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Magnetic and magneto-optical properties of CdS:Mn quantum dots in PVA matrix

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Abstract. We have studied the magnetic and magneto-optical properties of CdS:Mn quantum dots in polyvinyl alcohol matrix synthesized by co-precipitation method. The size of quantum dots was estimated by means of absorption spectroscopy. The results of measurements of magnetic susceptibility as a function of temperature and spectral dependence of the Faraday rotation of CdS:Mn quantum dots / polyvinyl alcohol composites are presented. In this work magnetic susceptibility was investigated by Faraday's method at the temperatures of (78-300) K in magnetic fields of (0.05-0.8) T. The inverse magnetic susceptibility as a function of temperature follows a Curie Weiss law. Formation of ferromagnetic coupling between magnetic ions is supposed. Magneto-optical Faraday rotation has been investigated in the wavelength region (400-700) nm at temperature 300 K in a magnetic field up to 5 T. Sign of the Verdet constant is found to be negative.

1. Introduction

At present many studies in the field of nanotechnology are dedicated to search of bottom-up approaches for the preparation of device structures analogous to those grown by molecular beam epitaxy or related vacuum deposition techniques. The preparation and characterization of polymer/inorganic nanoparticles composites have received increasing attention in recent years because materials in the nanometer scale have provided not only new physics in reduced dimensions, but also the possibility of fabricating novel materials. Recently the attention to inorganic nanoparticles has shifted toward doping of colloidal semiconductor quantum dots (QD) by direct chemical methods because of the vast untapped potential to control their physical properties through the introduction of impurities. Diluted magnetic semiconductor (DMS) nanostructures are the basic working components of many existing and proposed devices in the emerging field of semiconductor spin-based electronics. These materials attract an increasing interest because of unusual combination of optical, magnetic and semiconducting properties. Magnetic and magneto-optical properties of DMS materials are governed by the exchange interactions between the local magnetic moments introduced by magnetic ions and band carriers, or so called s p- d exchange interactions [1-3].

In this work, to probe s p-d exchange interaction static magnetic susceptibility and Faraday rotation (FR) measurements have been carried out. The CdS:Mn quantum dots / polyvinyl alcohol (PVA) nanocomposites were synthesized by wet chemical method. The size of QD was estimated by means of absorption spectroscopy. The temperature dependences of the static magnetic susceptibility and spectral dependence of FR angle are presented. The results are analyzed from the viewpoint of contribution of Mn^{2+} ions into the observed properties.

2. Experimental

2.1. Synthesis

A CdS:Mn quantum dots / PVA composite films have been prepared by means of in situ synthesis method via the reaction of Cd^{2+}, Mn^{2+} - dispersed PVA with sodium sulfide at room temperature. The concentrations of salt solutions of $CdCl_2$, $MnCl_2$, Na_2S and the pH value were selected to optimize the QD yield, i.e. the molar concentrations of precursors and the pH value were within the range of (10^{-4} – 10^{-2}) mol/l and (3-6), respectively. The films of the CdS:Mn quantum dots / PVA composite were formed by adsorptive desiccation method.

2.2. Optical, magnetic and magneto-optical measurements

Measurements of the optical absorption spectra have served for revealing of quantum-size effect and estimation of the average size of CdS:Mn quantum dots.

Static magnetic susceptibility of CdS:Mn quantum dots / PVA composite films was measured by Faraday's method. The experiment was made at the temperature range of (78 – 300) K in magnetic fields (0,05 – 0,8) T. The force on a sample in an inhomogeneous magnetic field was measured with an electronic balance device (resolution of the order of 10^{-3} milligram) at which the sample is suspended. The measurements were calibrated using a NaCl crystal standard. The measurements of external magnetic fields applied to a sample done by a Hall probe. The chamber was firstly degazed to 10^{-3} Pa and then filled in with helium of high purity up to $1{,}3\cdot10^{3}$ Pa. Cooling of samples is accomplished by a regulated flow of nitrogen gas. The temperature is measured with copper-constantan thermocouples placed close to the sample. The temperature was changed in steps of 10 to 15 degrees and with an isothermal exposition during 5-10 min at each temperature.

Magneto-optical Faraday rotation was measured at wavelength of (400-700) nm in magnetic field up to 5 T. These experiments were performed at room temperatures. The FR was studied with a measuring setup which included diffraction monochromator, Roshon prisms, and water-cooled electromagnet.

3. Results and discussion

Figure 1 shows the optical density spectra of CdS:Mn quantum dots / PVA composites. The position of exciton peaks remained almost unchanged at 2.75 eV regardless of the precursors concentrations in the range $5\cdot10^{-4}$ – $5\cdot10^{-2}$ mol/l, therefore the size of the CdS:Mn quantum dots was also invariable. The average size of QD was calculated [4,5] to be 18 nm in diameter. However, slight increase of the amplitude of exciton peak with an increase of the amount of Na_2S precursor can be attributed to increase of the concentration of QD.

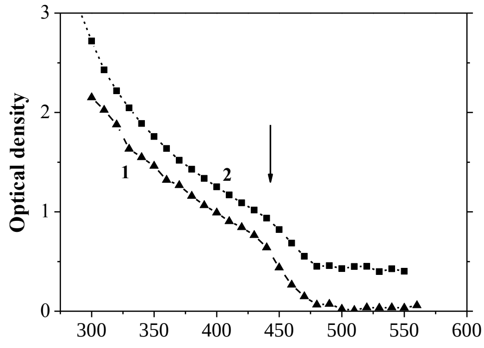

Figure 1. Optical density as a function of wavelength for CdS:Mn quantum dots / PVA composites at $[MnCl_2]$:$[CdCl_2]$ ratio is 1:9. Curves 1 and 2 correspond to $[CdCl_2]$:$[Na_2S]$ is 9:1 and $[CdCl_2]/[Na_2S]$ is 4:1, respectively.

3.1. Magnetic properties

In II-VI compounds Mn ions are divalent and assume the high spin d^5 configuration characterized by S = 5/2 and g = 2. The Mn ions neither introduce nor bind carriers, but give rise to the presence of the localized spin in II-VI based DMS. The spin dependent hybridization between anion p and Mn d states leads to the superexchange a short-range antiferromagnetic coupling among the Mn moments. However, the antiferromagnetic superexchange can be overcompensated by ferromagnetic interactions mediated by band holes [6].

The temperature dependence of the magnetic susceptibility is shown in Figure 2. The plot clearly shows a paramagnetic system with a temperature dependent susceptibility. Undoped CdS quantum dots /PVA composites show diamagnetic properties, which can be seen from the Figure 2.

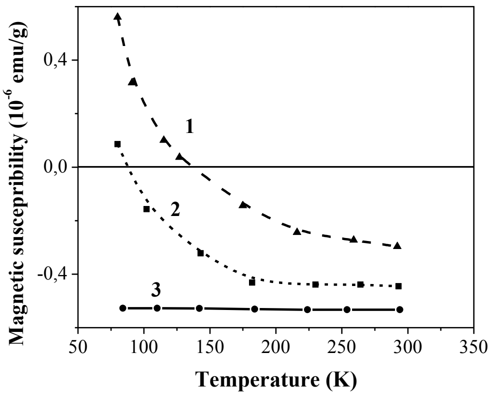

Figure 2. Temperature dependence of magnetic susceptibility of the composites. Curves 1 and 2 correspond to the samples mentioned in Figure 1, curve 3 correspont to CdS quantum dots/PVA composite.

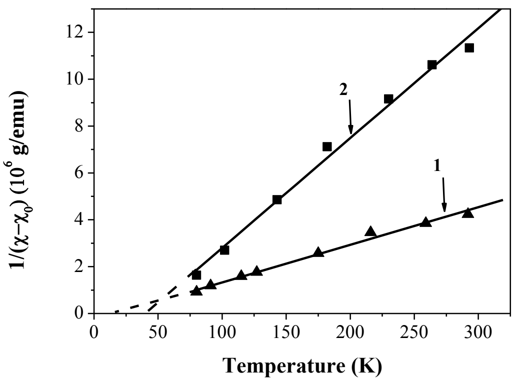

Figure 3. Inverse susceptibility as a function of temperature plotted on the base of data from Figure 2.

In the temperature interval of (75-300) K magnetic susceptibility for both samples decreases following Curie-Weiss law. The inverse susceptibility is plotted as a function of temperature in Figure 3. From the linearity of this graph it is apparent that CdS:Mn quantum dots are paramagnetic materials above 78 K. The result is consistent with the Curie–Weiss equation

$$\chi = \chi_0 + \frac{C}{T - \theta} \quad , \qquad (1)$$

where C is Curie constant, Θ is paramagnetic Curie temperature and χ_0 is the temperature-independent susceptibility (diamagnetic contribution).

Analysis of experimental data was performed by a liner Curie-Weiss model. The Curie constants were obtained from the slopes of the lines and the effective Curie–Weiss temperatures by extrapolation to the temperature axis. From this fit the temperature axis intercept is found to be +17,6 K and +40,3 K for 1 and 2 samples, respectively. This indicates the ferromagnetic interactions between Mn magnetic moments in these composites below Curie–Weiss temperatures.

The features observed in the magnetic measurements of two samples are very similar, for exception of the ferromagnetic coupling between Mn^{2+} ions, which is stronger in sample 2 likely due to the fact that the Mn-Mn distance is shorter in sample 1. The increase of the ferromagnetic coupling value between Mn^{2+}ions was accompanied with an increase of the CdS phase amount. The more the amount of the phase the stronger an interaction. We admitted that these changes are caused by the embedded Mn^{2+}ions into CdS QD, because the QD size to a great extent exceeds the distance between magnetic ions which influences on a type of interaction.

3.2. Magneto-optical properties
Figure 4 shows the spectral dependence of the Faraday rotation angle of the nanocomposites after subtraction of the rotation angle of the PVA matrix.

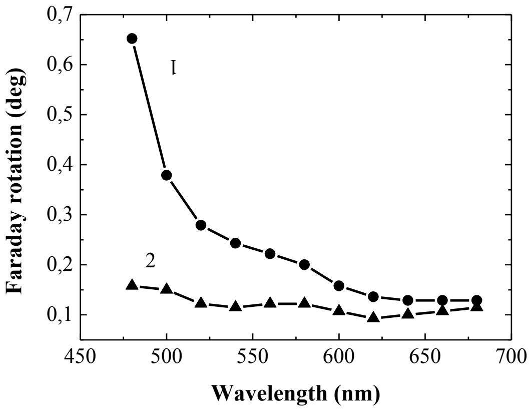

Figure 4. Spectral dependence of the Faraday rotation for PVA film samples containing CdS:Mn (1) and CdS (2) QD at 300K.

It was observed that Faraday rotation angle of semiconductor quantum dot phase has positive sign for undoped CdS quantum dots, but negative sign in case of CdS:Mn quantum dots. The revealed reversal of the direction of the Faraday rotation in its spectral dependence is associated with the competition between the paramagnetic term due to the magnetization of the Mn^{2+} ions and the diamagnetic term due to the interband transition in the CdS crystal.

Nevertheless, the calculated value of the Verdet constant in case of CdS:Mn quantum dots is - 0.16 deg/mT×cm at 475 nm at room temperature. This value is the same order as for bulk non-magnetic CdS crystals [2] because of low magnetization at room temperature and small content of Mn in the quantum dots.

4. Conclusions
We have studied magnetic and magnetooptical properties of CdS:Mn quantum dots / PVA composites. From the magnetic susceptibility data presented it is evident that nanocomposites behave as a typical Curie–Weiss paramagnet over the temperature range studied with ferromagnetic interactions between the Mn^{2+} moments. Effect of the CdS phase amount in composite on magnitude of ferromagnetic interactions can be argument for the stage of embedded magnetic ions. In the Faraday rotation spectra negative sign of the angle of rotation has been revealed in case of CdS:Mn quantum dots / PVA composites like to bulk DMS crystals.

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