Magnetic Properties of Nanocrystalline $Pb_{1-x}Mn_xSe$

Tianhao Ji, Wen-Bin Jian, Jiye Fang, Jinke Tang, Volodymyr Golub, and Leonard Spinu

***Abstract*—Mn-doped diluted magnetic semiconductors are important semiconductor materials and have received much attention due to their application in magnetooptics, spintronics, displays, and lasers. The authors present the magnetic properties of Mn-doped PbSe nanocrystals (NCs) based on electron paramagnetic resonance and superconducting quantum interference device measurements, demonstrating that the electron spin-nuclear spin interactions, hyperfine interactions, in NCs are enhanced due to the quantum confinement effects.**

***Index Terms*—Diluted magnetic semiconductors, magnetic properties, nanocrystals, spin.**

I. Introduction

DILUTED magnetic semiconductors (DMS) are semiconductor materials in which a fraction of sublattice (usually made of metal cations) are replaced by other metal ions having magnetic moment [1]. These materials exhibit a wide range of magnetic properties including paramagnetic, spin glass, or ferri/ferro-magnetic behavior [2]. Our motivation is to transfer these interesting materials into nanophase, as their forming into nanocrystals may have more exotic behavior due to exchange interactions, which will be enhanced by the confinement of electrons and holes [3]. Another objective of this research is that DMS nanocrystals can be used to study and to manipulate a small number of spins that are trapped in semiconductor quantum dots. In addition, such materials can also provide a useful model system for spintronics.

In this paper, based on the recent success in synthesis and self-assembly of PbSe nanocrystals [4], Mn-doped PbSe nanocrystals (NCs) were prepared and investigated for the first time by using electron paramagnetic resonance (EPR) and superconducting quantum interference device (SQUID) magnetometer.

II. Experiment

A. Materials

The starting materials in this investigation include Lead (II) 2-ethylhexanoate (Alfa Aesar), selenium (Aldrich, 99.99+%), oleic acid (Aldrich, 90%), pentacarbonylmanganese bromide (Alfa Aesar), methyllithium in diethyl ether (1.6M, Aldrich), trioctylphosphine (TOP) (Aldrich, 90%), and trioctylphosphine oxide (TOPO) (Aldrich, 90%). The precursor of $Mn_2(\mu\text{-SeMe})_2(CO)_8$ was prepared according to the experimental procedure in Mikulec's paper [5]. TOP-Se (1 M) was preprepared by adapting Murray's method [6].

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B. Preparation Procedures

A high-temperature organic solution approach was employed to prepare Mn-doped PbSe NCs. In a typical experiment, organometallic precursors including 2 mg of $Mn_2(\mu\text{-SeMe})_2(CO)_8$, 0.5 ml of 1 M lead (II) 2-ethylhexanoate in TOP and 0.7 ml of 1 M Se-TOP solution were premixed with an additional 3 ml of TOP. Under a stream of argon on an Schlenk line, 20 g of TOPO with 0.5 ml of oleic acid was heated to 260 °C and the above mixed solution was then rapidly injected into this TOPO hot solution. The reaction mixture was agitated for 30 s at 260 °C and the growth of NCs was subsequently terminated by cooling down the system to room temperature. Mn-doped PbSe NCs were separated from solution by size selective precipitation using methanol and toluene. Surface ligand exchange with pyridine was also performed as described in [7].

C. Method of Characterization

Transmission electron microscopy (TEM) was conducted on JEOL 2010. The TEM sample was prepared by dropping the suspension of Mn-doped PbSe NCs in toluene on a copper grid. Room temperature (9.87 GHz) EPR spectra were recorded using a Bruker ER041XG. Before the EPR measurement, the capping-ligand on $Pb_{1-x}Mn_xSe$ NCs was exchanged by immersing the sample into pyridine for three days to remove physically absorbed Mn^{2+} ions on the surface of these nanocrystals. Direct magnetization measurement on powders of nanocrystalline samples was carried out in the temperature range of 5–300 K by using a SQUID magnetometer at a magnetic field of 1 T.

III. Results and Discussion

Fig. 1 shows a typical TEM image of the as-prepared Mn-doped sample, $Pb_{0.953}Mn_{0.047}Se$ NCs, demonstrating a close-packed pattern of the NCs in short range. The percentage of Mn ions in this image was determined as 4.7 mol% by using energy-dispersive X-ray spectroscopy (EDS) combined with a scanning electron microscope. We note that a majority of spherical particles are observed here; whereas, the numbers of cubic NCs decrease with a reduction of Mn^{2+} concentration in $Pb_{1-x}Mn_xSe$ NCs. Based on the TEM image, it was calculated that the standard deviation of crystalline size is less than 8%, and the mean size of the crystallites is about 10.5 nm in diameter. This result is in agreement with the size estimated from XRD pattern.

EPR spectra of different Mn^{2+} concentration in $Pb_{1-x}Mn_xSe$ NCs are shown in Fig. 2. The broad curve and six split peaks between 3250 and 3750 G come from the electron's spin interactions between Mn^{2+} ions. The broad curve is due to electron's spin–spin interactions ($1/2 \rightarrow -1/2$) of substituted Mn^{2+} ions

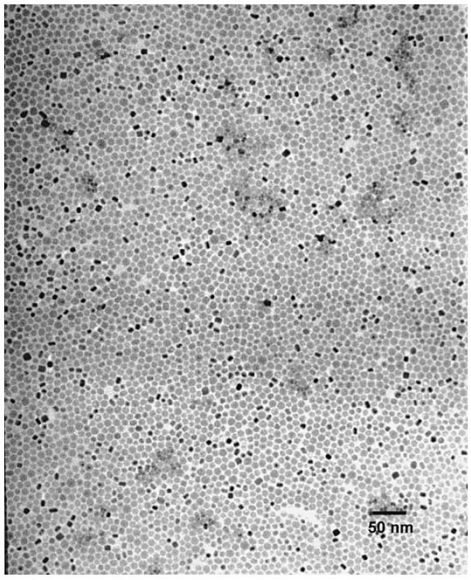

Fig. 1. TEM micrograph of the sample $Pb_{0.953}Mn_{0.047}Se$ NCs. Standard deviation of crystalline size was calculated as $\delta \leq 8\%$.

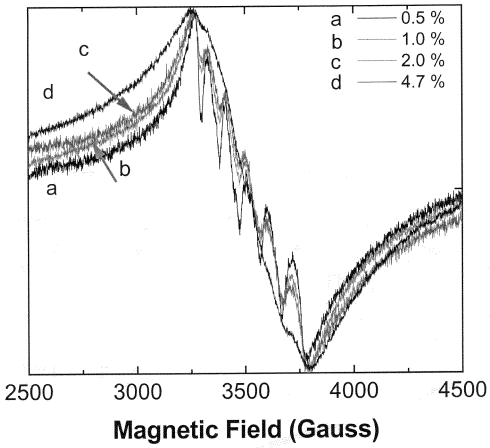

Fig. 2. EPR spectra of pyridine-washed $Pb_{1-x}Mn_xSe$ NCs (10.5 nm), measured at room temperature. Curve a: $x = 0.005$; curve b: $x = 0.010$; curve c: $x = 0.020$; and curve d: $x = 0.047$.

in $Pb_{1-x}Mn_xSe$ NCs, whereas the six sharp splitting lines (hyperfine splittings) are due to electron spin-nucleus spin interactions. Because of $I = 5/2$ for nuclear spin of Mn, spin-nucleus interactions of Mn^{2+} ions lead to the six splitting peaks. The hyperfine constant of the Mn-doped nanocrystals was reported as 83×10^{-4} cm^{-1} for Mn-CdSe system [5] and as 65×10^{-4} cm^{-1} and 83×10^{-4} cm^{-1} (two separate signals) for Mn-ZnS system [8], respectively. In our EPR measurement, the hyperfine constant in $Pb_{1-x}Mn_x$ Se NC's system was, for the fist time, determined as 86×10^{-4} cm^{-1} for all the samples. It is much larger than the hyperfine constant of Mn^{2+} in bulk crystalline PbSe (67.6×10^{-4} cm^{-1} [9]). We present an intriguing effect that the hyperfine constant is enhanced in quantum-confined nanocrystals, as electrons confined in nanocrystals promote the enhancement of electron spin-nuclear spin interactions between Mn^{2+} ions. At the same time, we obtained a significant dependence of electron-nucleus interaction on the ratio of the Mn^{2+} ions inside the NCs. When increasing the Mn^{2+} concentration from $x = 0.5\%$ to $x = 4.7\%$ by doping more paramagnetic Mn^{2+} ions into a nanocrystallite, we find that the signal of hyperfine splitting decays rapidly and finally vanishes at $x = 4.7\%$ (see Fig. 2), indicating a change of the environment and site of Mn^{2+} ions in PbSe lattice and the enhancement of exchange interaction intra-NCs.

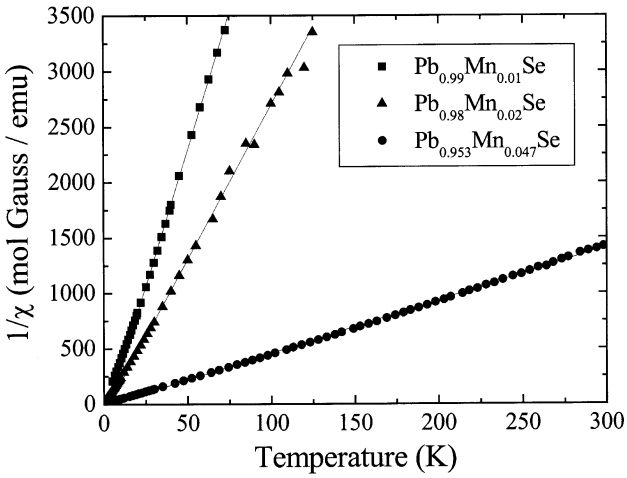

Fig. 3. Inverse susceptibility of $Pb_{1-x}Mn_xSe$ NCs measured by SQUID at a field of 10 000 Gauss displaying linear dependence on temperature. Slope of each line is inversely relative to Mn^{2+} concentration.

Analysis of the magnetic data measured by SQUID indicates that all the doped nanocrystals are paramagnetic materials, which is clearly different from the pure bulk PbSe, a diamagnetic material. We also prepared PbSe NCs and our measurement demonstrates that PbSe NCs are diamagnetic as well. The magnetic susceptibility χ (T) can be represented by the Curie–Weiss law

$$\chi(T) = [xN_A g^2 s(s+1)\mu_B^2]/[3k_B(T - \theta_s)] \qquad (1)$$

where x is the fitted result of Mn^{2+} concentration, g is the spin-splitting g factor, s is electron spin of magnetic ion ($s = 5/2$), μ_B is the Bohr magneton, N_A is Avogadro's number, θ_s is Curie temperature, and k_B is the Boltzmann constant. As illustrated in Fig. 3, a plot of $1/\chi$ versus temperature (T) reveals the Curie–Weiss linear behavior. The lines are fitted within a temperature range of 20 K–300 K. We can estimate the Mn^{2+} concentration and Curie temperature from linear least square fits. For instance, the fitted concentration of our $Pb_{0.953}Mn_{0.047}Se$ sample is 0.0481 and the fitted Curie temperature is 4.36 K.

IV. Conclusion

By employing a high-temperature organic solution approach, we have successfully synthesized nanocrystalline $Pb_{1-x}Mn_xSe$. The magnetic properties of these novel DMS NCs have been, for the first time, characterized using EPR and SQUID. The hyperfine constant estimated from EPR results implies that the electron spin-nuclear spin interactions are enhanced in DMS NCs. These phenomena are different from those in the bulk phase. Furthermore, the enhancement of exchange interactions intrananocrystals is greatly dependent on the amount and the site of the Mn dopants in $Pb_{1-x}Mn_xSe$ NCs.

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