Structure and Spin-Glass Properties of $Cd_{0.5}Mn_{0.5}S$ Diluted Magnetic Semiconductor Quantum Dots

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Abstract - $Cd_{0.5}Mn_{0.5}S$ diluted magnetic semiconductor (DMS) quantum dots (QDs) of crystallite size ranging from 24 Å to the bulk have been chemically synthesized using an aqueous solution precipitation method and thermal annealing. Subsequent characterization indicates that the "as prepared" material is of the cubic zinc blende structure which evolves with increasing size to the bulk hexagonal wurtzite structure. Magnetic properties of the DMS QDs have been measured with a SQUID magnetometer. A transition from a paramagnetic to a spin-glass (SG) state at a critical temperature T_f has been observed. Size dependence measurements on T_f indicate a minimum size for SG formation. Relaxation in isothermal remanent magnetization has also been measured and shows a power law decay.

I. Introduction

The physical properties of nanostructured materials including semiconductor quantum dots (QDs) have been an important and interesting subject for many years. For semiconductors, dramatic changes in their optical properties are expected when the dimension of the semiconductor approaches the corresponding Bohr radius of excitons [1,2] (bound state of the electron-hole pairs) which sets the natural length scale for all optical processes. These QDs have potential applications in non-linear optics, fast optical switching devices, and memory devices. In the area of magnetics, the study of nanophase magnetic systems and the concomitant effects of reduced dimensionality have generated tremendous interest. Both quasi-2D layered magnetics [3,4] and 0D particle [5] magnets have shown a variety of phenomena including changes of magnetic coupling, enhanced magnetic moment, enhanced coercivity, and changes in the Curie temperatures. These phenomena are interesting both in terms of theory and applications.

Diluted magnetic semiconductors (DMS), also known as semimagnetic semiconductors have been studied for many years because of their uniqueproperties which promise many potential applications. However, three dimensional confined systems, i.e. nanoparticles or QDs, of diluted magnetic semiconductors (DMS) have not been studied extensively. In such systems the physical properties are expected to be different from their bulk materials due to the effects of quantum confinement on their semiconductor properties, and reduced size on their magnetic properties. In this paper we address the effects of size on the properties of $Cd_{0.5}Mn_{0.5}S$ DMS QDs.

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II. Experimental Techniques

The $Cd_{0.5}Mn_{0.5}S$ DMS QDs used in this study were prepared from a combination of aqueous solution precipitation and scintering. The "as prepared" QDs were characterized using X-ray diffractometry (XRD) and the Scherrer formula [6] to have a size of 24 Å. With subsequent thermal annealing under an Ar atmosphere these sizes were increased and could be controlled. This is shown in Table I where the mean crystallite size is listed along with the corresponding annealing temperature for a few temperatures.

Table I. Mean crystal size of $Cd_{0.5}Mn_{0.5}S$ QDs under different annealing temperatures.

Annealing Temp (°C)	Crystal Size (Å)
24	24
200	24
300	74
400	160
450	350
500	500
550	610

Characterization of the QDs were carried out using XRD, transmission electron microscopy (TEM), Raman spectroscopy, and chemical analysis. The Mn composition was determined at three different stages of the synthesis: from the starting materials,

the "as prepared" samples, and the annealed samples, using three different techniques. The measured composition agreed very well in all three methods with the nominal concentration [7].

The magnetic properties were measured using a SQUID magnetometer. Since the materials under investigation were in powder form, they were placed in gelcaps and inserted into the SQUID for measurements. In all measurements the amount of sample used was kept constant at a mass of 10 mg with $\pm$ 1% uncertainty in its mass.

III. Experimental Results

An interesting feature observed in the X-Ray analysis of the $Cd_{0.5}Mn_{0.5}S$ QDs was that, apart from the change in size with increasing annealing temperature, it also changed in structure. The samples prior to any thermal annealing were of the cubic, zinc blende crystalline structure [8]. With subsequent thermal annealing this structure evolved to the bulk hexagonal, wurtzite structure [9]. This change has been previously observed to occur in a temperature region around 300°C for CdS thin films prepared by chemical bath deposition (CBD) [10]. Our data corroborates this result for the $Cd_{0.5}Mn_{0.5}S$ DMS QDs. Fig. 1 shows XRD spectra for $Cd_{0.5}Mn_{0.5}S$ taken at five different annealing temperatures which are plotted along with the corresponding JCPDS (Joint Committee on Powder Diffraction Standards) spectra for the zinc blende (····) and wurtzite (————) structures of CdS and MnS. A single peak in the angular range between 20^0 and 30^0 for the "as prepared" QDs canthe be seen evolving into a three peak pattern with increasing annealing temperature, indicating a change in the crystalline structure from a cubic to the bulk hexagonal structure for increasing QD size. The structure phase transition can be estimated occurring at a temperature between 200 and 300 °C.

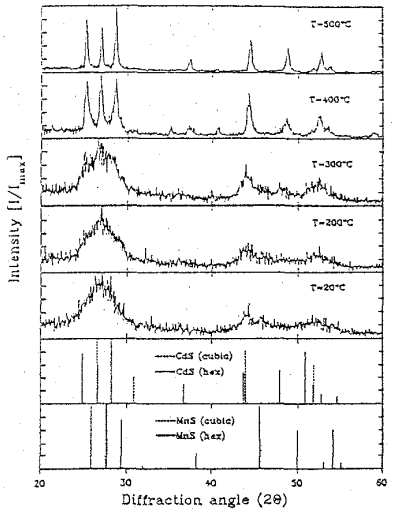

Fig. 1. X-Ray diffraction spectra for $Cd_{0.5}Mn_{0.5}S$ QDs taken for five different annealing temperatures. Diffraction peaks for both zinc blende and wurtzite structures of CdS and MnS, respectively, obtained from JCPDS data base are also shown.

Zero field cooled (ZFC) magnetization measurements of the QDs indicated a transition from a paramagnetic to a spin-glass (SG) state at a transition temperature T_f. The dependence of this transition temperature T_f on the QD size was systematically investigated for $Cd_{0.5}Mn_{0.5}S$ DMS QDs and is shown in Fig. 2, where susceptibility vs. temperature is plotted for four representative sizes. The transition temperature T_f is determined from the position of the cusp in these plots which occur between 14 and 18 K. Here we see that T_f increases with particle size until it reaches a maximum at the bulk DMS T_f value [11].

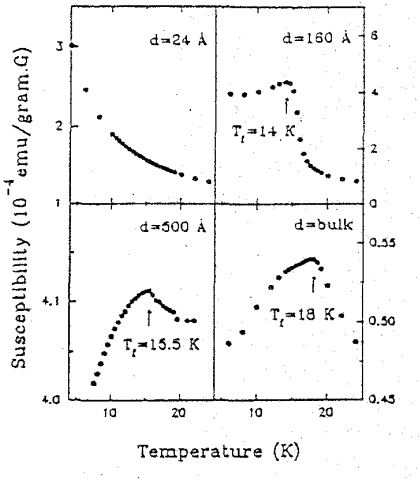

Fig. 2. Susceptibility of $Cd_{0.5}Mn_{0.5}S$ QDs of different size. Data were taken under ZFC with a field of 100 G applied after cooling. The transition temperature T_f is determined from the position of the cusp in these plots.

An important observation obtained from the size dependence measurements was that in small QDs (d < 30 Å) no SG transition is observed. This can be seen clearly in the first quadrant of Fig. 2. A possible explanation for this behavior is that there may be a critical size for SG formation in DMS.

This can be understood by a SG empirical picture for DMS [12].

One of the characteristic features of a SG system is the presence of a time and history dependent remanent magnetization below the critical temperature T_f [13]. The results presented in Fig. 3 show the relaxation of isothermal remanent magnetization (IRM) for $Cd_{0.5}Mn_{0.5}S$ QDs of size 74 Å. The IRM relaxations were measured as a function of temperature with the sample cooled under ZFC from 300 K to the measuring temperature. An external field of 5 kG was applied at this temperature for a period of 300 sec before being turned off and the magnetization measured as a function of time.

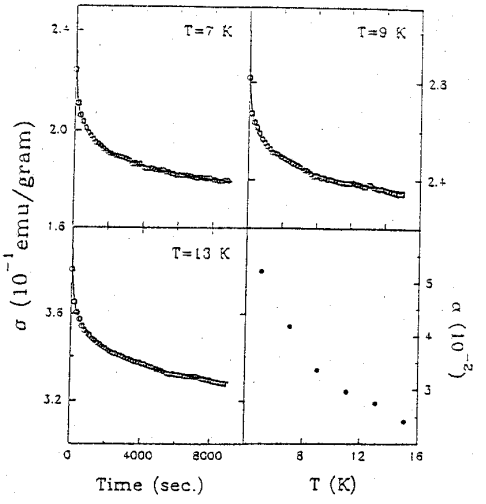

Fig. 3. Temperature dependence of the IRM relaxation in $Cd_{0.5}Mn_{0.5}S$ QDs of size d=74 Å. The samples were cooled under ZFC to the desired temperature, and an external field of 5 kG applied for 300 sec. A small measuring field of 10 G was used during data collection. The solid lines are the least squares fits using a power law decay $M(t)=M_o t^{-\alpha}$. The decay parameter α is plotted as a function of temperature in the fourth quadrant.

The measurements indicate a power law decay $M(t)=M_o t^{-\alpha}$, which is typical for SG relaxation [14]. The decay exponent α was found to decrease with increasing temperature. Similar observations were made for the corresponding bulk material. The decay exponent α for the QDs when compared with the bulk material was almost one order of magnitude smaller [11]. However, the initial magnetization M_o for the QDs was about two orders of magnitude larger than in the bulk.

IV. Conclusions

In conclusion $Cd_{0.5}Mn_{0.5}S$ DMS QDs have been synthesized using an aqueous solution precipitation method. The "as prepared" QDs were found to have a cubic structure which evolved to the bulk hexagonal structure with increasing annealing temperature (QD size). A magnetic phase transition from a paramagnetic to a SG state was observed. QD's size dependence on the critical temperature T_f indicates a minimum size for SG formation. IRM relaxations indicate a power law decay with the decay exponent α decreasing with increasing temperature.

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