MAGNETIC INTERACTIONS IN Hg$_2$Mn$_2$Te$_3$Se$_x$

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Abstract. Electron paramagnetic resonance has been studied in diluted magnetic semiconductor Hg$_2$Mn$_2$Te$_3$Se$_x$ with $x=0.01$ and $x=0.03$, 0.05 and 0.14 in the temperature range 20-290 K. From the high-temperature linewidth dependence the paramagnetic Curie-Weiss temperature is estimated as $0=10$ K for the sample with $x=0.01$, $x=0.01$, and $0=18$ K for $x=0.03$, $x=0.01$. These values of 0 together with those obtained in the magnetic susceptibility measurements give the nearest-neighbour exchange constant in Hg$_2$Mn$_2$Te$_3$Se$_x$ with $x=0.01$, $x=0.01$, and $x=5.4$ K. We find that the magnitude of the EPR linewidth is mainly determined by superexchange interaction and unresolved hyperfine structure. An analysis of the exchange scattering of the free charge carriers on the Mn$^{2+}$ ions suggests that this mechanism might be effective in the line broadening at high temperatures.

1. Introduction

Hg$_2$Mn$_2$Te$_3$Se$_x$ is a member of the A$^{1+}$, Mn$^{3+}$, family of diluted magnetic semiconductors (DMSs) in which a fraction of nonmagnetic cations is replaced randomly by Mn$^{2+}$ ions [1, 2]. Hg$_2$Mn$_2$Te and Hg$_2$Mn$_2$Se are typical representatives of the narrow-gap DMSs. It has been found that Hg$_2$Mn$_2$Te has p-type conductivity [2, 3], while Hg$_2$Mn$_2$Se always has n-type conductivity with high electron concentration [4]. In Hg$_2$Mn$_2$Te the acceptor defects are vacancies in the mercury sublattice, and in Hg$_2$Mn$_2$Se the donor defects are mercury atoms at interstitial positions and vacancies in the selenium sublattice. One may assume that the variation of the selenium content in Hg$_2$Mn$_2$Te$_1$Se$_x$ could make it possible to regulate the type of the conductivity and concentration of the free charge carriers in this four-component system. The galvanomagnetic properties were studied as a function of manganese and selenium content [5, 6, 7]. The temperature and magnetic field dependences of the Hall coefficient have been explained by the existence of three groups of current carriers, electrons and two types of holes with different mobilities. In the present work the magnetic properties of Hg$_2$Mn$_2$Te$_3$Se$_x$ are examined by electron paramagnetic resonance (EPR). This method enables us to study the magnetic interactions in the material and the most important mechanisms responsible for the line broadening.

2. Experiment

Single crystals of Hg$_2$Mn$_2$Te$_3$Se$_x$ were grown by the Bridgman method. After synthesis the crystals were annealed in Se vapour at 250°C for 200 h. The samples used in the EPR experiment were cut from ingots by electro erosion. The manganese concentration was determined from the magnetic susceptibility at room temperature measured by a Faraday method in the magnetic field B=0.1 T. The selenium concentration was estimated from the leading of the amoule.

The EPR measurements were performed on a Varian spectrometer operating at the nominal frequency $v=9.5$ GHz. The first derivative of the absorption lines was recorded in the temperature range 20-290 K. The samples were cooled in an open-cycle cryogenic refrigerator using flowing hydrogen gas.

3. Results and discussion

In the studied manganese concentration range the EPR spectrum of Hg$_2$Mn$_2$Te$_3$Se$_x$ is characterized by a single resonance line. An increase of the linewidth is found with decreasing temperature for the samples with $x=0.01$, $y=0.01$ and $x=0.03$, $y=0.01$. For the samples with $x=0.05$ and $0.14$, the observed temperature dependence of the linewidth was much weaker than it is expected on the basis of the theory developed for the EPR line broadening in Mn-substituted II-VI DMSs [8].

The high temperature EPR linewidth has been analysed using the theoretical expression for the linewidth behaviour in Mn-DMSs in the high-temperature limit [8]:

$$\Delta B = \Delta B_0 \left(1 + \frac{a}{T}\right)$$

(1)
where $\Delta B_{xy}$ is the infinite-temperature linewidth, and $0=0_1+0_2+0_3$, where $0_1$ is the paramagnetic Curie-Weiss temperature and $0_2$ is a spin temperature. The peak-to-peak linewidth for the samples with $x=0.01$ and $x=0.03$ is presented as a function of inverse temperature in Fig. 1. The straight lines in this figure represent a least-squares fit of expression (1) to the experimental data.

The values of $0$ obtained as fitting parameter in this experiment as well as those determined in the magnetic susceptibility measurements [5] are plotted against Mn concentration in Fig. 2. It is seen that the values of $0$ obtained in the EPR experiment fit well into the linear dependence of the paramagnetic Curie-Weiss temperature versus manganese concentration established in the magnetic susceptibility measurements.

#### Fig. 1. EPR linewidth for $\text{Hg}_2\text{Mn}_2\text{Te}_1\text{ySe}_y$ with $y=0.01$ and $x=0.01,0.03$ as a function of inverse temperature.

The high-temperature expansion of the magnetic susceptibility for random diluted magnetic system of magnetic ions having spin momentum only gives the Curie-Weiss law with the Curie-Weiss temperature in the form [9]:

$$0(x) = \frac{2}{3} x(S+1) \sum_{k} \frac{j_k}{k_B} = 0_2 x$$  \hspace{1cm} (2)

where $x$ is the atomic fraction of magnetic ions, $S$ is the spin of magnetic ion ($S=5/2$ for Mn$^{2+}$), $j_k$ is the number of cations in the $k$th coordination sphere and $k_B$ is the Boltzmann constant. It is established that the exchange interaction in small-gap Mn-DMSS is of long-range [10] which can be described by a radial dependence on distance, $j_k = J_{nn}/R_k^n$, where $J_{nn}$ is the nearest-neighbour (NN) exchange constant, $R_k$ is the distance between $k$th neighbours in the units of the NN distance, and $n$ is the interaction range parameter. It was reported that $n=5$ for $\text{Hg}_2\text{Mn}_2\text{Te}_1\text{ySe}_y$ and $\text{Hg}_2\text{Mn}_2\text{Se}_1\text{y}[10]$. Then, the sum in equation (2) can be written as:

$$\sum_{k} \frac{j_k}{k_B} = J_{nn}/R_5^{5} = 3 \frac{0_2}{2(S+1)}$$  \hspace{1cm} (3)

Substituting in equation (3) the value of the parameter $0_2=\text{50.8 K}$, which is obtained by fitting the linear dependence $0(x)=0_2 x$ on the experimental data (Fig. 2), the NN exchange constant in $\text{Hg}_2\text{Mn}_2\text{Te}_1\text{ySe}_y$ with $y=0.01$ is found as $J_{nn}/k_B = (54 \pm 2) K$. This value falls just between the NN exchange constants of the constituent systems. $J_{nn}/k_B = 5.1$ K for $\text{Hg}_2\text{Mn}_2\text{Te}_1\text{ySe}_y$ and $J_{nn}/k_B = 6.0$ K for $\text{Hg}_2\text{Mn}_2\text{Se}_1\text{y}[11].$

It is known that a perturbation due to spin-orbit coupling with a superexchange mechanism can lead to the anisotropic superexchange of Dzyaloshinsky-Moriya (DM) type [12] of the form $H_{xy} = -\sum_{l} D_{l} (\mathbf{r}_{l} \times \mathbf{S}_{l}) \cdot \mathbf{S}_{i}$. The parameter $D_{l}$ between the NNs in $\text{Hg}_2\text{Mn}_2\text{Te}_1\text{ySe}_y$ with $y=0.01$ is estimated from the expression $D_{l} = 3 \frac{1}{l} D_{l} / k_B$ [13, 14]. Taking for tellurides $l=0.34$ eV, $U_{se}=7$ eV [8] at the infinite temperature EPR linewidth due to anisotropically diluted system in the approximation $\delta(\Delta B_{xy}) = 2\frac{\Delta B_{xy}}{k_B T}$.

The calculated values $\Delta B_{xy}^{DM}$ for four manganese compositions are listed in Table 1.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\Delta B_{xy}^{DM}$ (mT)</th>
<th>$\Delta B_{xy}^{exp}$ (mT)</th>
<th>$\delta(\Delta B_{xy})$ (mT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>1.70</td>
<td>0.04</td>
<td>0.0</td>
</tr>
<tr>
<td>0.03</td>
<td>4.70</td>
<td>0.11</td>
<td>0.0</td>
</tr>
<tr>
<td>0.05</td>
<td>7.20</td>
<td>0.12</td>
<td>0.0</td>
</tr>
<tr>
<td>0.14</td>
<td>16.14</td>
<td>0.36</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The total calculated infinite-temperature contributions $\Delta B_{xy}^{DM}$, $\delta(\Delta B_{xy})$ and $\delta(\Delta B_{xy})$ have been obtained for two samples of $\text{Hg}_2\text{Mn}_2\text{Se}_1\text{y}$ presented in Table 1. For two samples with 1% temperature linewidths are quoted. Comparison of the anisotropic superexchange mostly influence interactions is not significant. The maximal error is $\sim 5$%.

However, the estimated error cannot explain the experimental values $\Delta B_{xy}^{DM}$. The applied magnetic field splits the $t_2$ leading to the fine structure of the EPR spectrum from the coupling between the electron spin and the magnetic field into six levels, so that each line of Mn$^{2+}$ ions can be observed for very low intensity. The spectrum was observed for Mn$^{2+}$ in CdTe [15]. These lines of about A=6 mT are observed at lower temperatures, but also at room temperature [15].

As the amount of manganese increases, the splitting into a single line due to interaction is observed for $x=0.01,0.05$ with the linewidth $\gamma$. The range of the magnetic field is less than the range of individual lines are less than $5$% for the NNs (for Cd$^{2+}$, Mn$^{2+}$, Te$^{2-}$, Mn$^{2+}$, Se$^{2-}$), observed in Cd$^{2+}$, Mn$^{2+}$, Te$^{2-}$ and Cd$^{2+}$, Mn$^{2+}$, Te$^{2-}$ for $\gamma=0.01,0.05$ at structure. Since the parameters of exchange close to those in Cd$^{2+}$, Mn$^{2+}$, Te$^{2-}$, the width of interaction exchange between the NNs is expected to be similar in the high-temperature regime. So, the linewidths of the magnetic lines are expected to be similar.
from the expression $D_i = \lambda J_i / U_{\text{eff}}$ [13, 14], where $\lambda$ is the spin-orbit coupling constant and $J_i = J_{\text{NN}}$.

Taking for tellurides $\lambda = 0.34 \text{ eV}$, $U_{\text{eff}} = 7 \text{ eV}$ [8] and $J_{\text{NN}} = 5.4 \text{ K}$ one obtains $D_i / k_B = 0.26 \text{ K}$. The expression for the infinite temperature EPR linewidth due to anisotropic superexchange of DM type has been derived for a randomly diluted system in the approximation of NN interactions [13, 14].

$$\Delta B_{\text{e}} = \frac{1.105 D_i^2 \gamma^2}{\gamma + J_{\text{NN}}^{\text{NN}} + 0.1}$$

The calculated values $\Delta B_{\text{e}}$ for four manganese concentrations in Hg$_x$Mn$_{1-x}$Te$_y$Se$_{1-y}$ with $y=0.01$ are presented in Table 1.

The other possible sources of anisotropic spin interactions are the magnetic dipolar interaction, intramolecular Mn spin-orbit coupling and single-ion anisotropy. The EPR linewidth arising from these interactions has been derived [8] in the same approximation as equation (4) and here we present the calculated linewidth corrections $\Delta B_{\text{e}}$ for dipolar interaction, $\delta(\Delta B_{\text{e}})$ for Mn spin-orbit coupling and $\delta(\Delta B_{\text{e}})$ due to single-ion anisotropy for the studied Hg$_x$Mn$_{1-x}$Te$_y$Se$_{1-y}$ samples (Table 1).

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\Delta B_{\text{e}}$</th>
<th>$\Delta B_{\text{e}}^{\text{SO}}$</th>
<th>$\delta(\Delta B_{\text{e}})$</th>
<th>$\delta(\Delta B_{\text{e}})$</th>
<th>$\Delta B_{\text{e}}^{\text{an}}$</th>
<th>$\Delta B_{\text{e}}^{\text{ISP}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.70</td>
<td>0.04</td>
<td>0.07</td>
<td>0.07</td>
<td>1.88</td>
<td>24.2 ± 2.0</td>
</tr>
<tr>
<td>0.03</td>
<td>4.70</td>
<td>0.11</td>
<td>0.18</td>
<td>0.18</td>
<td>5.17</td>
<td>25.6 ± 2.0</td>
</tr>
<tr>
<td>0.05</td>
<td>7.29</td>
<td>0.17</td>
<td>0.28</td>
<td>0.28</td>
<td>8.02</td>
<td>29.0 ± 2.0</td>
</tr>
<tr>
<td>0.14</td>
<td>16.14</td>
<td>0.36</td>
<td>0.63</td>
<td>0.62</td>
<td>17.75</td>
<td>33.0 ± 2.0</td>
</tr>
</tbody>
</table>

The total calculated infinite-temperature EPR linewidth $\Delta B_{\text{e}}^{\text{ISP}}$ was determined as the sum of the contributions $\Delta B_{\text{e}}$, $\Delta B_{\text{e}}^{\text{ISP}}$, $\delta(\Delta B_{\text{e}})$ and $\delta(\Delta B_{\text{e}})$ (Table 1). The experimental infinite temperature linewidths have been obtained for two samples of Hg$_x$Mn$_{1-x}$Te$_y$Se$_{1-y}$ with $y=0.01$ and $x=0.01$ and 0.03, and they are also presented in Table 1. For two samples with higher manganese concentrations, $x=0.05$ and 0.14 the room temperature linewidths are quoted. Comparison of all the anisotropic spin interactions considered here shows that the anisotropic superexchange mostly influences the EPR linewidth, and the influence of other anisotropic interactions is not significant. The maximal error in the calculated linewidth $\Delta B_{\text{e}}^{\text{ISP}}$ was estimated to be ±30%. However, the estimated error cannot explain the large difference between the calculated linewidths $\Delta B_{\text{e}}^{\text{ISP}}$ and the experimental values $\Delta B_{\text{ISP}}$.

The applied magnetic field splits the two levels of Mn$^{2+}$ ions in the cubic crystal field into six levels leading to the fine structure of the EPR spectrum which consist of five lines. The hyperfine interaction arises from the coupling between the electron spin and nuclear spin of manganese. This interaction splits each fine structure level into six levels, so that each fine structure line is split into six hyperfine lines. The fine structure of Mn$^{2+}$ ions can be observed for very low manganese concentrations and at low temperatures. Such EPR spectrum was observed for Mn$^{2+}$ in CdTe [15]. The six well resolved hyperfine lines with splitting between these lines of about A=6 mT, are observed for manganese concentrations $x=0.005$ not only at low temperatures, but also at room temperature [15].

As the amount of manganese is increased, the individual lines become broader and the whole spectrum coalesces into a single line due to interactions between manganese ions. In Cd$_{1-x}$Mn$_x$Te the single line was detected for $x=0.01-0.05$ with the linewidth of about 10 mT at room temperature [16]. In this concentration range the widths of individual lines are less than 10 mT, even if one includes the superexchange interaction between the NNs (for Cd$_{1-x}$Mn$_x$Te $J_{\text{NN}}^{\text{NN}}=6.1$ K and $D_i/k_B=0.30$ K [8]). It seems that the width of single line observed in Cd$_{1-x}$Mn$_x$Te for $x=0.01-0.05$ at room temperature can be ascribed to the unresolved hyperfine structure. Since the parameters of exchange interaction $J_i$, and $D_i$ in Hg$_x$Mn$_{1-x}$Te$_y$Se$_{1-y}$ with $y=0.01$ are very close to those in Cd$_{1-x}$Mn$_x$Te, the width of individual lines, as well as the width of single line arising from the exchange interaction between the NNs are expected to be approximately the same for the two materials, at least in the high-temperature regime. So, the linewidth of about 10 mT originating from the unresolved hyperfine
structure is expected in the samples of Hg$_{1-x}$MnTe$_{1-x}$Se$_x$ with $x = 0.01, 0.03$ and 0.05 at room temperature. However, the experimental linewidths are about 2.5-3 times larger (Table I) suggesting that there are another mechanisms which are effective in the line broadening.

The effect of exchange scattering of the free charge carriers on the Mn$^{2+}$ ions will be shortly considered. The relaxation time of Mn$^{2+}$ ion spins due to this mechanism can be expressed as $\tau = \tau_{\text{exchange}}$, where $\tau$ is the free charge carrier scattering, $\tau_{\text{exchange}} = (3k_B T/\mu)^{1/2}$ is their thermal velocity, and $\sigma_{\text{exchange}}$ is the spin-flip scattering cross section. We take for $\sigma_{\text{exchange}} = \frac{3}{2\hbar^2}(\hbar/\pi \mu)^{1/2}(S+1)$ \cite{17}, where $\hbar$ is the Planck constant, $\pi$ is the Fermi velocity, $\mu$ is the magnetic moment of the Mn$^{2+}$ ion, and $S=5/2$ for Mn$^{2+}$. From the hole concentrations in the acceptor impurity band $p = 1.7 \times 10^{17} \text{cm}^{-3}$ at $T=4.2 \text{K}$, $E_F = 5 \text{meV}$ \cite{5} and $N_{\text{D}} = 0.6 \text{ eV}$ \cite{1}, we have estimated $\sigma_{\text{exchange}} = 10^{-13} \text{cm}^2$. Taking for the thermal velocity $v = 1.6 \times 10^7 \text{cm/s}$, we obtain $\tau = 4 \times 10^{-8} \text{s}$ at $4.2 \text{K}$, and EPR linewidth of about $0.1 \text{mT}$, which means that the exchange scattering mechanism is not important for the relaxation of Mn$^{2+}$ ion spins at low temperatures. However, the concentration of the free charge carriers and thermal velocity increase with increasing temperature. From the galvanomagnetic measurements performed on Hg$_{1-x}$MnTe$_{1-x}$Se$_x$ with $x = 0.01$ and $x = 0.03$ and 0.05 at $T = 80 \text{K}$ \cite{5, 6, 7} we find $p = 5.8 \times 10^{17} \text{cm}^{-3}$, $v = 6.9 \times 10^7 \text{cm/s}$ and $\tau = 2.5 \times 10^{-8} \text{s}$ at $80 \text{K}$. This relaxation time corresponds to the linewidth of about $2 \text{mT}$ which is not small compared with the width of individual lines originating from the superexchange interaction at $x = 0.03$ and 0.05. One may expect that the influence of the exchange scattering mechanism on the EPR linewidth of Hg$_{1-x}$MnTe$_{1-x}$Se$_x$ will be even stronger at higher temperatures. For the precise determination of the relaxation time due to exchange scattering in the high temperature region the free charge carrier concentrations and their mobilities have to be known.

We can conclude that there are several mechanisms which are effective in the EPR line broadening of Hg$_{1-x}$MnTe$_{1-x}$Se$_x$ depending on temperature and manganese concentration. In the high temperature region the superexchange interaction and unresolved hyperfine structure can explain the linewidth of about $20 \text{mT}$ in the samples with $x = 0.01, 0.03, 0.05$ and about $20 \text{mT}$ in the sample with $x = 0.14$. An inspection of the exchange scattering of the free charge carriers on the Mn$^{2+}$ ions suggests that this mechanism might be effective in the line broadening at high temperatures.

References


OPTICAL PHONONS IN Hg$_{1-x}$MnTe$_{1-x}$Se$_x$

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Abstract. In these work far-infrared spectroscopic properties of a Hg$_{1-x}$MnTe$_{1-x}$Se$_x$ (x=0.01, 0.03, 0.05) system are studied. The ground state shows the intermediate "one-two" behavior. The random-element isodisplacement (RER) model and wavelength optical phonon frequencies are calculated.

1. Introduction

Hg$_{1-x}$MnTe and Hg$_{1-x}$MnSe are known systems. They are a solid solution with a zinc-blende structure, show the two-mode behavior \cite{3, 4}. However, the magnetic properties are well known \cite{5}. The ground state properties of Hg$_{1-x}$MnTe$_{1-x}$Se$_x$ (x=0.01, 0.03, 0.05) are reviewed in our previous work \cite{6}.

2. Experiment

Single crystals of Hg$_{1-x}$MnTe$_{1-x}$Se$_x$ (x=0.01, 0.03, 0.05) were grown by a pulling method in a flowing stream of Hg$_2$Te$_2$Se$_2$. The reflectivity was measured at room temperature using a modified factorized dielectric function method.

3. Results and discussion

The far-infrared reflection spectra of Hg$_{1-x}$MnTe$_{1-x}$Se$_x$ are shown in Fig. 1. The experimental data were fitted using a modified factorized dielectric function method.