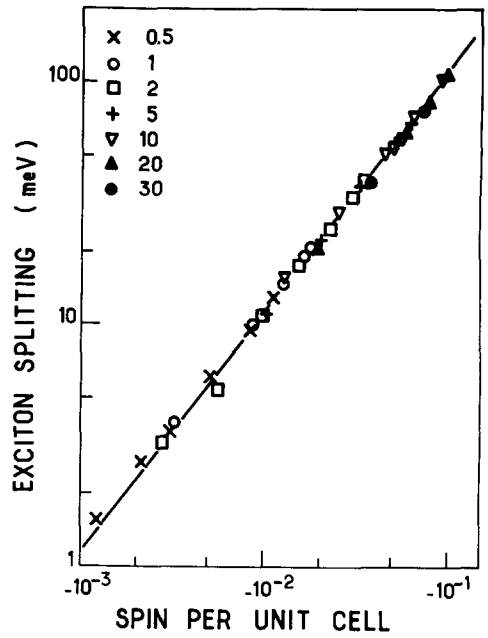

Fig. 2. Splitting of strong components of free exciton line in $Cd_{1-x}Mn_xTe$ plotted vs mean value per unit cell of the component of Mn^{2+} spin along the magnetic field. Composition values indicated in %.

represent all the data by a single pair of exchange integral values, namely:

$$N_0\alpha = 0.22 \pm 0.01 \text{ eV}$$

for the conduction band and

$$N_0\beta = -0.88 \pm 0.04 \text{ eV}$$

for the valence band. They are represented in Fig. 2 by a continuous line. These values differ slightly from those determined in [5] (0.19 and -0.75 eV, respectively), where an assumption of perfect manganese spin alignment at saturation was made. The magnetic measurements (Table 1) exhibit spin saturation values smaller that 5/2 even for samples of the smallest Mn concentration, that explains the origin of the discrepancy.

5. CONCLUSIONS

Simultaneous measurements of magnetoreflectivity and magnetic moment on $Cd_{1-x}Mn_xTe$ confirm fully the simple exchange interaction model and allow to determine precise values of exchange integrals for conduction and valence band. The experimentally established proportionality of exciton splittings to magnetization allows to use optical method as a tool for studying magnetic properties of disordered system of Mn^{2+} ions. In particular, extremely high values of Faraday rotation, observed in that material (7) allow to apply very low fields that may be essential for a system that can possibly exhibit spin glass properties.

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APPENDIX. DETERMINATION OF $\langle S_z \rangle$ FOR OPTICAL MEASUREMENTS

Under pumped helium conditions, optical measurements were done at temperatures T_{opt} slightly different from those T_m of magnetic experiment. Therefore, an adjustment was necessary to compare both series of measurements. It is seen from Table 1 that magnetization can be approximately represented by a Brillouin function of an argument $Sg\mu B/(T + T_0)$. An assumption was made that within a narrow range of temperature ($1.3 < T < 1.6$ K) magnetization depends on that argument with constant T_0 (it is not exactly true for the whole range between 1.4 and 4.2 K). Therefore, the experimental values of $\langle S_z \rangle$ for optical measurements were determined from following equation:

$$\langle S_z \rangle_{opt}(H) = \langle S_z \rangle_{mag}\left(H\frac{T_m + T_0}{T_{opt} + T_0}\right).$$

In other words values of $\langle S_z \rangle$ were read from magnetization curves for a slightly corrected value of magnetic field. The correction coefficient

$$\gamma = \frac{T_m + T_0}{T_{opt} + T_0}$$

never exceeded 1.1 (compare Table 1).

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