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Jonathan Alaria, Manel Bouloudenine, Guy Schmerber, Silviu Colis, Aziz Dinia, et al.. Pure paramagnetic behavior in Mn-doped ZnO semiconductors. *Journal of Applied Physics*, 2006, 99 (8), pp.08M118/1-3. <10.1063/1.2172887>. <hal-00204991>

HAL Id: hal-00204991

<https://hal.science/hal-00204991v1>

Submitted on 28 Aug 2024

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Pure paramagnetic behavior in Mn-doped ZnO semiconductors

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(Presented on 3 November 2005; published online 25 April 2006)

Polycrystalline Mn-doped zinc oxides ($\text{Zn}_{1-x}\text{Mn}_x\text{O}$) were synthesized by coprecipitation method with x varying between 0.01 and 0.1. Raman spectroscopy indicates the appearance of an additional mode which is an indicator for the incorporation of Mn ions into the ZnO host matrix. The magnetic properties have been studied by electron paramagnetic resonance (EPR) spectroscopy. The Mn-related EPR spectra exhibit the expected pattern for isolated Mn ions. Temperature dependence of the reciprocal integrated EPR signal follows a Curie law indicating a typical paramagnetic behavior for $x \leq 0.05$. © 2006 American Institute of Physics. [DOI: 10.1063/1.2172887]

The rapidly growing field of spintronics is driven by the prospect of using the properties of spin in semiconductor devices. One of the basic requirements for the realization of such devices is the generation of spin polarized currents. A class of materials called diluted magnetic semiconductors (DMS's) has emerged as the most promising candidate.¹ Among them, magnetic ion substituted ZnO knows an increasing interest since the prediction of room-temperature ferromagnetism by Dietl *et al.*² According to these theoretical calculations, room-temperature ferromagnetism is the stable phase for a p -type doped $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ with 5% Mn and 3.5×10^{20} holes/cm³. Although many preparation methods were used to produce high quality Mn-doped ZnO, the results are contradictory. Both ferromagnetism and absence of ferromagnetism were observed in doped ZnO thin films.³⁻⁶ In bulk system the same contradictions are observed.⁷⁻¹⁰ The magnetic properties of this compound seems to be very sensitive to the preparation method and the working conditions. It emphasizes how important it is to check that transition metal dopants occupy Zn sites without changing the ZnO host lattice, rather than precipitate, which can lead to ferromagnetic phases.

In the present paper we analyze the structural and magnetic properties of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($0.01 \leq x < 0.10$) using the Raman and electron paramagnetic resonance spectroscopies, respectively. We evidence a pure paramagnetic behavior in samples with $x \leq 0.05$ instead of the expected ferromagnetic character, although Mn ions are well inserted in the ZnO lattice.

$\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x=0.01, 0.03, 0.05, 0.09$) powders were prepared by coprecipitation technique. This is a suitable technique to obtain homogeneous ZnO:Mn solid solutions with a large enough magnetic signal. An additional advantage is the good reproducibility and the use of low temperature required to obtain the compound which limits the formation of parasitic phases. $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ was obtained from the decomposition of an oxalate precursor in which Mn and Zn ions are already intimately mixed. The oxalate precursor

$\text{Zn}_{1-x}\text{Mn}_x(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ was obtained by coprecipitation of 50 ml of a 0.4 mol/l aqueous solution of zinc and manganese acetates [$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$], respectively, with the same volume of 0.4 mol/l solution of oxalic acid at room temperature. The precipitate was thoroughly washed with distilled water and dried in air at 313 K for 12 h. The light white powders thus obtained were then heated at 1173 K for 15 min in air. The color of the final powder ranged from yellow brown to dark brown when increasing the Mn concentration.

The cationic composition of the sample was checked by means of inductive coupled plasma mass spectroscopy (ICP-MS) and energy dispersive x-ray spectroscopy (EDS). The samples are homogeneous and the Mn concentrations found by EDS are in agreement with the estimations given by the ICP-MS measurements and with the nominal Mn concentrations. The structural characterization and the size of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ particles are reported elsewhere.¹¹ We remind here that x-ray diffraction (XRD) in the θ - 2θ configuration showed diffraction patterns typical for a wurtzite structure with no additional peaks that would correspond to any second crystalline phase. The average crystallite size was about 44 nm.

In order to check the insertion of Mn ions into the ZnO lattice and due to the limited sensitivity of the XRD technique, Raman scattering experiments were carried out using a Renishaw micro-Raman system at room temperature. The 514.53 nm line of an Ar⁺ laser with an exposure time of 10 s was used for excitation. The ZnO wurtzite structure belongs to the $P6_3mc$ symmetry group. The Zn^{2+} ions have a T_d geometry with an irreducible representation: $\Gamma_v = A_1 + E + F_2$. Using the Halford site method we find the optical phonon irreducible representation: $\Gamma_{\text{opt}} = 2A_1 + 2B_1 + 2E_1 + 2E_2$ where the A_1 and E_1 modes are polar and can split into transverse optical (TO) and longitudinal optical (LO) phonons, both being active in Raman and infrared spectroscopies. Nonpolar E_2 modes are Raman active, while B_1 modes are Raman inactive. Figure 1 shows the room-temperature unpolarized Raman spectra of $\text{Zn}_{0.91}\text{Mn}_{0.09}\text{O}$ and pure ZnO powders. All the Raman peak frequencies have been extracted by Lorentz

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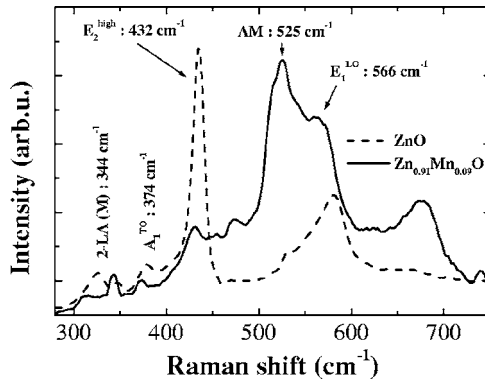


FIG. 1. Room-temperature micro-Raman of both $\text{Zn}_{0.91}\text{Mn}_{0.09}\text{O}$ and ZnO pellets.

fitting. The most intense Raman band at 432 cm^{-1} can be attributed to the nonpolar optical phonon mode of ZnO (E_2 modes). The Raman bands at 374 and 566 cm^{-1} are the TO mode with A_1 symmetry and the LO mode with E_1 symmetry, respectively. This second mode can be attributed to defects due to O vacancies, Zn-interstitial defect states, or free carriers.¹² The concentration of these defects increases with increasing the Mn concentration as shown by the increasing intensity of the E_1^{LO} phonon mode.

We will focus now on the origin of the vibration mode at 525 cm^{-1} . Previously, Bundesmann *et al.*¹³ have observed some additional vibration modes for different dopants. They suggested that these modes are related to defect-induced modes and can be used as indicator to check the dopant incorporation in the host matrix. In a similar manner, the vibration mode at 525 cm^{-1} can be associated with Mn^{2+} impurities. This can be explained by the larger size of Mn^{2+} compared to Zn^{2+} ionic radius. When Mn^{2+} substitute the Zn^{2+} ions, new lattice defects are created or intrinsic host lattice defects are activated. This presumption is in agreement with the increasing intensity of the E_1^{LO} mode (566 cm^{-1} in Fig. 1). Another indication of the insertion of Mn in the host matrix is the enhancement of the 684 cm^{-1} peak which may result from (a) the two phonon process [$A_1^{\text{LO}} + E_2^{\text{low}}$] and (b) the increase of the amount of Mn-based phases.¹⁴

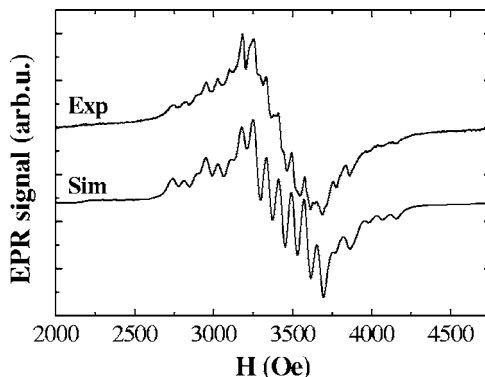


FIG. 2. Experimental (top trace) and simulated (bottom trace) spectra of $\text{Zn}_{0.99}\text{Mn}_{0.01}\text{O}$ recorded at room temperature. Simulation parameters: ^{55}Mn ; $S=5/2$; $I=5/2$; isotropic $g=2.001$; axial $D=250\text{ Oe}$; isotropic $A=79\text{ Oe}$; isotropic linewidth= 50 Oe .

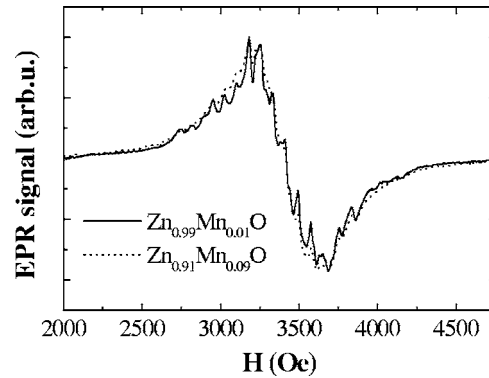


FIG. 3. Superimposed EPR spectra of $\text{Zn}_{0.99}\text{Mn}_{0.01}\text{O}$ (solid line) and $\text{Zn}_{0.91}\text{Mn}_{0.09}\text{O}$ (dotted line) compounds at room temperature.

The EPR measurements were performed with an X-band (9.5 GHz) spectrometer in the $4\text{--}300\text{ K}$ temperature range. The room-temperature $\text{Zn}_{0.99}\text{Mn}_{0.01}\text{O}$ EPR spectrum reported in Fig. 2 is well simulated according to a previous EPR study of Mn^{2+} ions in polycrystalline ZnO .¹⁵ The reported parameters of the EPR Hamiltonian were used to perfectly reproduce the observed sequence of the hyperfine pattern and of the fine structure (Fig. 2). A slight distortion and/or a slightly nonequivalent site for Mn ions may be responsible for the intermediate lines marked by arrows on Fig. 2.

This result further supports the high symmetry of the substitution sites of Mn in ZnO , as inferred from the XRD and Raman studies. Moreover, it suggests the almost isotropic neighborhood of the isolated Mn ions in this substitution pattern. As the amount of Mn is increasing, there is no indication for any increasing disorder or symmetry change of the ZnO host. This is evidenced by the very similar EPR spectra observed at room temperature for the $\text{Zn}_{0.99}\text{Mn}_{0.01}\text{O}$ and $\text{Zn}_{0.91}\text{Mn}_{0.09}\text{O}$ compounds (Fig. 3). The main difference simply corresponds to the expected line broadening attributed to dipolar interactions as the Mn concentration increases. For a given Mn concentration, a similar but less structured EPR spectrum is observed as the temperature decreases (Fig. 4), due to a slight line broadening. There is no indication for strong exchange interactions which could strongly affect the line shape and linewidth.

The overall picture of isolated Mn^{2+} ions is furthermore supported by the pure Curie-like behavior of the reciprocal

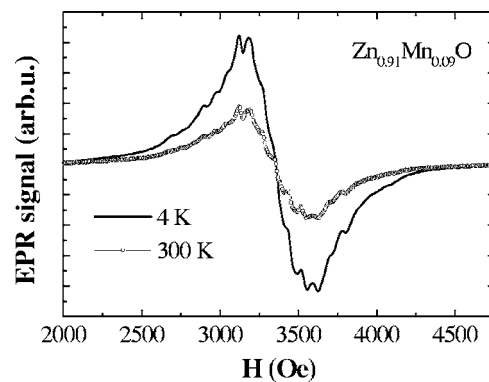


FIG. 4. EPR spectra of the $\text{Zn}_{0.91}\text{Mn}_{0.09}\text{O}$ compound at room temperature and at 4 K .

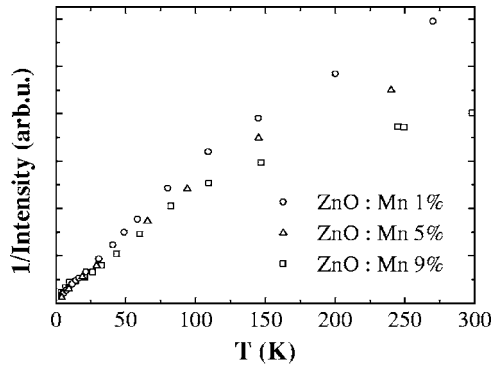


FIG. 5. Temperature dependence of the reciprocal integrated EPR signal for different Mn^{2+} concentrations.

EPR integrated signal intensity versus temperature in the 4–100 K range (Fig. 5), in agreement with the static susceptibility measurements. For Mn concentrations smaller than 5% the data are fitted to a Curie law $\chi=C/T$, whereas for Mn concentration higher than 5% a Curie-Weiss law $\chi=C/(T-\Theta)$ is needed to fit the experimental results. C and Θ are the Curie constant and the Curie-Weiss temperature, respectively. For $\text{Zn}_{0.91}\text{Mn}_{0.09}\text{O}$ we found, by fitting the curve in the high temperature range, a Curie-Weiss temperature about -250 K characteristic for an antiferromagnetic coupling between Mn^{2+} ions similar with the one reported by Chikoidze *et al.*¹⁶ To confirm the antiferromagnetic interaction observed in highly doped samples a calibration of the spin concentration has been performed at room temperature. As expected, the spin concentration increases linearly for low doped samples ($x \leq 0.05$), whereas it is smaller than the nominal Mn concentration for highly doped samples ($x > 0.05$). This observation confirms that some of Mn^{2+} ions couple antiferromagnetically. This antiferromagnetic interaction is solely due to the statistical distribution of Mn ions in ZnO which gives an increasing probability to find two Mn ions separated by an O ion as the Mn concentration increases. Therefore, the transition between the low and the

high doped regimes should not be seen as an abrupt transition. The Mn concentration of 5% is the upper range to make the approximation of pure paramagnetic behavior.

To conclude, we have shown by Raman scattering measurement the presence of Mn^{2+} in substitution of Zn^{2+} ions. The insertion of magnetic ions leads to the formation of defects in the host matrix. According to the EPR experiments no indication of ferromagnetism has been evidenced neither in low doped ($x \leq 0.05$) nor in highly doped ($0.05 < x < 0.10$) samples, which is probably due to a lack of free carriers. Instead, a pure paramagnetic behavior was observed for the low doped samples in agreement with the randomly character of the Mn distribution in the ZnO host matrix, as underlined by the observations of the typical EPR spectra of isolated Mn ions.

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