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2005 J. Phys.: Condens. Matter 17 2755

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Magnetic resonance in the $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{Se}_4$ dilute magnetic semiconductor system

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Received 9 December 2004, in final form 17 February 2005

Published 15 April 2005

Online at stacks.iop.org/JPhysCM/17/2755

Abstract

An electron paramagnetic resonance (EPR) study of the Mn concentration and temperature in the range of $4 \text{ K} \leq T \leq 300 \text{ K}$ for the dilute semimagnetic semiconductor $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{Se}_4$ is reported. The EPR spectra were measured for the concentrations $0.01 < x < 1.0$. For low Mn content the spectrum contains multiple resonances at $g = 2$, $g \sim 3$ and $g \sim 5$. The behaviour of the $g = 2$ signal linewidth ΔH_{pp} as a function of temperature was studied and it was related to the fitting parameters at the critical temperature and the Curie point. The j parameter of the modified expression of Silva was obtained and its role is shown for the particular transition of this system.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnetically dilute semiconducting systems (MDS) with controlled amounts of magnetic elements have received considerable attention, due to the interactions of interest that occur between their electronic and magnetic subsystems. The II–VI systems containing Mn [1, 2] are well known, and the more complex ternary and quaternary systems have been subjects of recent structural and magnetically studies [3] aiming to explore and manipulate the electronic, magnetic and structural interactions. An example is provided by the cationic disorder, which can be studied via its effects on the magnetic properties [4, 5].

The spin glass behaviour observed in the systems $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{Te}_4$ [6] and MnIn_2Se_4 as the limit of the $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{Se}_4$ series was investigated [7]. To the limit of low Mn

Table 1. Composition of $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{Se}_4$ alloys.

Nominal compositions (x)	Zn	Mn	In	Se
1.00	—	1	1.92 ± 0.05	4.51 ± 0.07
0.90	0.14 ± 0.01	0.86 ± 0.01	2.06 ± 0.02	4.06 ± 0.04
0.70	0.32 ± 0.02	0.68 ± 0.02	1.95 ± 0.03	3.77 ± 0.03
0.60	0.35 ± 0.01	0.65 ± 0.01	2.06 ± 0.04	3.95 ± 0.05
0.40	0.71 ± 0.03	0.29 ± 0.03	2.0 ± 0.1	3.9 ± 0.1
0.30	0.79 ± 0.01	0.21 ± 0.01	2.1 ± 0.1	4.0 ± 0.1
0.03	0.972 ± 0.004	0.028 ± 0.004	2.04 ± 0.01	4.02 ± 0.01
0.02	0.989 ± 0.002	0.021 ± 0.002	2.00 ± 0.01	3.98 ± 0.01
0.01	0.986 ± 0.003	0.014 ± 0.003	1.97 ± 0.03	3.82 ± 0.05

concentrations, the systems are structurally similar to the II–VI MDS, where the interchange between the Mn^{2+} ions was previously studied [8]. EPR has been used as a technique that allows the study of the interaction of spin–spin dynamics, as well as the related effects of the magnetic transition phases [9]. The resonance line broadening ΔH is a function of different processes relating the effects associated with the transition from the paramagnetic phase to the spin glass, spin–spin interactions, and spin–phonon and exchange interactions. It was found that the ΔH values show a rapid diminution with temperature decreasing towards the T_f temperature of the spin glass transition [10, 11]. It was suggested recently [12, 13] that the ΔH variation with temperature, namely the resonance line broadening, is due to the spatial inhomogeneity that could be present in the Mn distribution and that results in a progressive clustering of these atoms, as x increases toward unity. In this work we present a study of the dynamics of interaction between the spins in the system $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{Se}_4$, from the temperature dependence of the EPR spectra in the range of 4–100 K and of the Mn^{2+} ion concentration.

2. Experimental procedure

Single crystals of $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{Se}_4$ with nominal concentrations in the range of $0.01 \leq x \leq 1$ were prepared by chemical vapour transport (CVT), inside quartz ampoules of dimensions 20 cm length and 2 cm diameter, sealed in vacuum. The single crystals were obtained using AlCl_3 as the transport agent for compounds with relatively high concentrations of Mn ($x > 0.5$) [14] and I_2 for the lower concentration of Mn ($x < 0.5$) [15, 16]. Approximately 5 mg cm^{-3} of AlCl_3 and (4 mg cm^{-3} I_2) were added into the ampoule together with 1.5 g of additional reagents. The reaction process was carried out in a furnace at two temperatures of growth zones of 900 and 950 °C for AlCl_3 and 800 and 850 °C for I_2 . The reaction period lasted for about five days. The single crystals were obtained in sheets of 1 cm^2 area and with thicknesses between 20 and 30 μm . The Mn content was determined using the technique of x-ray fluorescence spectroscopy of dispersive energy (XDE) using a Shimadzu XDE-900 device as given in table 1. The Mn concentration data are in good agreement with those obtained by means of the Curie constant, extracted from measurements of magnetic susceptibility in the range of high temperatures [7]. The identification of the compounds was accomplished by means of the x-ray diffraction technique. The EPR measurements were performed using a Bruker ELEXSYS E580 spectrometer at a microwave frequency of 9.4 GHz (X-band) in the temperature range of $4 \text{ K} \leq T \leq 300 \text{ K}$, measured with calibrated non-magnetic charcoal-glass pieces.

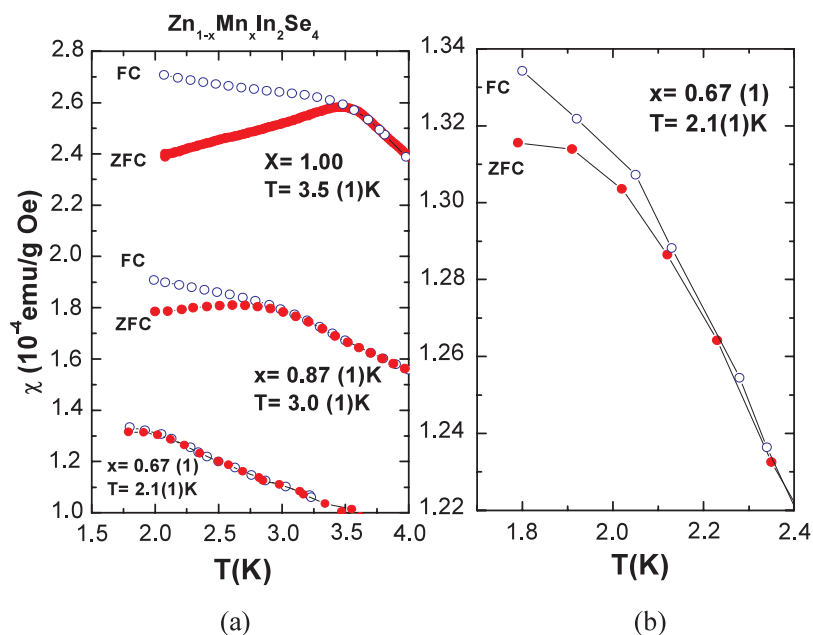


Figure 1. Magnetic susceptibility as a function of temperature (in the region of low temperature) in ZFC and FC modes; for the concentrations (a) $x = 1.00$, 0.87 and 0.67 . In (b) we show an enlarged view of the irreversibility (ZFC and FC) for the concentration $x = 0.67$.

3. Results and discussion

The $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{Se}_4$ system with x between 0.0 and 1.0 presents different crystallographic phases depending on the Mn ion concentration: one purely rhombohedral phase for $x \geq 0.87$, one mixture of phases for x between 0.67 and 0.35 and one tetragonal phase for concentrations below 0.25 [17]. At high Mn concentrations ($x \geq 0.67$) the observed magnetic behaviour is that of spin glass [7]. The observed phenomenon is attributed to the occurrence of a frustration in the system that may be due to a cationic ordering inside the structure, between the Mn ions, caused by the random replacement of Mn by Zn. Such replacement is expected to increase the degree of disorder in the structure via the competition between the interactions among the Mn^{2+} ions.

As shown in figure 1 the temperature dependences of the dc magnetic susceptibility in zero magnetic field (ZFC) χ_{ZFC} and when cooled in the presence of the field (FC) χ_{FC} for the $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{Se}_4$ system are different below a certain temperature. For $x = 0.67$, 0.87 and 1.00 in addition to the $\chi_{\text{ZFC}} - \chi_{\text{FC}}$ splitting a cusp of susceptibility (indicative of spin glass behaviour) is also found at about ~ 2.0 , 3.0 and 3.5 K.

The EPR spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{Se}_4$ crystal have been measured at different temperatures from 4 K up to 300 K. Their room temperature spectra are shown in figure 2. It seems that they are similar for all the compositions. They consist of a broad and isotropic line centred at $g \approx 2$ and the line shape turned out to be Lorentzian. This spectrum can be attributed to the strong interactions between the Mn ions. The only difference among these spectra is in their peak to peak (ΔH_{pp}) linewidth. It is broadened by dipole-dipole interaction and narrowed by exchange. As observed from these spectra, there are different behaviours, which are dependent on the replacement of zinc ions by manganese. For the concentrations of $x = 0.01$ – 0.02 , several

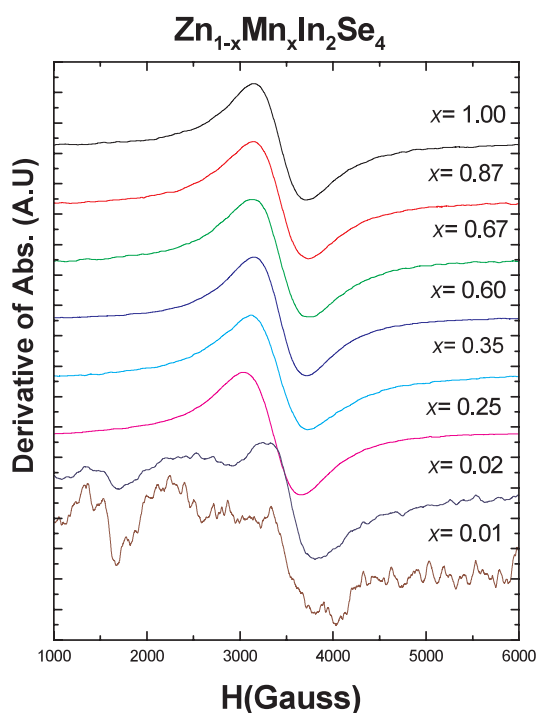


Figure 2. EPR spectra for the system $Zn_{1-x}Mn_xIn_2Se_4$ ($0.01 \leq x \leq 1.00$) at room temperature.

signals appear in the range $1 \text{ kOe} < H < 2.5 \text{ kOe}$ near the principal absorption (figure 2). This behaviour is associated with the increased dilution of the magnetic ions and the low field signals are perhaps due to small isolated Mn^{2+} ions.

The presence of several independent resonance modes suggests an increased magnetic inhomogeneity of the system and prevents, therefore, an analysis of the line shape and of the relaxation time for these samples. This behaviour is similar to those reported by Viticoli and co-workers [18], Sagredo *et al* [19] and Siebert [20]. The temperature behaviour in the range of $4 \text{ K} \leq T \leq 100 \text{ K}$ of the EPR spectra of $Zn_{1-x}Mn_xIn_2Se_4$ for $x = 0.02$ is plotted in figure 3. It can be seen that the EPR spectra present three resonances that remain almost unchanged as the temperature is decreasing. This behaviour is consistent with the negligible interaction between the magnetically dilute neighbouring Mn^{2+} ions. The characteristic Mn^{2+} resonances at $g \sim 2$, $g \sim 3$ and $g \sim 5$ are easily recognized.

The resonance observed at $g \sim 5$ can be associated with axial distortions of the crystalline field of manganese ions occupying In (external) sites, located outside the tetrahedron of Se ions occupying the vertices.

The resonance observed at $g \sim 3$ is typical for $E/D = 1/3$, where E is identified with rhombic distortion and D is the axial distortion of the crystalline field [21] at the site located at the centre of the Se tetrahedron (substitution) in the place of Zn, as deduced from the Aasa [22] diagram. For the compound of the type AB_2C_4 studied by us in the present work, the site A (Zn^{2+}) replaced by Mn^{2+} (d^5) is at the centre of a distorted tetrahedron of C (Se^{4-}) and the In^{3+} (or Mn^{3+}) ions remain at the two external B equivalent sites.

These distortions are associated with an increasing disorder in the tetrahedral structure at the sites of Zn, Mn and In [17, 20]. The resonance at $g \sim 2$ shows a faint hyperfine structure in

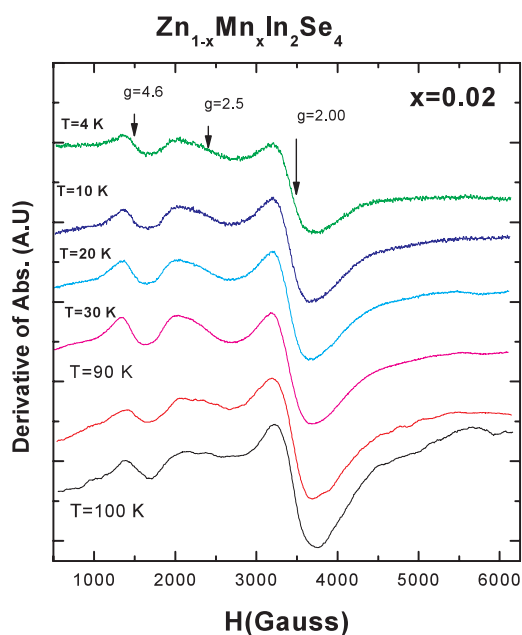


Figure 3. EPR spectra of the system $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{Se}_4$ for $x = 0.02$ as a function of temperature in the range $4 \text{ K} \leq x \leq 100 \text{ K}$. The characteristic Mn^{2+} lines are observed and their meaning is discussed in the text.

contrast to a much stronger profile observed, for example, in the systems $\text{BaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$ doped with Mn^{2+} [23–25].

Figure 4 shows the dependence of the EPR linewidths measured between the absorption maximum slopes as a function of temperature for different concentrations of Mn. It can be seen that for $x = 0.02$, the linewidth remains almost constant as the temperature decreases. This seems to be the usual behaviour for samples with low manganese content [26]. The small broadening can be associated with a decrease of the exchange narrowing due to a slowing down of the spin fluctuations at low temperatures [27].

With respect to the other samples ($0.35 \leq x \leq 0.87$), it can be observed that the linewidth ΔH_{pp} of the resonance above $T = 100 \text{ K}$ changes smoothly with temperature. This behaviour is expected for paramagnetic compounds and the line changes are small for higher temperatures. For temperatures $T \leq 50 \text{ K}$ the linewidth strongly increases. This behaviour was studied by Huber *et al* [28] in an antiferromagnetic system and by Oseroff *et al* [29] in a system with spin glass behaviour. However, for the compound MnIn_2Se_4 , one observes usual ‘motional narrowing’ in the temperature interval of $30 \text{ K} \leq T \leq 100 \text{ K}$, but on cooling from 30 to 4 K one observes a line narrowing. This behaviour is attributed to a transition from the paramagnetic phase to spin glass [7], which was also noticed for compounds of the type $\text{CdCr}_{2x}\text{In}_{2-2x}\text{S}_4$ [18]. A possible explanation for the different behaviour of the EPR line broadening observed (figure 4) can be given by considering that only the superparamagnetic clusters with a distribution of relaxation times, successively blocked, could provide such a behaviour. The coupling becomes collective and the relaxation modes of the different clusters are no longer independent. The change of the linewidth from 20 K towards lower temperatures can be related to the interchange and collective cooperative nature of the interaction processes on cooling.

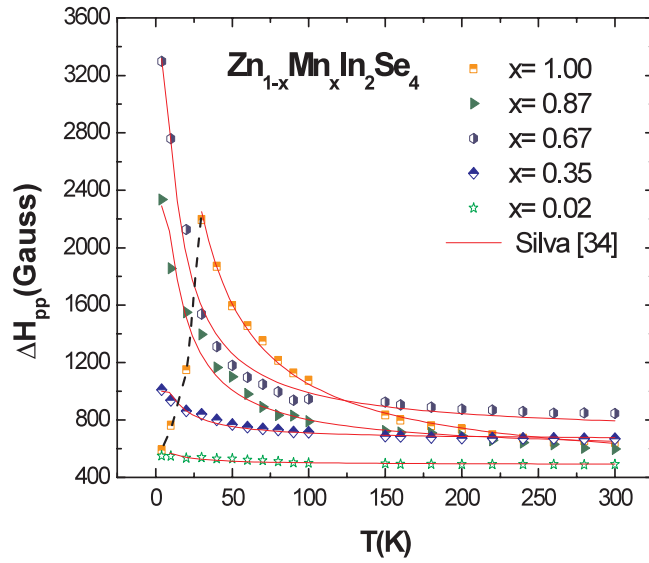


Figure 4. EPR linewidth ΔH_{pp} behaviour as a function of temperature and of Mn concentration for the system $Zn_{1-x}Mn_xIn_2Se_4$. The solid line is the adjustment performed using expression (3).

Huber [28] developed a theory for antiferromagnets where the broadening was associated with a critical increase of the relaxation time at temperature close to that of the AFM transition. He ended up with the following expression:

$$\Delta H_{pp} = A \left[\frac{T_N}{T - T_N} \right]^\alpha + B, \quad (1)$$

where A and α are two parameters calculated by fitting the experimental data, B is the high temperature linewidth and T_N is the Néel temperature. Oseroff [10], working with a large group of MDS, replaced the B value by a Curie paramagnetic term $B(1 - \Theta/T)$ with Θ being the Curie–Weiss temperature. Chehab *et al* [30] and Bhagat *et al* [31, 32] criticized the interpretation on the basis of the critical increase of the relaxation time and suggested that the ΔH_{pp} change with temperature is due to inhomogeneous line broadening produced by the random distribution of magnetic ions.

Wooley *et al* [11, 33] suggested an expression such as equation (2) where the first term takes into account the special inhomogeneity effects of the system and the second term accounts for the paramagnetic behaviour:

$$\Delta H_{pp} = A \exp\left[\frac{T}{T_0}\right] + B \left(1 - \frac{\Theta}{T}\right) \left[1 - \exp\left(-\frac{T}{T_0}\right)\right], \quad (2)$$

where A , B and T_0 are temperature-independent parameters to be calculated by fitting this equation to experimental data.

Finally, Silva *et al* [34] introduced a modification to equation (2) from the central idea of Oseroff [10] by adding an exponential part related to the reciprocal of the correlation time among the spins, somehow related to the spin–spin relaxation time, that allows explaining the temperature behaviour of ΔH_{pp} :

$$\Delta H_{pp} = \Delta H_\infty \left(1 - \frac{\Theta}{T}\right) \exp\left(-j\frac{T_f}{T}\right), \quad (3)$$

Table 2. Values of the parameter calculated by fitting Silva's relation given by equation (3) for the system $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{Se}_4$. Θ_{Sm}^* (K) are the Curie–Weiss temperatures obtained from magnetic susceptibility measurements performed at high temperatures [7, 35].

Mn (x)	ΔH_∞ (G)	Θ (K)	Θ_{Sm}^* (K)	T_f (K)	j
0.02	489 ± 10	-3.2 ± 0.3	-2.8 ± 0.3	0.03 ± 0.02	1
0.35	660 ± 16	-22 ± 2	-24 ± 3	0.8 ± 0.4	1
0.67	692 ± 11	-50 ± 2	-49 ± 2	2.1 ± 0.2	1
0.87	574 ± 24	-87 ± 5	-89 ± 5	3.1 ± 0.3	1
1.00	371 ± 12	-116 ± 14	-96 ± 5	4.3 ± 0.5	1

where ΔH_∞ is the linewidth at a very high temperature. This parameter contains information related to the magnetic ion concentration and about the kind of interaction, which dominates the signal behaviour at temperatures above the transition. The exponential term contains: the reciprocals of correlation times; the j parameter, a number between -1 and 1 that depends on the transition type (spin glass or antiferromagnetic nature) that could occur in the system; T_f the cooling temperature and Θ the Curie–Weiss temperature. We have found that our results can be explained using equation (3). Solid lines in figure 4 represent the calculated values. A good agreement between calculated and experimental linewidths has been reached. The adjustment data are shown in table 2.

From these results it may be observed that the Θ values increase with manganese content. The negative sign of the Weiss constant is indicative of the presence of dominant antiferromagnetic interaction. In table 2 it is shown that the measured values are in good agreement with those obtained from adjustments of experimental values of the magnetic susceptibility at high temperatures [7, 35]. The value obtained for j is equal to 1 , showing a possible phase transition to be present, from the paramagnetic phase to the spin glass, as can be seen for the compound MnIn_2Se_4 at $T_f = 4.25$ K.

4. Conclusions

A characterization was made of the influence on the EPR spectrum of the manganese concentration in the system $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{Se}_4$ as a function of the temperature. For the compound MnIn_2Se_4 on cooling from 30 to 4 K one observes a resonance line narrowing, attributed to a transition from the paramagnetic phase to spin glass. The EPR spectra of more dilute samples ($x = 0.01$ – 0.02) show the appearance of several signals probably associated with the formation of small isolated clusters reflecting an increased magnetic inhomogeneity with increasing manganese concentration associated with increasing cationic disorder in the tetrahedral structure at the sites of Zn (Mn) (substitution) and In (Mn) external. The analysis of the temperature dependence of the EPR linewidth ΔH_{pp} resulted in estimates for the Curie–Weiss temperature Θ and for the freezing temperature T_f of the spin glass. The value obtained for j is equal to 1 , showing a possible phase transition to be present, from the paramagnetic phase to spin glass, as can be seen for the compound MnIn_2Se_4 at $T_f = 4.25$ K.

Acknowledgments

The authors wish to thank FAPESP and CNPQ for the financial support and infrastructure made available to carry out this investigation.

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