

# Synthesis and Properties of $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ Diluted Magnetic Semiconductor Nanoparticles

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**Abstract**-- $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  diluted magnetic semiconductor (DMS) nanoparticles of crystallite size ranging from 20 to 300 Å and  $x$  from 0 to 0.65 have been chemically synthesized by using aqueous solution precipitation. Subsequent characterization has been carried out by X-ray diffractometry and TEM measurements. Magnetic properties of DMS nanoparticles have been measured with a SQUID magnetometer. A transition from a para-magnetic to a spin-glass state at a critical temperature  $T_f$  has been observed. The applied magnetic field dependence of  $T_f$  has also been measured.

## I. Introduction

The physical properties of systems of reduced dimensionality have been an important and interesting subject for many years.<sup>1,2</sup> For semiconductors, such systems have been realized in quasi-2D systems of quantum wells, quasi-1D systems of quantum wires, and quasi-0D systems of quantum dots (QDs). Because of their unique properties, these nanostructures have great potential for revolutionary applications. The study of nanophase magnetic systems and the concomitant effects of reduced dimensionality have also been an area of recent intensive interest. Both quasi-2D layered magnetics<sup>3,4</sup> and 0D particle<sup>5,6</sup> magnets have shown a variety of phenomena including changes of magnetic coupling, enhanced magnetic moment, enhanced coercivity, and changes in the Curie temperatures. Once again these phenomena are interesting from both a fundamental and applied point of view.

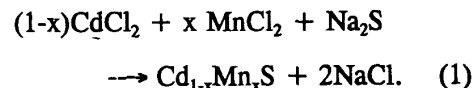
Diluted magnetic semiconductors (DMS) are a group of materials that have attracted a great deal of attention for many years because of their unique and far ranging properties.<sup>7,8</sup> It is well established in DMS that there exists a paramagnetic to a spin-glass (SG) transition at low temperatures because of the randomness of the magnetic ion distribution and spin-spin interactions. The transition temperature or freezing temperature  $T_f$  depends on magnetic ion composition,<sup>9</sup> magnetic field,<sup>10</sup> and the history of the system.

DMS nanoparticles are a unique system that combines both the semiconductor confinement

effects and magnetic finite size effects. Recent work on manganese-doped nanocrystals of ZnS suggests that doped nanocrystals are a new class of materials.<sup>11</sup> We thus expect DMS nanoparticles may also be a new class of materials. In this paper, we report the synthesis as well as subsequent characterization of DMS nanoparticles. The magnetic and spin-glass properties of these DMS nanoparticles are also reported.

## II. Synthesis

DMS nanoparticles of  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  in aqueous solutions were synthesized by reacting a  $\text{Na}_2\text{S}$  with a mixture of  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$  in aqueous solution. Aqueous solutions of 0.25M  $\text{CdCl}_2$ ,  $\text{MnCl}_2$ , and  $\text{Na}_2\text{S}$  were prepared in distilled and de-ionized water, which was deoxygenated with Ar gas. Solutions of  $\text{CdCl}_2$  and  $\text{MnCl}_2$  were then mixed together in compliance with the ratio of Cd:Mn concentration desired, and then the appropriate volume of  $\text{Na}_2\text{S}$  solution was added in accordance with the stoichiometry of the equation



For Mn concentrations of  $x > 0.5$ , low pH solutions, obtained by addition of HCl, were used in order to avoid oxidation. The precipitates obtained were sonicated for 15 minutes to break up large agglomerations of  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  nanoparticles. The precipitates were then washed with deoxygenated water, filtered, and dried in a desiccator in an oxygen purged atmosphere. The average crystallite size obtained was in the range of 20-35 Å. Subsequent annealing under an Ar environment increased particle size which can be controlled by the annealing temperature or the annealing time.

## III. Characterization

DMS nanoparticles have been characterized by TEM and X-ray diffractometry. Fig. 1 is a TEM photograph of the as prepared  $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{S}$  nanoparticles, where we can see that the particle size is in the range of about 30 Å. TEM photographs of  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  nanoparticles annealed at different temperatures and times show clearly that the particle size increases with annealing time and

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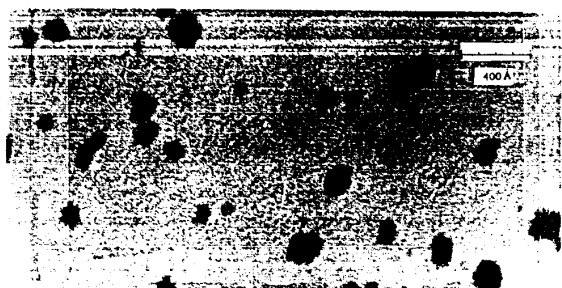


Fig. 1. TEM photograph of as prepared  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  DMS nanoparticles ( $x=0.5$ ).

temperature. Most TEM photographs indicate that nanoparticles form clusters. However, individual particles can be easily distinguished. The particle size indicated by TEM photographs is in general larger than that obtained from X-ray diffraction (XRD) data. This is also expected since XRD measures the crystallite size instead of particle sizes.

Fig. 2 shows the XRD results for  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  nanoparticles with different Mn composition  $x$  with annealing at a temperature of  $500^\circ\text{C}$  for 2.5 hours. Two peaks around  $29^\circ$  and  $37^\circ$  are the (101) and (102) diffraction peaks, respectively. We have also included in Fig. 2 the corresponding diffraction peaks of hexagonal structure bulk CdS and MnS. We see that both (101) and (102) diffraction peaks from the nanoparticles shift toward larger angles with increasing  $x$ . In Table 1, we list the diffraction angles of these two peaks which change from  $28.16^\circ$  and  $36.60^\circ$  to  $28.82^\circ$  and  $37.58^\circ$  for

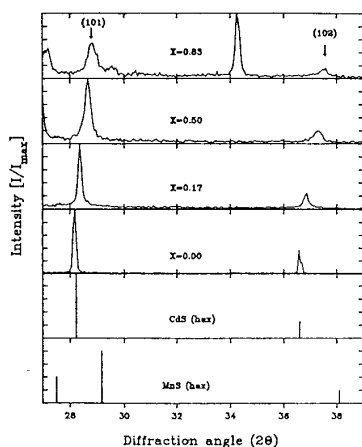


Fig. 2. X-ray diffraction of  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  nanoparticles with different Mn composition  $x$ . Nanoparticles were annealed at  $500^\circ\text{C}$  for about 2.5 hours. Diffraction peaks of hexagonal structure bulk CdS and MnS crystals are also included.

(101) and (102) as the synthesis composition  $x_{\text{syn}}$  increases from 0 to 0.83, respectively. From the data of these two diffraction peaks, with the assumption that the diffraction peak position shifts linearly with composition  $x$ , we have calculated the corresponding values of composition  $x$  which are listed in the third and fourth columns of Table 1. The average compositions,  $x_{\text{ave}}$ , of these two values is shown in column 5 of Table 1. The last column in Table 1 lists the synthesis composition,  $x_{\text{syn}}$ , which is the Mn composition expected from the starting chemical ratio of Mn:Cd. The averaged composition,  $x_{\text{ave}}$ , from XRD data agreed very well with the synthesis composition,  $x_{\text{syn}}$ , up to  $x=0.5$ . For the case of  $x_{\text{syn}}=0.83$ , XRD data indicate that nanoparticles with a Mn composition of 0.65 were formed. This is not surprising since one can only grow bulk  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  alloys with homogeneous phase up to  $x=0.5$ .<sup>7</sup>

Table 1. Diffraction angles of (101) and (102) XRD peaks of as prepared  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  nanoparticles with different synthesis Mn composition  $x$ . Composition  $x$  determined from these two diffraction peaks, the averaged composition  $x_{\text{ave}}$  and the synthesis composition  $x_{\text{syn}}$  as determined from the starting chemical Mn/Cd ratio are all listed.

	$2\theta$ (Diff. Angle)		$x$ (X-Ray)		$x_{\text{ave}}$	$x_{\text{syn}}$
	(101)	(102)	(101)	(102)		
CdS ↓ MnS	28.16	36.60	0.0	0.0	0.0	0.0
	28.36	36.90	0.16	0.20	0.18	0.17
	28.66	37.36	0.50	0.52	0.51	0.50
	28.82	37.58	0.66	0.65	0.66	0.83*

Magnetic properties of  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  nanoparticles have been measured by a SQUID magnetometer (Quantum Design). Fig. 3 shows the zero-field-cooled magnetic susceptibility of as prepared  $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{S}$  nanoparticles and measured at different applied magnetic fields. The experimental procedure is as follows: the sample was cooled from room temperature in absence of an applied magnetic field to the measuring temperature ( $T=5\text{ K}$ ); a magnetic field was then applied and the susceptibility was measured as a function of temperature as temperature rose. In the low magnetic field region ( $H=100\text{ G}$ ), the susceptibility increases monotonically with temperature until reaching a maximum, it then decreases as a result of further increasing of temperature. The behavior shown in Fig. 3 is very similar to that observed in bulk DMS.<sup>7</sup> Temperatures at which the

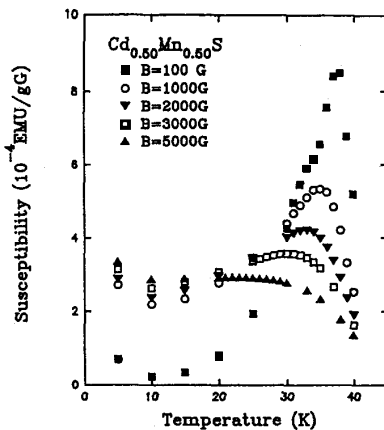


Fig. 3. Zero-field-cooled (ZFC) magnetic susceptibility as a function of temperature of as prepared  $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{S}$  nanoparticles of crystallite size of about 29 Å measured at different magnetic fields.

susceptibility reach a maximum define the spin-glass freezing temperature  $T_f$ . Above (below)  $T_f$ , the system is in a paramagnetic (SG) state. Thus, Fig. 3 indicates that the transition temperature depends on the applied magnetic field.

$T_f$  as a function of applied magnetic field is plotted in Fig. 4. The mean size  $\langle r_0 \rangle$  indicated in Fig. 4 is the mean crystallite size obtained from XRD using the Scherrer formula.<sup>12</sup> It clearly shows that  $T_f$  decreases with an increase of the applied magnetic field, similar to the behavior observed in the bulk. However, the variation in  $T_f$  with the applied magnetic field in DMS nanoparticles is larger than that in bulk materials. Another important observation here is that  $T_f$  in the nanoparticles of mean size 29 Å (38 K at  $H=0$ ) is

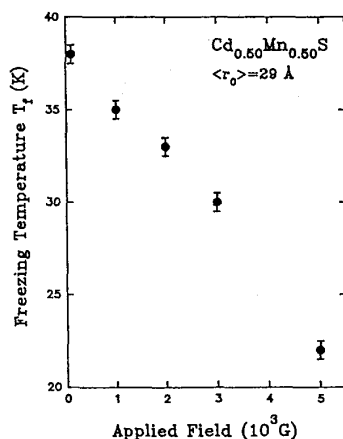


Fig. 4. The applied magnetic field dependence of the spin-glass freezing temperatures  $T_f$  of as prepared  $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{S}$  nanoparticles.

higher than that in the bulk DMS with the same Mn composition (18 K at  $H=0$ ).<sup>7</sup>

Our interpretation of the paramagnetic to SG transition in DMS nanoparticles is also supported by the following two additional observations: a) remanent magnetization below  $T_f$  and b) enhancement of coercivity in nanoparticles from the magnetic hysteresis measurements. The detailed results of these experiments will be published elsewhere. In conclusion,  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  nanoparticles have been synthesized and characterized. Magnetic properties have been studied. A phase transition from a paramagnetic to a SG state has been observed and the applied magnetic field dependence of SG freezing temperature has been measured.

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