

## Quantum-size-effect-enhanced dynamic magnetic interactions among doped spins in $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ nanocrystals

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Dynamic magnetic properties of spins from Mn ions doped in semiconductor nanocrystals ( $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ ) have been studied using an electron paramagnetic resonance method based on two different crystalline sizes and a series of Mn concentrations. By decreasing the size of the quantum dots, the electron spin-nuclear spin interactions are reduced due to enhanced magnetic interactions between Mn ions. A linewidth analysis was also carried out, showing longer spin relaxation times and supporting the enhancement of spin coherence. We suggest that the enhancement of Mn–Mn interactions results from the quantized electrons which have longer coherence length in quantum dots. Quantum size effects may benefit to control and manipulation of spins in a semiconductor nanocrystalline system in which the magnetic ions are incorporated. © 2003 American Institute of Physics. [DOI: 10.1063/1.1619564]

Materials of semiconductors in the states of clusters, nanocrystals (NCs), and quantum dots have been fabricated through either chemical synthetic route or physical deposition methods.<sup>1,2</sup> Such materials may create an avenue to control the physical properties for its applications. Recently, a field has emerged to control and to manipulate spins for applications ranging from semiconductor spin electronics (spintronics) devices to quantum computers.<sup>3</sup> In this territory, carrier spin, spin in introduced magnetic atoms, and nuclear spin of constituent atoms have been demonstrated to have functions by injecting, transporting, and controlling their spin states.<sup>4</sup> In addition to the importance of applications in spintronics, Mn doped CdSe, which plays an important role in optoelectronics as a typical example of diluted magnetic semiconductors (DMS), shows spin-glass, antiferromagnetic, and ferromagnetic behaviors.<sup>5,6</sup>

Quantum confinement effects providing a way to tune optical properties in semiconductor NCs have been extensively studied in literature. At the same time, the effects of quantum confinement on the exchange interactions in carrier spins and in spins from introduced magnetic ions (e.g.,  $\text{Mn}^{2+}$  ions) in DMS systems were also investigated.<sup>7,8</sup> Awschalom *et al.*<sup>9</sup> have reported that changes of magnetic behavior in CdMnTe thin films as a function of the layer thickness variation were observed. They suggested that quantum confinement effects should affect the Mn–Mn interactions (the  $d$ – $d$  exchange) as well. The  $sp$ – $d$  exchange interactions between the doped  $\text{Co}^{2+}$  and CdS semiconductor in the nanocrystalline state were also studied recently by nuclear spin resonance.<sup>10</sup> However, how the size dependence of the quantum confinement effect affects magnetic interactions in electron spins from doped magnetic atoms has not yet been well understood. Since long spin lifetime and sharp electron spin

resonance will be required for quantum computing,<sup>11,12</sup> we have a great interest to examine if it is possible to enhance spin coherence and magnetic interactions by changing the size of the NCs. We therefore prepared  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  nanocrystalline samples in two different sizes with a series variation of Mn concentration, and employed electron paramagnetic resonance (EPR) to study the dynamic magnetic properties of the electron spins from the doped Mn ions in NCs.

A high-temperature organic solution approach,<sup>6,13</sup> which has been applied to prepare Mn-doped PbSe NCs in our previous work,<sup>14</sup> was employed to prepare the  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  NCs. In a typical experiment, 2 mg of  $\text{Mn}_2(\mu\text{-SeMe})_2(\text{CO})_8$ <sup>14</sup> and 0.7 ml of 1 M Se-trioctylphosphine solution were premixed with additional 3 ml of trioctylphosphine in a glove box. The mixed solution was rapidly injected into 20 g of trioctylphosphine oxide (90%) with 0.5 ml of 1 M cadmium(II) acetate in oleic acid at 310 °C under a flow of argon on an Schlenk line. The hot mixture was vigorously agitated at 260 °C for 1 min–1 h to produce different average-sized crystals. The crystalline growth was subsequently terminated by cooling it to room temperature once the dispersion reaches the desired size. Monodispersed  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  NCs in different sizes were finally separated from the multidisperse mixture by a size selective precipitation.<sup>14</sup> The samples with two different crystalline sizes, 5 and 8 nm according to our transmission electron microscopy (TEM) observation carried out on a JEOL 2010, were chosen for the further characterization. In both samples, the size distribution ( $\delta$ ) was less than 7%. In order to remove all the physically adsorbed Mn ions at the surface of NCs, we performed a surface ligand-exchange treatment by immersing samples into pyridine<sup>14</sup> before all the characterizations. A Bruker EPR EMS spectrometer in the X band (9.86 GHz) was used for EPR measurements at room temperature. The EPR instrument was calibrated by

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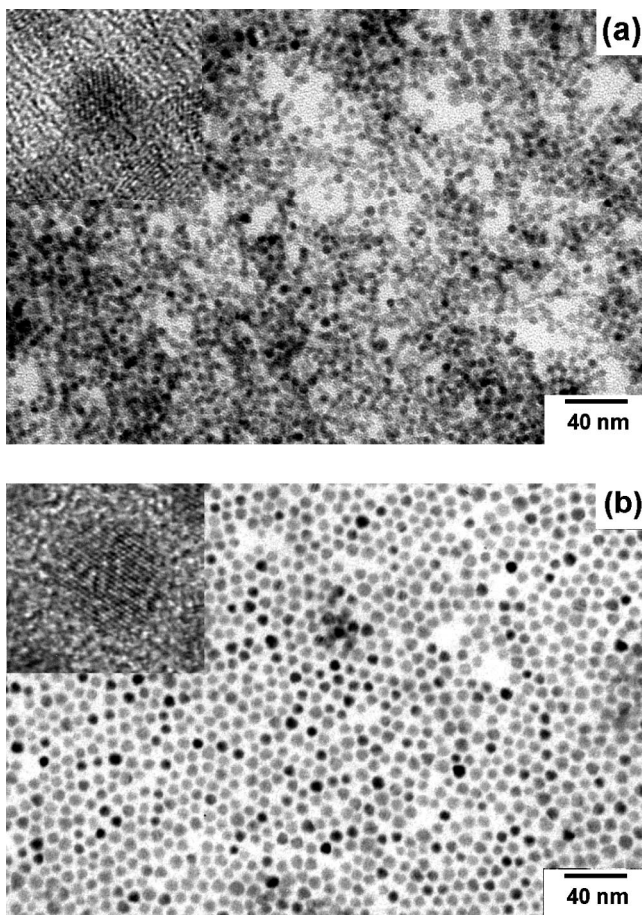


FIG. 1. TEM images of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  nanocrystals with sizes of (a) 5 and (b) 8 nm. Dark gray and light gray spheres indicate the same concentration but different rotation of lattice direction among nanocrystals. Insets: high-resolution TEM images showing nanocrystalline structure.

using a DPPH magnetic field marker with the  $g$ -factor value of  $2.0036 \pm 0.0003$ . The EPR samples for  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  NCs were prepared either using dry powders or toluene suspension, both of which give consistent results.

The size and structure of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  DMS NCs were characterized by TEM (see Fig. 1). The NCs appear spherical in shape and crystalline in lattice structure (see the insets in Fig. 1) even after the substitution of  $\text{Cd}^{2+}$  cations by magnetic  $\text{Mn}^{2+}$  ions. From the TEM analysis, the sizes of these NCs are calculated to be 5 and 8 nm in Figs. 1(a) and 1(b), respectively. We found that the crystalline size does not vary with the Mn concentration. The random orientation of lattice directions among NCs in Fig. 1 can be observed obviously through the contrast of different gray scale in NCs since a change of lattice direction results in different scattering intensity of the electron beam.

Figure 2 shows normalized EPR spectra. The spectra were fitted with a Lorentzian function and then normalized by itself assuming the same peak to peak intensity. The  $\text{Mn}^{2+}$  electron spin Hamiltonian,  $H$ , in the CdSe NCs is given by<sup>15</sup>

$$H = g \mu_B \mathbf{H} \cdot \mathbf{S} + A \mathbf{I} \cdot \mathbf{S}, \quad (1)$$

where  $\mu_B$  is the Bohr magneton,  $\mathbf{H}$  is applied magnetic field,  $\mathbf{S}$  is electron spin angular momentum,  $\mathbf{I}$  is nuclear spin angular momentum, and  $A$  is the hyperfine constant. Since the

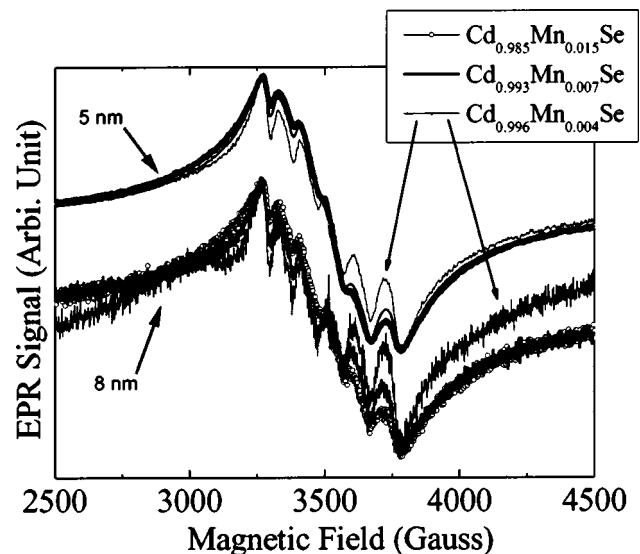


FIG. 2. EPR spectra recorded at 9.86 GHz and at room temperature for  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  nanocrystals with sizes of 5 and 8 nm. Hyperfine structures can be observed for all samples with Mn concentration lower than 1.5 at. %.

skin depth of CdSe semiconductors is in the range of submillimeter,<sup>16,17</sup> which is much greater than the size of our NCs, and the NCs are randomly oriented with its lattice direction, we observed only the mainly symmetrical line shape from the electron spin-spin ( $1/2 \rightarrow -1/2$ ) interactions (Lorentzian distribution). The EPR spectra are grouped based on the size of NCs, and exhibit a systematic result with an increase of Mn dopants inside the NCs. In addition to the main line shape, we have also observed hyperfine splitting which displays six sharp lines between 3200 and 3800 G. The six-line pattern is from the  $^{55}\text{Mn}$  nucleus ( $I=5/2$ ) and corresponds to the transition of  $\Delta m_S = \pm 1$  and  $\Delta m_I = 0$ , where  $m_S$  and  $m_I$  are electron spin and nuclear spin quantum numbers, respectively. The  $g$  factors obtained from the EPR measurements are  $2.0084 \pm 0.0010$  and  $2.0123 \pm 0.0005$  for the sizes of 5 and 8 nm, respectively. We noted that for the

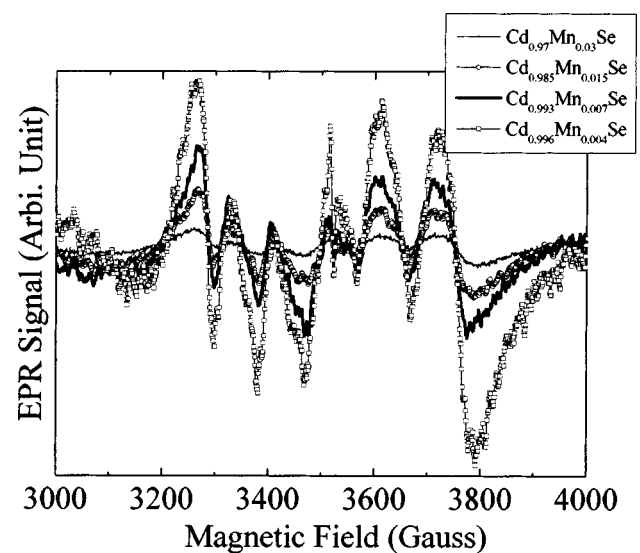


FIG. 3. Electron spin-nuclear spin interactions after normalization and a subtraction of spin-spin interactions from EPR spectra for  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  nanocrystals with a size of 8 nm. Even the lowest signals of hyperfine structures for the  $\text{Cd}_{0.97}\text{Mn}_{0.03}\text{Se}$  nanocrystals can be clearly observed.

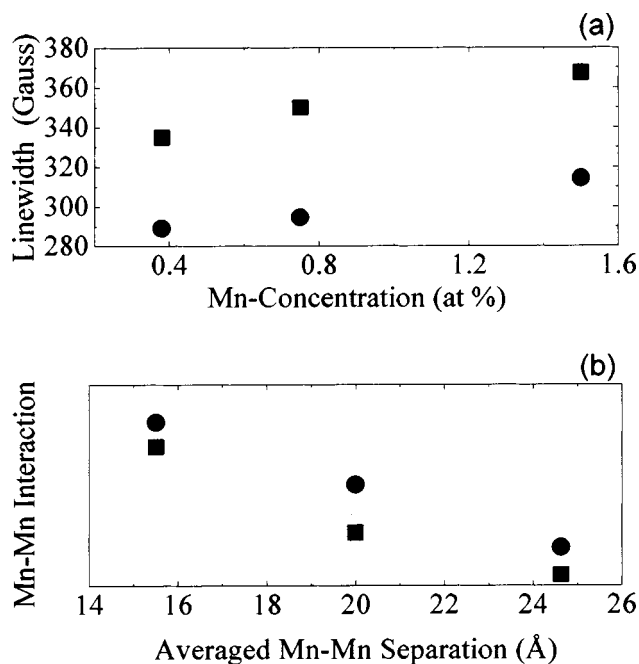


FIG. 4. (a) A linewidth analysis of EPR spectra for the two sizes (filled spheres and squares representing the sizes of 5 and 8 nm, respectively) of nanocrystals with a serious variation of Mn concentration. For the same concentration of Mn ions, the linewidth is broader in large-size nanocrystals than that in small-size ones. (b) The Mn–Mn interactions estimated from the inverse of peak to peak intensities of hyperfine splittings from Fig. 3. The Mn–Mn interaction in small-size nanocrystals is enhanced.

small size NCs (5 nm) the  $g$  factor is a little bit smaller than that for the large size NCs (8 nm). The hyperfine splitting is 9.06 mT and the hyperfine constant  $A$  is  $85 \times 10^{-4} \text{ cm}^{-1}$  for all the samples regardless of their size and Mn concentration.

In order to study the hyperfine structures, we subtracted the fitted and normalized Lorentzian curve (electron spin–spin interactions) from the EPR spectra. Since the main line shape of EPR spectra in Fig. 2 does not make a lot of difference, we assume that the spin–spin interaction is the same and quantify the hyperfine interactions from their peak to peak intensity as shown in Fig. 3. The quantitative result of electron spin–nuclear spin interactions can then be extracted. The electron spin–nuclear spin interactions do decrease gradually until vanishing with increasing Mn concentration. The Mn–Mn interactions, which inversely relate to hyperfine interactions, become stronger as more and more Mn ions are introduced into CdSe NC(s). The hyperfine structures are depicted much more obviously in Fig. 3, in which five peak to peak breadths of hyperfine splittings are 6.3, 8.5, 9.5, 10, and 11 mT with an average value of 9.06 mT.

Since the EPR linewidth is a measure of the transverse relaxation rate (inversely dependent on dephasing time  $T_2$ ) for spin fluctuations perpendicular to the field,<sup>18</sup> as illustrated in Fig. 4(a) we obtained the linewidth versus Mn concentra-

tion in NCs of two sizes by fitting the EPR spectra. The fitting range excludes the field between 3200 and 3800 G in order to reduce the effects coming from hyperfine interactions. The linewidth analysis displays a broadening effect with increasing Mn concentration. The broadening effect is due to dipolar broadening and exchange narrowing as reported in the literature. In addition, we have observed the narrowing effects when the size of the NCs was decreased. The narrowing effects correspond to longer dephasing time ( $T_2$ ). As a result, the quantum size effects enhance the phase coherence of the electron spins from doped ions in the NCs. In Fig. 4(b), we demonstrated the Mn–Mn interaction versus an averaged Mn–Mn separation. The Mn–Mn interaction was obtained from inverse intensities of hyperfine structures and the averaged Mn–Mn separation was estimated from the Mn concentration in NCs. The size-effect-enhanced Mn–Mn interactions can be observed clearly.

In summary, from EPR results we have observed that the size-effect-enhanced dynamic magnetic interactions in electron spins from the  $\text{Mn}^{2+}$  ions, which were doped in the CdSe NCs. The Mn–Mn interaction is enhanced and the transverse relaxation time ( $T_2$ ) is increased due to quantum confinement effects. The quantized electrons enhance spin phase coherence and Mn–Mn interactions in the nanocrystalline quantum dots. Electron spins from doped magnetic ions in NCs may provide long spin lifetime and may benefit the application in quantum computing.

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