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Dynamic susceptibility measurements at the spin-glass transition in the $Zn_{1-x}Mn_xIn_2Se_4$ semiconductor

J Mantilla[1], **E Ter Haar**[2], **J A H Coaquira**[3] **and V Bindilatti**[2]

[1] Laboratório de Física Molecular, Universidad Central de Venezuela, Caracas 1040, Venezuela
[2] Instituto de Física, Universidade de São Paulo, C.P. 66318, 05315-970, São Paulo, SP, Brazil
[3] Instituto de Física, Universidade de Brasília, C.P. 70919-970, Brasília, Brazil

E-mail: jmantilla@fisica.ciens.ucv.ve

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Abstract

Measurements of the magnetic properties of the magnetic semiconductor $Zn_{1-x}Mn_xIn_2Se_4$ for two Mn compositions ($x = 0.87$ and 1.00) are presented in this work. The localized Mn ions in the layered rhombohedral structure undergo a spin-freezing transition below 3.5 K. The frequency-dependent freezing temperature T_f varies as $\Delta T_f/(T_f \Delta \log \omega) \approx 0.022$, indicating a spin-glass behaviour. From the frequency dependence of T_f, the validity of the critical slowing down associated with a true phase transition is tested. For $T > T_c$, the dynamic scaling of the imaginary component of ac susceptibility data yields the following set of critical parameters: $z\nu = 9.7 \pm 1.0$, $\beta = 1.18 \pm 0.20$ and $T_c = 2.61 \pm 0.06$ K for $x = 0.87$ and $z\nu = 10.7 \pm 0.9$, $\beta = 1.20 \pm 0.20$ and $T_c = 3.43 \pm 0.01$ K for $x = 1.00$. These values are in good agreement with reported values for other spin glasses.

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

1. Introduction

Although spin-glass behaviour in semiconductors with short-range antiferromagnetic interactions has been studied for a long time, their relation to canonical spin glasses is still under investigation [1–3]. The variety of experimental realizations of the spin-glass state is due to the different ways in which the two main ingredients, randomness and frustration, may be present [4, 5]. In fact, a random distribution of magnetic interactions may be achieved either by a topological disorder or by mixing magnetic ions, as well as being generated in compounds with short-range interactions [6, 7].

We report here the magnetic properties of another site-disordered semiconductor $Zn_{1-x}Mn_xIn_2Se_4$, with short-ranged antiferromagnetic super-exchange interaction between Heisenberg spins but with a quasi-two-dimensional structure. As was established by Range *et al* [8] and confirmed by us for a Mn concentration of $x \geqslant 0.87$ [9], this structure consists of slabs of four Se layers which are van der Waals coupled to each other. Within the slabs the metal cations are distributed over three triangular layers between the Se layers, in a tetrahedral–octahedral–tetrahedral site sequence.

The Mn^{2+} ion provides localized, pure spin ($s = 5/2$) magnetic moments which interact through short-range antiferromagnetic super-exchange. For ions in the tetrahedral layers the exchange paths are similar to those of zinc-blende II–VI diluted magnetic semiconductors which have an exchange constant J of order -12 K [10]. In this work we have investigated the dynamics of spin freezing observed in the $Zn_{1-x}Mn_xIn_2Se_4$ system by means of ac magnetic susceptibility measurements.

2. Experimental details

Single crystals of $Zn_{1-x}Mn_xIn_2Se_4$ with nominal Mn concentrations $x = 0.87$ and 1.00 were prepared by a vapour phase chemical transport technique (CVT). A detailed explanation of the thermal procedure is given in [9].

The determination of the Mn content was made using the technique of x-ray fluorescence spectroscopy of dispersive energy (XDE) (Shimadzu XDE-900 device). Values of the Mn concentration were in good agreement with those extracted from the analysis of magnetic susceptibility data in the range of high temperature [10]. Room-temperature x-ray power diffraction was used to confirm the rhombohedral structure (space group $R\bar{3}m$) described above.

Low-field magnetic measurements were carried out using a commercial SQUID magnetometer in a broad range of temperature (2 K $\leqslant T \leqslant$ 300 K). The diamagnetic contribution of the sample holder was subtracted from the sample signal. In order to characterize the frequency dependence of the freezing temperature, experimental data for ac magnetic susceptibility (in-phase $\chi'(T)$ and out-of-phase $\chi''(T)$ components) were obtained using excitation frequencies in the range of 100 mHz $\leqslant f \leqslant$ 1 kHz.

3. Results and discussion

Figure 1 shows the temperature dependence of zero-field cooled (ZFC) and field cooled (FC) curves for samples $x \geqslant 0.87$ obtained with a magnetic field of 100 Oe. Plots for both samples show quite similar features, namely a clear irreversibility between ZFC and FC curves and a sharp peak in the ZFC curves. These features are the fingerprints of a spin-glass behaviour and confirm the results previously reported for the $Zn_{1-x}Mn_xIn_2Se_4$ system (see [11]).

In the high-temperature region the susceptibility data follow the Curie–Weiss behaviour with $\theta = -89$ and -96 K for $x = 0.87$ and 1.00, respectively. These values make evident the existence of strong antiferromagnetic interactions in both samples [10]. Values of T_f, represented in figure 1, are consistent with those values obtained using electronic paramagnetic resonance (EPR) [11].

Figure 2 shows the temperature dependence of the ac magnetic susceptibility. These measurements were carried out with an ac field $h = 5$ Oe and in a set of five frequencies from 0.1 Hz to 1 kHz. The temperature dependence of the in-phase component (χ') obtained at the lowest frequency (0.1 Hz) shows a peak at $T_f \sim 2.9$ and 3.5 K for $x = 0.87$ and 1.00, respectively. The imaginary part (χ'') exhibits a sudden rise at the temperature T_i, slightly above T_f ($T_i \approx 4.0$ and 3.5 K for $x = 1.00$ and 0.87, respectively). The freezing temperature (T_f) strongly depends on the excitation frequency, as can be observed in figure 2. $T_f(f)$ decreases with the decrease of frequency, as is expected for a spin-glass system. T_i

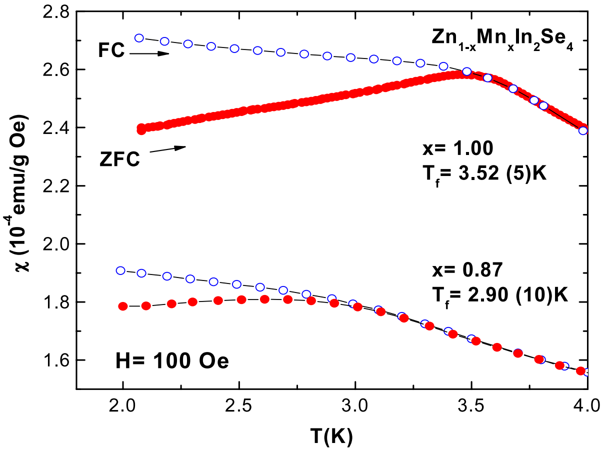


Figure 1. Temperature dependence of the dc zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibility for $Zn_{1-x}Mn_xIn_2Se_4$. (Plot partially reproduced from [11].)

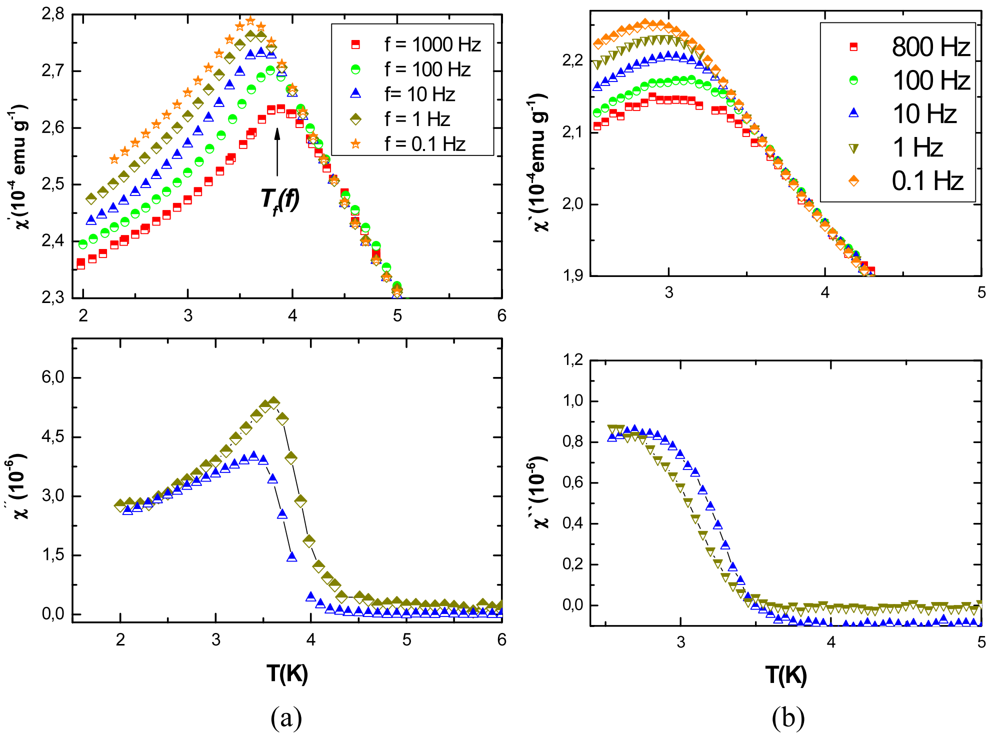


Figure 2. Temperature dependence of the in-phase (χ') and out-of phase (χ'') components of the ac susceptibility measured for $Zn_{1-x}Mn_xIn_2Se_4$ with (a) $x = 1.0$ and (b) $x = 0.87$.

indicates the onset of weak irreversibility and is related to the freezing of the transverse spin components, whereas T_f is related to the strong irreversibility and thus to the freezing of the longitudinal spin component [12, 13]. Similar results have been reported for other spin-glass systems [14–19]. It is worth mentioning that essentially the same spin-glass behaviour was

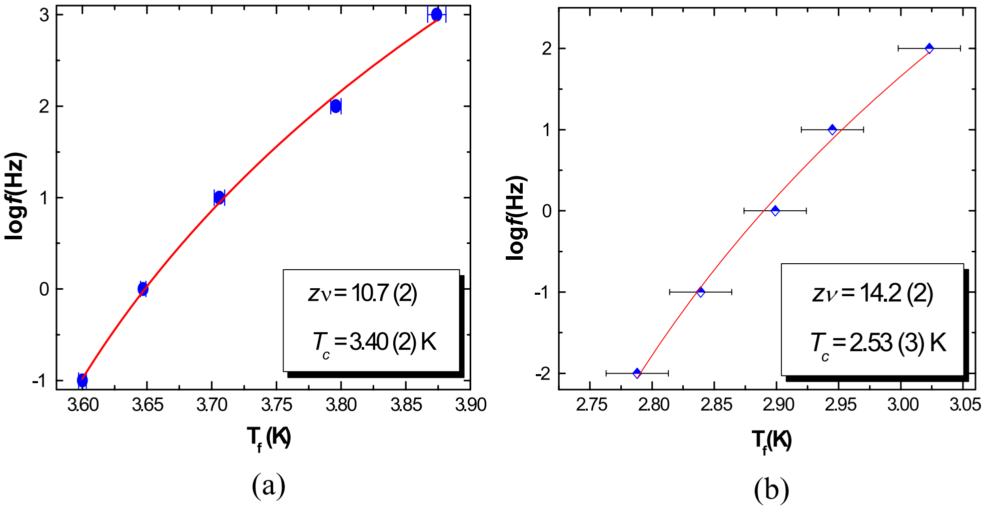


Figure 3. The frequency dependence of the freezing temperature T_f for $Zn_{1-x}Mn_xIn_2Se_4$ with (a) $x = 1.00$ and (b) $x = 0.87$.

reported for the isostructural $Zn_{1-x}Mn_xIn_2Te_4$ system [18]. The substitution of Se by Te ions produces slightly higher freezing temperatures.

As a preliminary analysis and to facilitate the comparison with other works we chose the frequency-dependent freezing temperature, T_f as the maximum of the in-phase magnetic susceptibility. The relative variation of T_f per frequency decade $(\Delta T_f/T_f)/\Delta \log f \approx 0.022$ was determined [20]. Despite the very different structure of the present materials, $(\Delta T_f/T_f)/\Delta \log f$ is intermediate between those typically reported for metallic spin glasses ($\approx 0.7 \times 10^{-2}$) [21] and for the insulator $Eu_{0.6}Sr_{0.4}S$ (5×10^{-2}) [22], but is similar to other reported spin glasses [18, 23]. Taking the temperature corresponding to the cusp of the in-phase ac magnetic susceptibility as the onset of the strong irreversibility of each measuring time $t_{meas} = 1/f$ (f being the frequency of the ac magnetic field) and studying the dependence of T_f on the ac field frequency, the dynamic properties of a true phase transition can be checked [24]. Our analysis of the critical dynamics is based on the conventional slowing down, which is valid for a spin-glass phase transition at finite temperature, T_c. The divergence of the relaxation time as the transition is approached from above is described by the power law [25]

$$f = f_0 \tau^{z\nu}, \tag{1}$$

where τ is related to the reduced temperature, $\tau = (T_f - T_c)/T_c$, ν is the critical exponent of the correlation length ξ, and z is the dynamic exponent relating ξ and f by $1/f \cong \tau_0 \xi^z$. Typical values for f_0 are in the range of 10^{11}–10^{13} Hz for canonical spin glasses.

The frequency dependence of T_f has been analysed using equation (1). Different T_c values were tested for the best fit of data points. The best fitting curve to the experimental data is shown in figure 3. From this analysis, we have obtained the $z\nu$ exponent and T_c for both investigated samples with $x = 0.87$ and 1.00 (see figure 3). For $MnIn_2Se_4$ the value $z\nu$ is close to the values ($z\nu \approx 8$–10) reported for spin glasses [26], as well as for the non-conventional spin-glass-like system $La_{0.95}Sr_{0.05}CoO_3$ [27]. We note also that the $z\nu$ value increases when the Mn concentration is decreased. A similar trend has been reported for other spin-glass systems [14, 28].

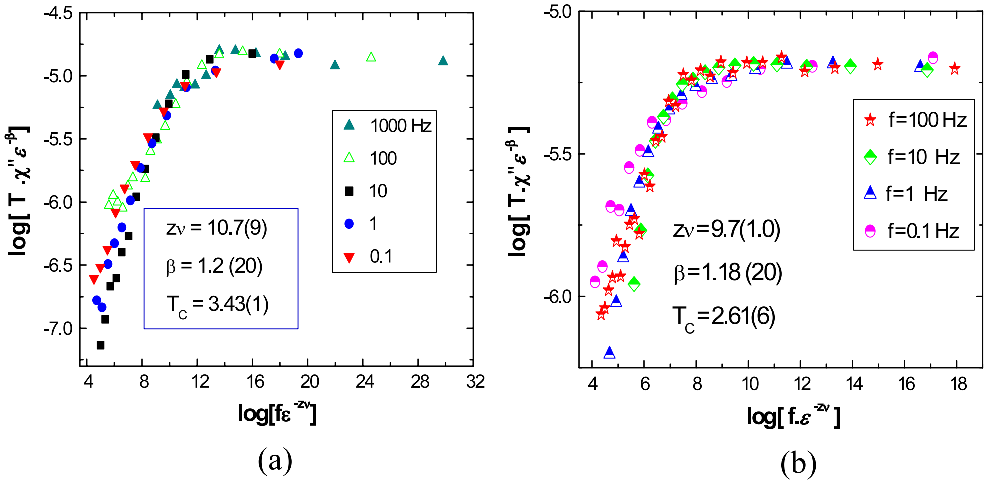


Figure 4. Scaling of $\chi''(T, f)T$ performed according to equation (2) for $Zn_{1-x}Mn_xIn_2Se_4$. (a) Corresponds to $x = 1.00$ and (b) corresponds to $x = 0.87$.

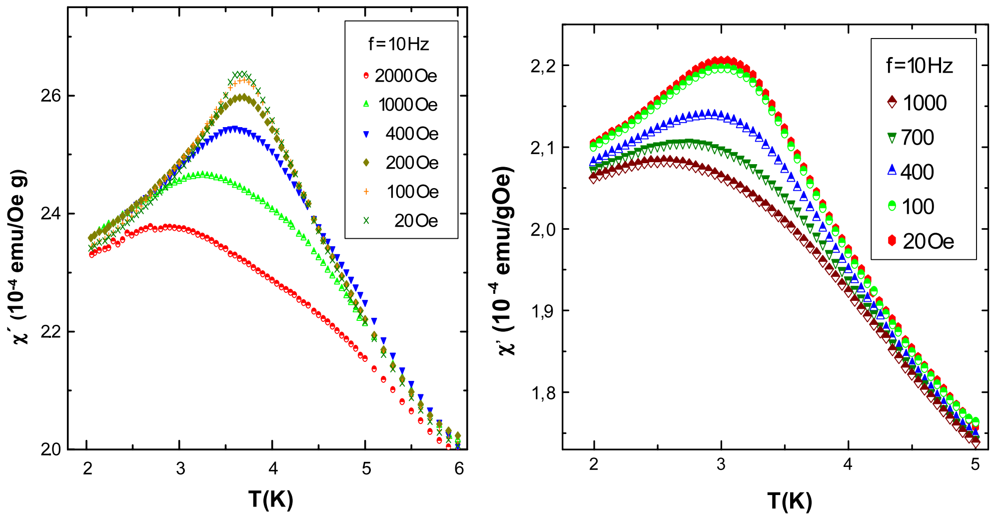
In a more complete analysis, we tested the scaling relation for the dynamic critical properties derived from the linear response theory [6]:

$$T\chi''(f, T) \sim \varepsilon^{\beta} G[f\varepsilon^{-z\nu}]. \tag{2}$$

Here, $G(x)$ is a universal function of x, β is the exponent of the order parameter, $\tau = \tau_0\varepsilon^{z\nu}$ and $\varepsilon = T/T_c - 1$ is the zero-field reduced temperature. In figure 4 we show the result obtained using the dynamic scaling law (equation (2)) for all data collection of $\chi''(f, T)$ at different frequencies. The best data collapsing corresponds to a set of values $z\nu = 10.7(9)$, $\beta = 1.20(20)$ and $T_c = 3.43(1)$ K for $MnIn_2Se_4$ ($x = 1.0$), and $z\nu = 9.7(1.0)$, $\beta = 1.18(20)$ and $T_c = 2.61(6)$ K for the sample with $x = 0.87$. These values are in good agreement with these previously published for semimagnetic systems [29, 30], and also with data obtained by numerical simulation for the case of three-dimensional spin glasses with short range interactions [15].

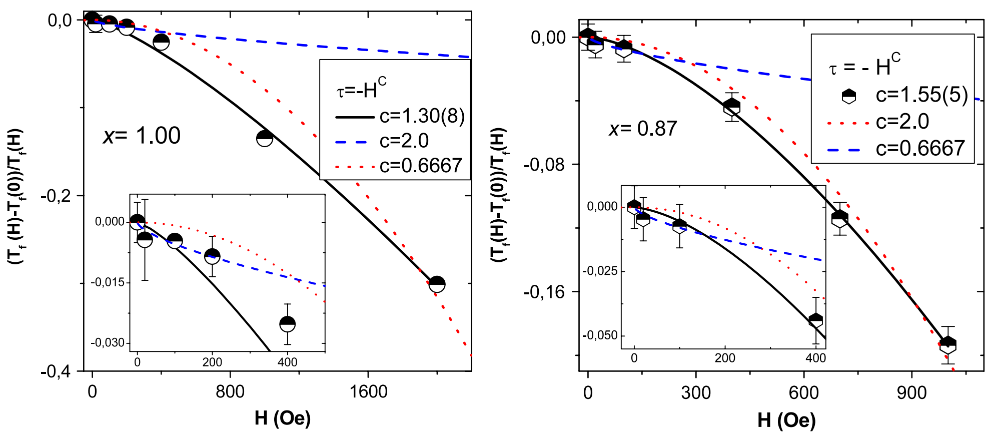
We have also checked the behaviour of the system under the influence of a dc magnetic field, H. In a Heisenberg spin glass, both strong and weak irreversible lines were first derived by Almeida and Thouless (AT) [13, 20]. In Ising spin glasses, treated in the Sherrington–Kirkpatrick (SK) molecular field approximation for purely random interactions of infinite range, an H–T instability was evidenced (the AT line), which corresponds to the onset of irreversibilities with the equation $H_c \approx (-\tau)^{\frac{\phi_{H-T}}{2}}$, where $H_c = \mu H/k_B T_f(0)$ is the reduced magnetic field, $\tau = (T_f(H) - T_f(0))/T_f(H)$ is the reduced temperature, T_f is the transition temperature and ϕ is a critical exponent [31]. This line was first interpreted by Toulouse as due to a true phase transition. In the case of an isotropic Heisenberg spin-glass system, they predicted the freezing of the transverse spin components (perpendicular to the applied field) following a Gabay–Toulouse-like (GT) behaviour ($\tau \propto h^2$) [12, 13]. To determine the (H, T_f) phase diagram, figure 5 shows the temperature dependence of the real part of the complex susceptibility measured in various dc magnetic fields (from 20 to 2.0 kOe) and with 10 Hz of ac frequency for both Mn concentrations ($x = 0.87$ and 1.00).

As a preliminary analysis and for the sake of simplicity, we defined the temperature $T_f(H)$ at the maximum of the in-phase magnetic susceptibility. This critical temperature decreases with increasing dc field, which is similar to other reported results for spin-glass systems [17].



(a) (b)

Figure 5. Temperature variation of the real part of the ac susceptibility obtained for different values of dc fields and $f = 10$ Hz: (a) $x = 1.00$ and (b) $x = 0.87$.



(a) (b)

Figure 6. H–T_f diagrams for $Zn_{1-x}Mn_xIn_2Se_4$ with (a) $x = 1.00$ and (b) $x = 0.87$. The solid curves represent the fit of data; dashed and dotted curves represent the AT and GT lines, respectively.

The best fit to experimental data is shown in figure 6. From this analysis we have obtained values of $\phi_{H-T} = 1.29(6)$ and $\phi_{H-T} = 1.54(7)$ for compounds with $x = 0.87$ and 1.00, respectively. From the analysis of H–T plots (figure 6), we can determine that the experimental data for both samples seem to be more consistent with the GT line. However, at low magnetic field ($H \leqslant 200$ Oe) the AT-like line [32] better describes the experimental points (see insets in figure 6). AT-like behaviour (weak irreversibility line) has been also observed in other spin-glass systems [12]. The evolution from AT-like behaviour to the GT line as the magnetic field is increased suggests the presence of small amount of random anisotropy (weak), which seems to play an important role in the spin-glass phase transition [33, 34].

4. Conclusions

The dynamic magnetic properties of $Zn_{1-x}Mn_xIn_2Se_4$ with Mn concentration $x \geqslant 0.87$ have been investigated in the range of $2\ K \leqslant T \leqslant 300\ K$. From high-temperature data ($T > 100$ K) the Mn concentration x and the Curie–Weiss parameter, θ, were estimated, which are in good agreement with those obtained from EPR. For samples with $x \geqslant 0.87$, irreversibility features of a spin-glass transition have been observed at temperatures below 4 K. Values of critical exponents $z\nu$ and β are consistent with those reported for conventional spin glasses. Results obtained from dynamic scaling analysis for $MnIn_2Se_4$ and $Zn_{0.13}Mn_{0.87}In_2Se_4$, prove that the freezing at ~3.43 and ~2.61 K, respectively, can be considered as a true phase transition of a spin glass.

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