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# OPTICAL OBSERVATION OF A MAGNETIC MOLECULE IN $Cd_{1-x}Mn_xTe$

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Bound magnetic polarons - molecules consisting each of a hole localized at an acceptor center and a number of $Mn^{++}$ ions within its orbit - are experimentally observed by spectroscopic methods. Unusual temperature shift of a bound exciton line and some polarization properties of bound exciton luminescence of CdMnTe are consistently explained in terms of creation of bound magnetic polarons.

## I. Introduction

The idea of a bound magnetic polaron (BMP) has been used to explain transport properties of magnetic semiconductors in the vicinity of a transition to a magnetically ordered phase [1]. In a BMP, a gain in free energy is achieved by spontaneous ordering of magnetic moments within the range of a localized electron state - e.g. a shallow impurity. Under favourable conditions, creation of BMP-s may occur also in paramagnetic materials. In a system such as a BMP, temperature should be an important factor, strongly influencing the energy and even the excitance itself of the system.

The paper contains a photoluminescence study of bound excitons in $Cd_{1-x}Mn_xTe$. Pronounced changes in their binding energy with temperature - a phenomen unknown in nonmagnetic semiconductors-lead naturally to the idea of a BMP.

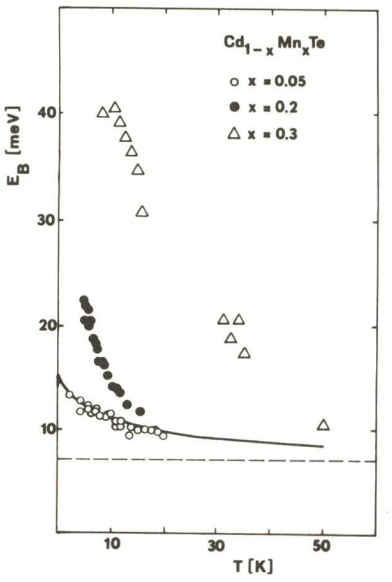


Figure 1. Binding energy of excitons to neutral acceptors in $Cd_{1-x}Mn_xTe$ versus temperature for three values of x indicated: Continuous line - theor. model (see text)

## II. Photoluminescence measurements

Photoluminescence of $Cd_{1-x}Mn_xTe$ in the energy gap region reveals a rather broad peak associated with recombination of excitons bound to neutral acceptors [2]. The energy of that peak, measured at its maximum, is plotted versus temperature in Fig.1 for several values of manganese mole fraction x. Values plotted in Fig.1 are in fact those of binding energy $E_B$ of the exciton to the neutral acceptor, since they

are measured related to the free exciton energy, determined from simultaneous reflectivity measurements on the same samples. The measured binding energy is generally greater than that in CdTe $E_B^o$ . The observed excess $\Delta = E_B - E_B^o$ increases with increasing manganese mole fraction x and decreasing temperature and reaches values several times higher than the binding energy in CdTe. Such big changes can hardly be accounted for by variation of the effective mass and/or dielectric constant.

## III. Interpretation

In order to explain the observed behaviour let us first consider a hole localized at an acceptor center, interacting with paramagnetic ions within its orbit. Our approach will be, similarly to that of Goncalves da Silva [3], based on molecular field approximation. However, conditions in CdMnTe containing a not too high Mn mole fraction allow to apply further approximations, essentially simplifying the model. Apart from the molecular field approximation following assumptions will be made:

1° Localized hole wave function has a form:

$$\Psi(\bar{r}) = F(\bar{r})\, u_o(\bar{r}) = \frac{1}{\sqrt{\pi a^3}} \exp(-r/a)\, u_o(\bar{r}) ,$$

where $u_o(\bar{r})$ is a periodic Bloch function at $\bar{k} = 0$.

2° Any modifications of that function (including possible changes of the effective Bohr radius a) due to interaction with $Mn^{++}$ ions will be neglected.

3° Exchange hamiltonian of the system has a Heisenberg form:

$$\mathcal{H} = -\sum |F(\bar{r}_i)|^2 \beta\, \bar{\sigma}\cdot\bar{S}_i = -\tfrac{1}{3} \sum |F(\bar{r}_i)|^2 \beta\, \bar{j}\cdot\bar{S}_i ,$$

where $\bar{\sigma}$ and $\bar{j}$ are hole operators of spin and total momentum respectively, $\beta$ is the exchange integral and index i numbers manganese ions of positions $\bar{r}_i$ and spin operators $\bar{S}_i$.

4° The $Mn^{++}$ ion system considered separately is perfectly paramagnetic lack of terms containing products $\bar{S}_i\, S_j$ in the hamiltonian .

It is obvious that under the above assumptions, appearance of a net magnetic moment would cause a gain in energy. It seems reasonable to expect (in analogy to previous works on BMP) that at sufficiently low temperature that gain will outweight the loss in entropy and that a local magnetization will appear.

A similar type of ordering by exchange interaction has been predicted by Pashitskii and Ryabchenko [8] in heavily doped materials with paramagnetic ions, they consider however only bulk magnetization and not local centers.

It must be pointed out that the total energy of the system is related to the hole, whereas a fraction of energy per one $Mn^{++}$ ion is much smaller (number of $Mn^{++}$ ions within a sphere of a radius equal to the expectation value $\langle r \rangle$ for the hole function is in $Cd_{0.95}Mn_{0.05}Te$ more than 15). That may justify the next approximation:

5° Throughout the temperature range of the experiment, the hole is totaly spin-polarized ($j_z = 3/2$ in localy chosen coordinate

system).

It means that the hole is equivalent to an effective magnetic field, nonhomogenous but constant in time, acting on spins of the $Mn^{++}$ ions.

Now the magnetic part $E_M$ of the acceptor energy $E_A$ can be calculated:

$$E_M = -\frac{5}{4} x N_0\beta \int |F(r)|^2 B_{5/2}\left(\frac{5\beta}{4kT}|F(r)|^2\right) d_3r$$

In order to obtain a value of effective Bohr radius, effective mass in a simple hydrogenic model is adjusted to obtain the ionization energy determined by Svob et. al for CdTe [5]. Taking thus obtained value a = 12 Å, lattice constant $a_o$ = 6.47 Å [6] and the exchange integral $N_0\beta$ = 0.88 eV [7], $E_M$ was evaluated numerically.

In order to compare $E_M$ with the experimental data, we shall proceed to the last rough approximation:

6° Magnetic part of the binding energy of an exciton to the neutral acceptor is proportional to the magnetic part of the acceptor ionization energy.

Now the values of $E_M$ must be compared with an adjustible coefficient to the magnetic part $\Delta$ of the measured exciton binding energy. That was done in Fig.1 for x = 0.05, assuming that the nonmagnetic part of the exciton binding energy is independent of composition and equal to its value $E_B^o$ in CdTe.

For crystals containing more manganese the assumption of noninteracting $Mn^{++}$spins is clearly unjustified (as well as assumption 2°).

## IV. Polarization measurements

The model presented above can be used as well to explain results of luminescence polarization measurements. A small magnetic field was applied in Faraday configuration and a difference in luminescence

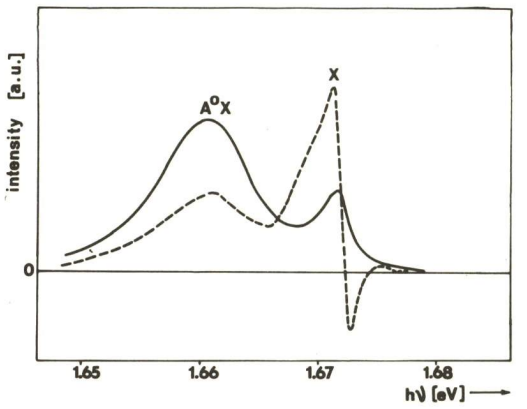


Figure 2. Photoluminescence spectrum (continuous line) and polarization differential spectrum (dashed line) of a $Cd_{0.95}Mn_{0.05}Te$ sample at 15 K and 0.1 T

intensities between two circular polarizations $\sigma^+$ and $\sigma^-$ was directly measured by a modulation technique. The results are shown in Fig.2. The free exciton line X behaves in a standard manner - almost symmetrical splitting of the luminescence structure into two components allowed in $\sigma^+$ and $\sigma^-$ respectively produces a derivate-like polarization spectrum. On the contrary, polarization spectrum of the bound exciton line $A^oX$ repeats the shape of the total luminescence spectrum. This may be explained assuming that the bound exciton state is already split by the exchange field of a local $Mn^{++}$ spin polarization and thermalized in the ground state. External magnetic field only aligns random directions of local polarization, producing the observed effect.

## V. Summary

A bound magnetic polaron - a magnetic molecule of giant spin - is experimentally observed in CdMnTe by means of photoluminescence measurements. An extremely simple model explains semi-quantitatively the behaviour of the exciton binding energy with temperature in crystals of low Mn concentration ($x = 0.05$) as well as the low-field polarization of luminescence. Optical experimental methods provide an efficient tool to study such local magnetic complexes in contrast to magnetization or ESR measurements that generally integrate magnetic properties over the bulk.

## VI. Acknowledgment

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## References

1) P. Kuivalainen, J. Sinkkonen, K. Kaski, T. Stubb: phys. stat. sol. (b) 94 (1979) 181 and references cited therein.
2) R. Planel, J.A.Gaj, C. Benoit à la Guillaume: J. Physique 41 (1980) C5-39.
3) C.E.T. Goncalves da Silva: Sol. State Comm. 17 (1975) 677.
4) G. Bastard, C.Rigaux, Y. Guldner, J. Mycielski, A. Mycielski: J. de Phys. 39 (1978) 87.
5) L. Svob, Y. Marfaing, M. Hoclet, P. Plumelle, M. Vandevyver: Sol. State Comm. 28 (1978) 895.
6) U. Sondermann: J. Magnetism and Mag. Mat. 2 (1976) 216.
7) J.A. Gaj, R. Planel, G. Fishman: Sol. State Comm. 29 (1979) 435.
8) E.A. Pashitskii, S.M. Ryabchenko: Fiz. Tver. Tela 21 (1979) 545.