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Electron paramagnetic resonance studies of $Zn_{1-x}Mn_xTe$

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Abstract. Electron paramagnetic resonance has been studied in $Zn_{1-x}Mn_xTe$ over a wide temperature range 20 K $\leqslant T \leqslant$ 290 K and a wide manganese concentration range $0.013 \leqslant x \leqslant 0.81$. Our results show that, for lower manganese concentrations $x \leqslant 0.23$, the EPR line can be represented by the Bloch model modified for broad resonance in the entire range of temperatures. For $x \geqslant 0.37$ the resonance is detected at higher temperatures. The values of the relaxation time τ and the g-factor are obtained by fitting an expression for the EPR absorption line in the modified Bloch model to the experimental data. The high-temperature linewidth for $x \leqslant 0.37$ is analysed within the exchange narrowing model. The calculated infinite-temperature linewidths are in good agreement with the extrapolated experimental values. It is found that the main contribution to the linewidth arises from the anisotropic superexchange.

1. Introduction

$Zn_{1-x}Mn_xTe$ is a member of the $A^{II}_{1-x}Mn_xB^{VI}$ family of diluted magnetic semiconductors (DMSs) where a fraction of the group-II ions are replaced at random by Mn^{2+} ions [1]. These materials are the subject of extensive studies because of interesting structural, optical and magnetic properties. The most important magnetic properties originate from the Mn–(sp band) exchange and from Mn–Mn exchange. A theory of the electronic structure and magnetic properties of DMSs has been proposed [2]. This theory establishes the superexchange as the dominant Mn–Mn exchange mechanism at near-neighbour distances. The inclusion of the anion spin–orbit coupling has shown that the anisotropic superexchange of Dzyaloshinski–Moriya (DM) type is the dominant anisotropic spin–spin interaction in DMSs such as $Cd_{1-x}Mn_xTe$ [3]. Calculated infinite-temperature EPR linewidths in some Cd-based DMSs, including DM exchange as the anisotropic spin–spin interaction, were found to be in good agreement with the experimental values [4, 5]. It was shown that the line broadening in these DMSs could not be explained by dipolar interaction.

In the present paper we have performed an EPR experiment on $ZN_{1-x}Mn_xTe$ in order to obtain better insight into the magnetic properties and magnetic interactions of this material and to establish the most important mechanism responsible for the line broadening. $Zn_{1-x}Mn_xTe$ is similar to $Cd_{1-x}Mn_xTe$ in its crystal structure, electronic structure and magnetic properties. Both materials crystallize in the zincblende structure and belong to the class of wide-gap semiconductors. The substitution of Zn for Cd has only an indirect effect on the band-structure features which are relevant for superexchange. Zn has a smaller tetrahedral convalent radius than Cd, leading to a shorter cation–anion distance in the Zn alloy than in the Cd alloy [1]. As a result, the isotropic and anisotropic exchange constants at nearest-neighbour (NN) distance in $Zn_{1-x}Mn_xTe$ are larger than those in $Cd_{1-x}Mn_xTe$ [3]. Relatively large exchange constants in $Zn_{1-x}Mn_xTe$ lead to a very broad EPR line. Nevertheless, we have succeeded in measuring the resonance line in $Zn_{1-x}Mn_xTe$ by the

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conventional EPR technique over a wide range of temperatures and compositions, except in samples with a high manganese concentration.

2. Experimental details

The samples used in the experiment were in the single-crystal form and were grown by the Bridgman method. The manganese concentration was determined by atomic absorption analysis. The measurements were performed on a Varian spectrometer with a 9 in magnet operating at the nominal microwave frequency $\nu = 9.5$ GHz. Details of this spectrometer have been described elsewhere [6]. The first derivative of the absorption lines was recorded. The peak-to-peak width, defined as the separation between the minimum and maximum of the first derivative, was measured. No dependences of the lineshape nor of the linewidth on the single-crystal orientation were observed. The samples were cooled in an open-cycle cryogenic refrigerator using flowing hydrogen gas. The temperature was measured with an iron-doped gold–chromel thermocouple. The error in the linewidth measurements was estimated to be within ±5%, and the error in the g-factor measurements to be within ±1%.

3. Results and discussion

The temperature dependence of the observed EPR linewidth in $Zn_{1-x}Mn_xTe$ is presented in figure 1 for several manganese concentrations. A significant increase in the linewidth is found with decreasing temperature and increasing manganese concentration. The apparent turnover in ΔH versus temperature observed in some samples at around 20 K is probably connected with the presence of a temperature gradient.

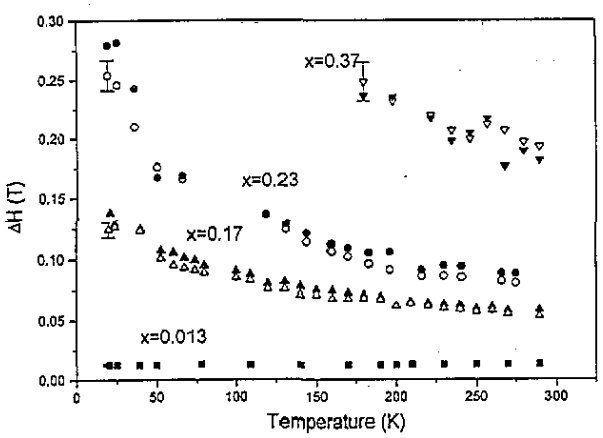

Figure 1. Temperature dependence of the EPR linewidth for $Zn_{1-x}Mn_xTe$ with $x = 0.013$, 0.17, 0.23 and 0.37: open symbols, observed values; full symbols, fit of the modified Bloch model to the experimental data.

From the Bloch equation of motion of the magnetization modified for the case of short relaxation times, the expression for the dynamic magnetic susceptibility can be obtained [7] with the imaginary part of the susceptibility in the form $\chi'' = \chi_0\omega_0\tau/[1 + (\omega \mp \omega_0)^2\tau^2]$, where χ_0 is the static magnetic susceptibility, ω_0 is the microwave frequence, τ is the

relaxation time, ω is the Larmor frequency given by $\omega = g\mu_B H/\hbar$, and H is the DC applied magnetic field. Since the absorbed energy in the EPR experiment is proportional to χ'', we have described the intensity of the absorption line in $Zn_{1-x}Mn_xTe$ by the expression

$$I = I_0\omega_0\tau/[1 + (\omega - \omega_0)^2\tau^2] + \omega_0\tau[1 + (\omega + \omega_0)^2\tau^2]. \quad (1)$$

The first and second terms in the above expression refer to the two opposite circular polarizations of the microwave. The first derivative of the dependence (1) was fitted to the experimental traces of the absorption lines using τ, g and I_0 as fitting parameters. The parameters g and τ are the most important because they are related to the resonance position and linewidth. Figure 2 shows the experimental trace of the absorption line in the sample with $x = 0.17$ at $T = 250$ K (full curve), and fit of the Bloch model to the experimental data (broken curve). We find that the shape of the resonance line for $Zn_{1-x}Mn_xTe$ can be described by the modified Bloch model expressed through equation (1).

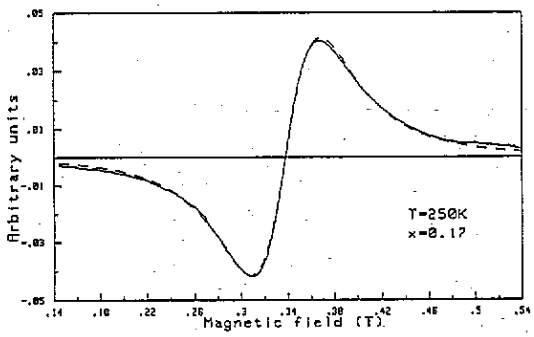

Figure 2. The first derivative of the EPR line as a function of applied magnetic field for a $Zn_{1-x}Mn_xTe$ sample with $x = 0.17$ at $T = 250$ K: ——, experiment; – – –, fit of the EPR line intensity in the modified Bloch model to the experimental EPR line.

The values of the inverse relaxation time τ^{-1} and of the g-factor, obtained in the fitting procedure, are presented as functions of temperature in figures 3 and 4 respectively, for the $x = 0.17$, 0.23 and 0.37 samples. The inverse relaxation time is in fact proportional to the EPR linewidth. If we take the fitting values of the parameters τ and g and calculate the linewidth from the relation $\Delta H = (4m/3^{1/2}eg)\tau^{-1}$, where $eg/2m = \gamma$ is the gyromagnetic ratio, we obtain the linewidth values which lie very close to the observed linewidths (figure 1).

The g-factor defines the resonance position. In figure 4 the g-factors obtained as fitting parameters for the samples with $x = 0.17$, 0.23 and 0.37 are compared with the directly measured values. It is seen that the discrepancy between the fitting values and measured values is less than the experimental error in measurements of the g-factor. A larger dissipation of the g-factor data, which can be seen for higher manganese concentrations and at lower temperatures, is connected with the difficulties in performing the EPR experiment when the resonance becomes very broad, $\omega_0\tau \simeq 1$.

We find that for lower manganese concentrations there is no shift in the resonance position and the g-factor does not change with respect to its high-temperature value. Even in the sample with $x = 0.17$ the g-factor remains at almost 2.0 over the entire temperature range and all the deviations in the g-factors from $g = 2.0$ lie within the error in measurements (figure 4). However, as the manganese concentration increases and the

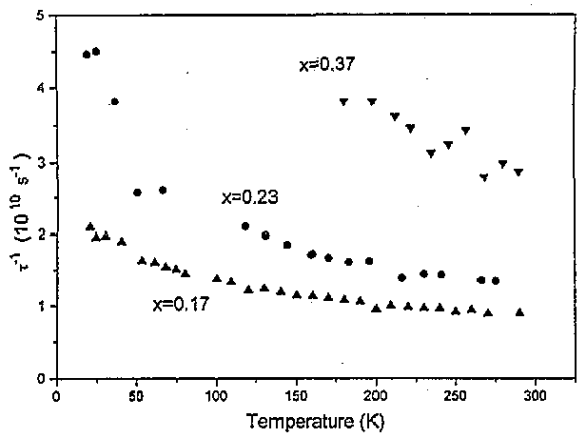

Figure 3. Temperature dependence of the inverse relaxation time τ^{-1} for $Zn_{1-x}Mn_xTe$ with $x = 0.17$, 0.23 and 0.37 obtained by fitting the EPR line intensity in the modified Bloch model to the experimental EPR line.

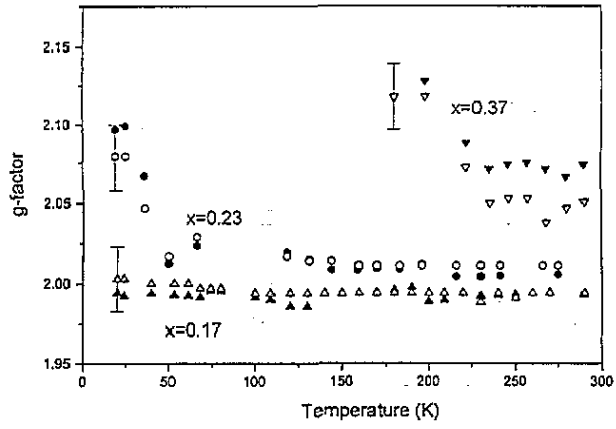

Figure 4. Temperature dependence of the g-factor for $Zn_{1-x}Mn_xTe$ with $x = 0.17$, 0.23 and 0.37: open symbols, observed values; full symbols, values obtained as fitting parameters.

temperature decreases, a shift in the resonance position to lower fields appears. This shift is described by an increase in the g-factor and this is shown in figure 4 for the samples with $x = 0.23$ and 0.37. It was suggested that the shift in the resonance position, which was also observed for $Cd_{1-x}Mn_xTe$, could be explained by the presence of internal fields [7]. However, such a description is only phenomenological and requires an explanation on the basis of microscopic theory.

Our analysis shows that the EPR line for $Zn_{1-x}Mn_xTe$, its position, shape and linewidth, can be described by the Bloch model modified for broad resonance in the samples with $x = 0.013$, 0.15, 0.17, 0.22 and 0.23 over the entire temperature range. In the sample with $x = 0.37$ the resonance is very broad at low temperatures and cannot be detected in the conventional EPR experiment. However, at higher temperatures ($T > 180$ K), the resonance in this sample is well defined and can be represented by the Bloch model. For the highest manganese concentrations studied in the present work ($x = 0.72$ and $x = 0.81$),

the resonance is no longer observable except at temperatures near room temperature.

The high-temperature EPR linewidth for $Zn_{1-x}Mn_xTe$ has been analysed using the theoretical expression for the linewidth behaviour in DMSs in the high-temperature limit [3]:

$$\Delta H = \Delta H_\infty (1 + \Theta/T) \tag{2}$$

where ΔH_∞ is the infinite-temperature linewidth, and $\Theta = \Theta_p + \Theta_d$, where Θ_p is the paramagnetic Curie–Weiss temperature and Θ_d is a spin temperature. In figure 5 the EPR linewidth for the $Zn_{1-x}Mn_xTe$ samples with $x = 0.013$, 0.17, 0.23 and 0.37 is presented as a function of inverse temperature. The straight lines in this figure represent a least-squares fit of equation (2) to the experimental data. We find that the observed linewidth can be described by the dependence (2) in the samples with $x = 0.17$ and $x = 0.23$ approximately above 100 K and in the sample with $x = 0.37$ above 200 K. Below these temperatures there is a pronounced deviation in the observed linewidth from the high-temperature dependence. This behaviour of the linewidth at lower temperatures probably reflects the spin-glass dynamics in this DMS.

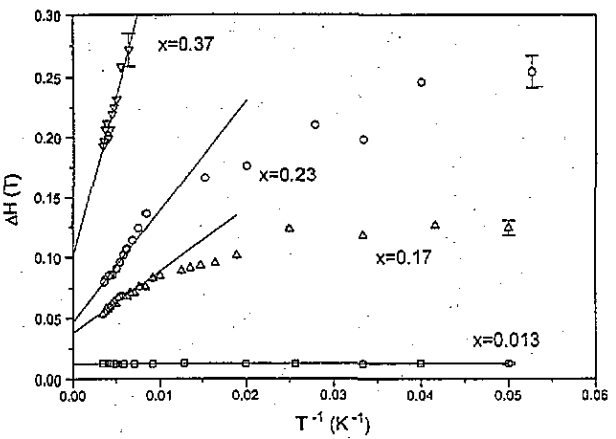

Figure 5. EPR linewidth for $Zn_{1-x}Mn_xTe$ with $x = 0.013$, 0.17, and 0.37 as a function of inverse temperature: ——, least-squares fit of equation (2) to the experimental data.

The values of the fitting parameters ΔH_∞ and Θ are shown in table 1. The Curie–Weiss temperature Θ_p, taken from the high-temperature magnetic susceptibility measurements [8], is also shown. For the concentration $x = 0.013$ the linewidth does not change in the entire temperature range, so that we have taken for ΔH_∞ the value observed at finite temperatures. For the other concentrations it is seen that the dominant part of the parameter Θ arises from Θ_p. The spin temperature parameter Θ_d seems to be small compared with Θ_p and cannot be determined precisely from such an experiment.

We start the analysis of the magnetic interactions in $Zn_{1-x}Mn_xTe$ by considering the anion spin–orbit coupling. This coupling leads to the anisotropic superexchange of DM type [9] in DMSs having the form $H_{DM} = -\sum D(R_{ij}) \cdot (S_i \times S_j)$. Since the DM interaction decreases rapidly with increasing distance, the strength of this interaction D_1 between the NNs is taken into account. The anisotropic exchange constant for $Zn_{1-x}Mn_xTe$ has been calculated in the theoretical work by Larson and Ehrenreich [3]: $D_1/k_B = 0.43$ K. On comparison of the DM exchange constant with the isotropic exchange constant J_1, which is

Table 1. Linewidth parameters for $Zn_{1-x}Mn_xTe$

x	ΔH_∞ (10^{-4} T)	Θ (K)	Θ_p (K)
0.013	130	—	—
0.15	363	127	123
0.17	378	135	139
0.22	480	192	183
0.23	469	196	188
0.37	1000	267	306

determined experimentally in high-field magnetization measurements [10] and in the neutron scattering measurements [11], $J_1/k_B = -9.1 \pm 0.3$ K, it is found that $|D_1/J_1| \simeq 0.05$.

We examine the infinite-temperature EPR linewidth using the exchange narrowing model. In this model the isotropic exchange narrows the line, which is in fact broadened by some anisotropic spin–spin interaction. Assuming that this anisotropic interaction is the anisotropic superexchange of DM type, Samarth and Furdyna [4] have derived an expression for the infinite-temperature linewidth for the case of a randomly diluted system in the approximation of NN interactions:

$$\Delta H_\infty^{DM} = (1/\sqrt{3})(10.5/\gamma)(D_1^2/\hbar J_1)(x/\sqrt{x+0.1}) \tag{3}$$

where D_1 is the NN isotropic exchange constant, J_1 is the NN isotropic exchange constant, $\gamma = eg/2m$ is the gyromagnetic ratio, x is the concentration of magnetic ions, and the factor $\sqrt{3}$ determines the peak-to-peak linewidth. Taking the values of the parameters $D_1/k_B = 0.43$ K and $J_1/k_B = 9.1$ K, we have calculated the infinite-temperature linewidth for $Zn_{1-x}Mn_xTe$ in the case of DM anisotropic exchange interaction for all the manganese concentrations studied in the present work (table 2).

Table 2. Calculated theoretical and experimental infinite-temperature linewidths for $Zn_{1-x}Mn_xTe$

x	ΔH_∞^{DM} (10^{-4} T)	ΔH_∞^{dip} (10^{-4} T)	$\delta(\Delta H'_\infty)$ (10^{-4} T)	$\delta(\Delta H_\infty)$ (10^{-4} T)	Total ΔH_∞^{calc} (10^{-4} T)	ΔH_∞^{exp} (10^{-4} T)
0.013	36	0.5	6	0.7	43	130 ± 10
0.15	271	3	47	5	326	363 ± 70
0.17	295	3	51	6	355	378 ± 70
0.22	355	4	62	7	428	480 ± 100
0.23	361	4	63	7	435	469 ± 100
0.37	491	5	86	9	591	1000 ± 400
0.72	725	7	126	14	872	
0.81	775	7	135	14	931	

The effect of magnetic dipolar interaction on the EPR linewidth is also examined. The strength of this interaction is $d_{dip} = g^2\mu_B^2/2r^3$, where r is the NN distance. For $Zn_{1-x}Mn_xTe$, $r \simeq 0.44$ nm and $d_{dip}/k_B = 0.015$ K. The dipolar-broadened EPR linewidth has been derived [4] in the same approximation as equation (3):

$$\Delta H_\infty^{dip} = (1/\sqrt{3})(88/\gamma)(d_{dip}^2/\hbar J_1)(x/\sqrt{x+0.07}). \tag{4}$$

The calculated values of dipolar linewidth are also presented in table 2.

The intra-ion Mn spin–orbit coupling may have a certain influence. The additional DM coupling constant D_1' can be estimated from Moriya's [9] expression $D_1' \sim (\Delta g/g)J_1$, where Δg is the deviation in the spectroscopic splitting factor of Mn^{2+} ions from the free-electron value. It was found that the g-factor for Mn^{2+} ions in ZnTe is 2.0105 [12], so that $\Delta g = 0.008$ and $D_1'/k_B = 0.04$ K. Larson and Ehrenreich [3] have evaluated the expression for the linewidth correction $\delta(\Delta H_\infty')$ due to Mn spin–orbit coupling:

$$\delta(\Delta H_\infty') = (1/\sqrt{3})(10.5/\gamma)(D_1'^2/\hbar J_1)[(1 + D_1'/D_1)^2 - 1]x/\sqrt{x + 0.1}. \quad (5)$$

The calculated linewidth correction $\delta(\Delta H_\infty')$ are given in table 2.

Single-ion anisotropy is also taken into account. According to Larson [3], the origin of single-ion anisotropy is the crystal-field effect, which causes the fine structure in EPR spectra. The fine-structure parameter is not large for cubic symmetry and for $Zn_{1-x}Mn_xTe$ it was found to be $a_{cub}/k_B = 0.004$ K [12]. The linewidth correction $\delta(\Delta H_\infty)$ due to single-ion anisotropy has been estimated in [3]:

$$\delta(\Delta H_\infty) = (2/\sqrt{3})(10.5/\gamma)(D_1 a_{cub}/\hbar J_1)(x/\sqrt{x + 0.1}). \quad (6)$$

The calculated linewidth corrections $\delta(\Delta H_\infty)$ are also shown in table 2.

The total calculated infinite-temperature EPR linewidth ΔH_∞^{calc} is determined as the sum of the contributions ΔH_∞^{DM}, ΔH_∞^{dip}, $\delta(\Delta H_\infty')$ and $\delta(\Delta H_\infty)$. The experimental infinite-temperature linewidths obtained in the extrapolation procedure are also shown in the last column of table 2 for comparison. The error in the calculated linewidth was estimated to be ±30% because of error in the input exchange constants [3]. The accuracy of the extrapolated experimental values of the linewidth is found to depend on the manganese concentration (table 2).

It is seen that the calculated linewidths for the samples with $x = 0.15$, 0.17, 0.22 and 0.23 are in very good agreement with the experimental values. The difference between ΔH_∞^{calc} and ΔH_∞^{exp} for these concentrations is less than the estimated error in the determination of both these quantities. However, in the sample with $x = 0.37$ the calculated linewidth is smaller than the experimental value by a factor of 1.7. We think that such a discrepancy mainly arises from the relatively large error in the experimental linewidth for this concentration. One possible source of this disagreement may lie in the theoretical approximation of a randomly diluted system which is assumed in the theoretical derivation of equations (3)–(6), whereas the real distribution function differs from random for higher manganese concentrations [13].

The predicted linewidth in the sample with the lowest manganese concentration $x = 0.013$ is less than a third of the experimental value. The experimental linewidth for this concentration is obtained with good accuracy. The linewidth intensity for this sample shows that almost all the magnetic ions participate in the absorption. On the other hand, almost all the magnetic ions in this sample are 'isolated' ions which have no other manganese ions as NNs. However, the magnetic ions have next-nearest and more distant magnetic neighbours. The small calculated value of the linewidth might arise from the theoretical assumption of the NN interactions. Such an approximation neglects the anisotropic interactions with more distant neighbours and underestimates the anisotropy of single ions. In any case, in the region of low manganese concentrations, some additional interactions, which are not included in the theory, seem to play a role.

Except for the region of low manganese concentrations, the theoretical calculation correctly predicts the values of the infinite-temperature EPR linewidth. It is seen that the

main part of the linewidth arises from the anisotropic superexchange, which is the dominant anisotropic spin–spin interaction in $Zn_{1-x}Mn_xTe$ with a magnitude of about 5% of isotropic exchange. The intra-ion Mn spin–orbit coupling is not large. However, it accounts for about 14% of the total linewidth. The dipolar interaction and the interaction with crystal field are weak magnetic interactions and their effect on the linewidth can be neglected.

A similar situation concerning the magnetic interactions and their implications with respect to the EPR linewidth is found for $Cd_{1-x}Mn_xTe$. DM exchange accounts for the majority of the line broadening for $Cd_{1-x}Mn_xTe$, and the corrections to the linewidth due to other anisotropic spin–spin interactions are even smaller than for $Zn_{1-x}Mn_xTe$ [3].

4. Conclusions

The analysis of the EPR absorption line for $Zn_{1-x}Mn_xTe$ has shown that over a wide range of temperatures and compositions the EPR line can be described by the Bloch model modified for broad resonance. In this region, where the resonance is Lorentzian in nature, the linewidth can be studied within the relaxation time approximation. For higher manganese concentrations and at lower temperatures the resonance becomes so broad that it is no longer observable in the conventional EPR experiment. In the high-temperature region and over a wide range of compositions the linewidth behaves in accordance with the '$1/T$' law. An analysis of the infinite-temperature linewidth shows that the anisotropic superexchange interaction is predominantly responsible for the linewidth. The effect of the intra-ion Mn spin–orbit coupling is not negligible and should be taken into account. The dipolar interaction and the interaction with the crystal field are weak magnetic interactions and do not contribute to the linewidth significantly.

Acknowledgments

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