

ELECTRON PARAMAGNETIC RESONANCE STUDIES OF $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$

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Abstract. The EPR linewidth has been studied in four samples of $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ with $x=0.09$, 0.11 , 0.15 and 0.18 as a function of temperature in the range $19 \text{ K} < T < 290 \text{ K}$, and as a function of dose of ^{60}Co gamma irradiation up to 500 kGy . It was found that EPR linewidth depends on temperature as $1/T$ in the range $50 \text{ K} < T < 290 \text{ K}$ for the samples with $x=0.15$ and 0.18 , and in the range $25 \text{ K} < T < 290 \text{ K}$ for the samples with $x=0.09$ and 0.11 . Using Anderson's model for the EPR linewidth, the exchange integral between the nearest neighbours Mn^{2+} ions was found to be $J_1/k \cong 0.05 \text{ K}$ in the sample with $x=0.18$. The observed variation of the linewidth with the applied doses of gamma rays in the sample $x=0.09$ are discussed in terms of the indirect exchange interaction.

1. INTRODUCTION

The mixed crystals of $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ are solid solutions of a zero gap semiconductor HgSe and a magnetic semiconductor MnSe and crystallize in the zinc blende structure. The manganese ions substitute mercury ions and are randomly distributed over the mercury sublattice with a pronounced tendency of cluster formation. The absence of the long range magnetic order, the large increase of the g value at low temperatures, the exotic temperature dependence of the amplitude of Shubnikov-de Haas oscillations /1/, /2/ and other specific properties make these crystals different from typical magnetic semiconductors. It is believed that such unusual properties are due to the exchange interaction between highly localised 3 d electrons on manganese ions and mobile band electrons.

/1/ S. Takeyama and R.R. Galazka, Phys. Stat. Sol. (b) 96, 413 (1979).

Electron paramagnetic resonance (EPR) has been found to be a useful technique to study spin-spin interaction and also the effects related to the magnetic phase transitions. A pronounced increase of the EPR linewidth with decreasing temperature and increasing manganese concentration is observed in $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$, /3/, /4/, as well as in other semimagnetic semiconductors. Such linewidth behaviour must depend on the Mn-Mn interaction. Therefore, systematic studies of the EPR in these crystals should contribute significantly to the understanding of their magnetic properties.

In the present work the EPR linewidth was measured in $\text{Hg}_{x-1}\text{Mn}_x\text{Se}$ crystals in the range $19 \text{ K} \leq T \leq 290 \text{ K}$ and as a function of dose of ^{60}Co gamma irradiation up to 500 kGy.

2. EXPERIMENT

The samples, used in the EPR experiment, were prepared at the Institute of Physics of the Polish Academy of Sciences. The EPR measurements were performed on a Varian spectrometer at microwave frequency $\nu = 9.4 \text{ GHz}$. The samples were cooled in an open cycle cryogenic refrigerator using the flowing gas of hydrogen. The temperature was measured by a Au-Fe/chromel thermocouple. The first derivative of the absorption line was recorded, where the resonance field is defined as zero of the derivative curve. No shift of the resonance field with temperature in the measured range was observed.

3. RESULTS AND DISCUSSION

The temperature dependence of the EPR linewidth in $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ crystals with manganese concentration $x = 0.09, 0.11, 0.15$ and 0.18 is presented in Fig.1. Significant increase of the linewidth is observed as the temperature is lowered, specially for higher manganese concentrations. Such behaviour has been observed in concentrated magnetic systems as MnTe, MnSe, MnS, but also in $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ for $x > 0.20$ /3/. In the first case such temperature dependence of the linewidth is

/2/ P.Buszewski, M.Z.Cieplak and A.Mongird Gorska, J. Phys.C: Solid St. Phys. 13, 5383 (1980),

/3/ K.Leibler, A.Sienkiewicz, K.Checinski, R.Galazka and A.Pajaczkowska, 3rd Internat. Conf. Phys. of Narrow-Gap Semicond. Warsaw, September 1977.

/4/ D.P.Mullin, R.R.Galazka and J.K.Furdyna, Phys. Rev. B 24, 355 (1981).

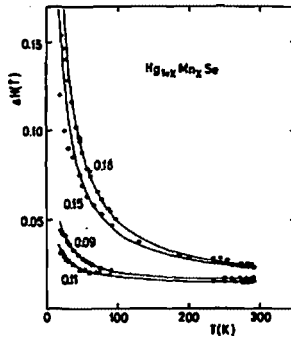


Fig.1. Temperature dependence of the EPR linewidth in $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ for $x=0.09, 0.11, 0.15$ and 0.18 .

interpreted as due to a transition from a paramagnetic to an antiferromagnetic state. In the case of $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ with higher manganese concentration, it seems that such temperature dependence of the linewidth is due to a transition from a paramagnetic to a spin glass state. But, in our experiment, the temperature range $T \geq 19$ K is far from the critical temperature of the transition to the spin glass state in the sample with $x=0.18$ /5/. For lower manganese concentration, the spin glass state in $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ was not observed at temperatures $T \geq 1$ K /5/. If it exists, than it should be at very low temperatures /6/.

In the present work it was found that the temperature dependence of the EPR linewidth in $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ can be approximated by a formula

$$\Delta H = a + b/T \quad (1)$$

in the temperature range $50 \text{ K} \leq T \leq 290 \text{ K}$ for the samples with $x=0.15$ and 0.18 , and in the temperature range $25 \text{ K} \leq T \leq 290 \text{ K}$ for $x=0.09$ and 0.11 . Full lines in Fig.1. represent a least squares fit of the above formula to the experimental data. The values of fitting parameters are shown in Table 1.

Table 1.

x	a(T)	b(TK)
0.09	1.46×10^{-2}	0.6620
0.11	1.44×10^{-2}	0.3882
0.15	1.42×10^{-2}	2.8451
0.18	1.05×10^{-2}	3.9106

/5/ G.D.Khattak, C.D.Amarasekara, S.Nagata, R.R.Galazka and P.H.Keesom, Phys. Rev. B 23, 3553 (1981).

However, for temperatures below 50 K for the samples with $x=0.15$ and 0.18 , and below 25 K for $x=0.09$ and 0.11 the formula (1) for the temperature dependence of the EPR linewidth is no longer valid (Fig.1). An analysis of the experimental data has shown that the temperature variation of the linewidth in the samples with $x=0.15$ and 0.18 , in the range $19 \leq T \leq 50$ K, can be well described by a dependence:

$$\Delta H = a + ce^{-T/T_0} \quad (2)$$

It is interesting to note that such temperature dependence of the EPR linewidth was proposed by Bhagat et al. in a number of metallic spin glasses. The formula (2) also represents well the temperature variation of the EPR linewidth in wide gap semimagnetic semiconductor $Cd_{1-x}Mn_xTe$ (see /7/ and references therein) with the transition temperature to the spin glass state at low T.

The above expressions (1) and (2) are only empirical and require an explanation on the basis of microscopic theory.

The width of the exchange narrowed absorption line in Anderson's model /8/ is given by:

$$\Delta H_{pp} = \frac{1}{2\sqrt{3}} \frac{(\Delta H_{pp})_{dip}^2}{\omega_e / \gamma} \quad (3)$$

where ΔH_{pp} is peak-to-peak width of the derivative of the absorption line in field units which is observed in an experiment, ω_e is a part of the fourth moment of the absorption frequency which depends on the exchange interaction, $\gamma = g\beta/\hbar$, and $(\Delta H_{pp})_{dip}$ is peak-to-peak width originating from the dipole-dipole interaction only. From Van Vleck expression for the second moment of the absorption frequency /9/ we have deduced $(\Delta H_{pp})_{dip}$ for a polycrystalline sample in the approximation of the nearest neighbours, where all nearest neighbours ions are assumed to be magnetic:

$$(\Delta H_{pp})_{dip} = 6\left(\frac{2}{5}\right)^{1/2} \frac{g\beta\sqrt{S(S+1)}}{r_0^3} \sqrt{x} \quad (4)$$

where S is the spin of the magnetic ion, r_0 is the distance between the two nearest neighbours magnetic ions and x is the magnetic ion concentration. An analysis of the above expression (4), applied to $Hg_{1-x}Mn_xSe$ with $x=0.18$, where the temperature dependence $r_0(T)$ was estimated on the basis of the known coefficient of thermal expansion in similar systems, has shown that the temperature variation of the interionic distance between 300 K and 20 K is

/6/ N.B. Brandt, V.V. Moshchalkov, A.O. Orlov, L. Skrbek, I.M. Tsidilkovskii and S.M. Chudinov, Zh. eksp. teor. Fiz., 84, 1059 (1983).

/7/ H.A. Sayad and M. Bhagat, Phys. Rev. B 31, 591 (1985).

/8/ P.W. Anderson and P.R. Weiss, Rev. Mod. Phys., 25, 269 (1953).

about $\Delta r_0 \cong 0.004 \times 10^{-8}$ cm and that such decrease of the interionic distance would increase the linewidth due to dipol-dipol interaction from about 0.1141 T to about 0.1138 T ($\sim 0.3\%$), which is negligible. We have concluded therefore, that the dipol-dipol interaction cannot be responsible for the observed temperature variation of the EPR linewidth in $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ and that the explanation should be found in the exchange interaction.

Taking the calculated high temperature value of $(\Delta H_{pp})_{\text{dip}} = 0.1127$ T at 970 K for the sample with $x=0.18$ (expression (4)), we have determined $\omega_e = 1.48 \times 10^{11} \text{ s}^{-1}$ from (3). Then, the exchange integral between the nearest neighbours magnetic ions was calculated from the expression for the fourth moment of the absorption frequency /9/ taking that the magnetic ions are distributed over an fcc lattice as in $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$. It was found that $J_1/k = 0.05$ K. The details of this calculation will be discussed in a separate paper.

The samples of $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ were irradiated with ^{60}Co gamma rays at room temperature. The maximal doses were 500 kGy. The interesting dependence of the EPR linewidth was obtained (Fig.2). In the sample with $x=0.18$ the linewidth decreases monotonously with increasing dose, whereas in the sample with $x=0.09$ a maximum is observed around 100 kGy. It seems that the observed dependence of

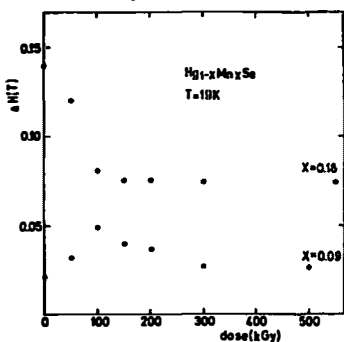


Fig. 2. The EPR linewidth in $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ as a function of dose of ^{60}Co gamma irradiation at $T=19$ K.

the linewidth on the applied doses of gamma rays cannot be explained by dipol-dipol interaction as well. The sample of $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ with $x=0.11$ was irradiated with gamma rays and then put on a powder X-ray diffractometer. It was found that a dose of about 100 kGy changes the crystal lattice parameter by about $\Delta a \sim 0.01 \times 10^{-8}$ cm. Such change of the lattice parameter has a negligible influence on the strength of dipol-dipol interaction as well as on the EPR linewidth (3). However, in the Hall effect measurements it was found that a

/9/ J.H. Van Vleck, Phys. Rev. 74, 1168 (1948).

dose of 70 kGy reduces the conduction electron concentration in $Hg_{1-x}Mn_xSe$ with $x=0.09$ by about 2.6 times at room temperature. We suppose that the reduction of conduction electron concentration influences the indirect exchange interaction. If this interaction becomes weaker as the electron concentration is reduced, then according to expression (3) the EPR linewidth should increase, as was observed in the sample $x=0.09$ for doses up to 100 kGy (Fig.2). For a better understanding of the effects of gamma irradiation on the EPR linewidth in $Hg_{1-x}Mn_xSe$, the transport properties should be measured as a function of dose at low temperatures.