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Optical and magnetic resonance investigations on Mn doped CdS nanocrystals

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Abstract. Mn doped CdS nanocrystals have been studied by electron paramagnetic resonance and optically detected magnetic resonance. It was found that Mn^{2+} which is located in the centre of the nanocrystals or on near surface positions create the large polarisation of the excitonic sublevels of the nanocrystals.

Introduction

The doping of sulfide nanocrystals with isoelectronic Mn has reached attention as it results in a bright yellow luminescence with quantum efficiencies of about 20% [1]. The emission originates from the ${}^4\text{T}_1 - {}^6\text{A}_1$ crystal field transition of Mn^{2+} and peaks around 2.1 eV.

Electron paramagnetic resonance (EPR) is an appropriate tool to study the local environment of Mn^{2+} in the nanocrystals, i.e. to get information whether Mn^{2+} is located inside the nanocrystals, or near the surface, or is purely located in the matrix in which the nanocrystals are typically dispersed [2, 3]. A direct correlation to the optical properties of the nanocrystals can be obtained by optically detected magnetic resonance (ODMR). We will show that in an external magnetic field the absorption of the quantum confined states of the nanocrystals are polarised by the orientation of the spins of paramagnetic Mn^{2+} (electron spin 5/2). For low doping concentrations (one Mn per nanocrystal) ODMR shows Mn^{2+} located on tetrahedral sites in the CdS lattice (hyperfine splitting 6.9 mT). For higher Mn concentrations (three Mn per nanocrystal) Mn^{2+} which is located near the surface of the nanocrystals dominates the spectrum (hyperfine splitting 9.5 mT).

1 Experimental

The CdS:Mn nanocrystals were synthesised as follows. In a first step the precipitation of the particles is achieved in ethylene glycol by the simple mixing of one solution containing cadmium and manganese acetate and the other containing sodium sulfide. The cadmium concentration is constant to 0.1 mol/l, and the manganese concentration is varied from 0 to 0.4 mol/l. The sulfide concentration is stoichiometric. A turbid yellow-orange suspension is obtained, consisting of partially agglomerated crystallites. The solution is centrifuged and washed two times with methanol. The deagglomeration of the particles into a clear colloid is then obtained through a thermal treatment of the precipitate for 1 hour in tri-ethylenephosphate at 215 °C. The disjunction of the particles occurs through the grafting of phosphate molecules at the surface of the particles. The obtained colloidal solution can

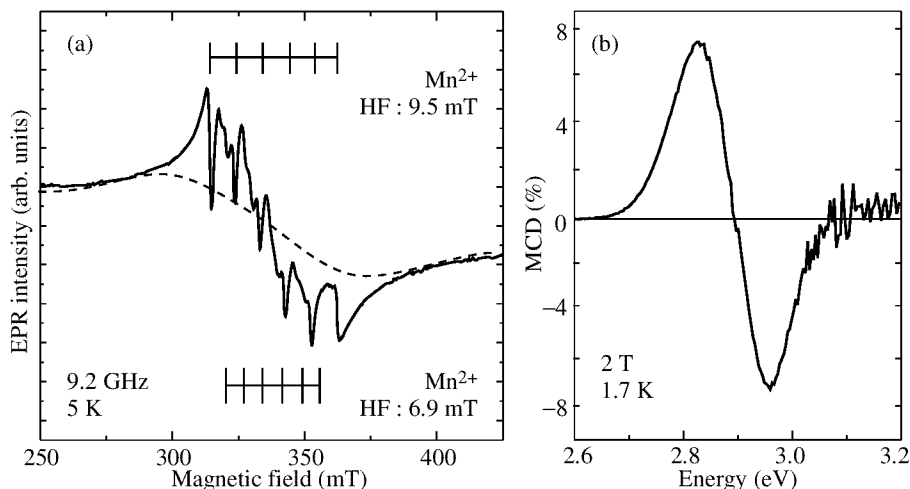


Fig. 1. (a) Electron paramagnetic resonance (EPR) spectrum of CdS nanocrystals doped with three Mn per nanocrystal. (b) Magnetic circular dichroism (MCD) of the excitonic absorption of CdS:Mn nanocrystals.

be destabilised upon the addition of heptane in excess. The flocculate is then washed two more times with heptane, and the resulting powder can be dispersed in methanol with high concentrations (> 1 mol/l).

Further incorporation of the particles in sol-gel silica matrices can be achieved using the process described in previous works [4, 5].

EPR experiments were performed on a commercial Bruker 300E spectrometer equipped with a Oxford ESR 900 flow cryostat. The setup for the optical detection of magnetic resonance (ODMR) consists of a Helium bath cryostat with a superconducting magnet. The maximum magnetic field is 4 T, the microwave frequency 24 GHz. The magnetic circular dichroism (MCD) of the absorption was detected by a photo-elastic modulator (50 kHz) in combination with a linear polarizer.

2 Results and discussion

Figure 1 shows a typical EPR spectrum of CdS nanocrystals doped with on average 3 Mn ions per quantum dot. The procedure to determine the Mn concentration is described in detail in Ref. [5]. The spectrum consists of three overlapping signals.

(a) A six line pattern of Mn^{2+} with a hyperfine splitting of 6.9 mT. This hyperfine splitting is typical for Mn^{2+} located on cation sites in tetrahedral semiconductors, thus it has been attributed to Mn^{2+} in or near the centre of the nanocrystals [2].

(b) A Mn^{2+} spectrum with a hyperfine splitting of about 9.5 mT. The increased hyperfine interaction is an indication for a reduced covalent bonding of Mn, which is likely to be the case for Mn located near the surface of the nanocrystals.

(c) A broad unresolved spectrum which arises from Mn-Mn dipolar interactions similar to heavily doped bulk materials, or Mn^{2+} located in an environment of varying crystal field strength, i.e. amorphous material, like the matrix in which the nanocrystals are embedded. These three signals are always present in our samples, independent of the Mn doping concentration. But it should be noted that signal (a) is more intense compared to signal (b) for nanocrystals which are doped only with one Mn per nanocrystal.

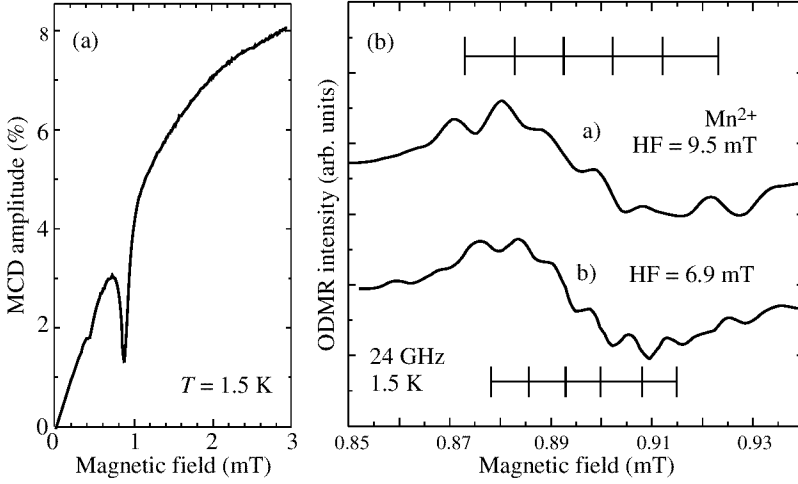


Fig. 2. (a) Optically detected magnetic resonance (ODMR) spectrum of CdS nanocrystals doped with Mn, detected on the excitonic MCD (24 GHz, 100 mW). (b) ODMR spectra measured with low microwave power (-30 dB) of CdS nanocrystals doped with three Mn (a) and one Mn (b) per nanocrystal.

The presence of Mn in the nanocrystals largely modifies its near bandgap magneto-optical absorption properties. A giant splitting of the exciton spin sublevels is observed which results in a MCD signal of several percent intensity [6]. The MCD has a derivative lineshape typical for excitonic transitions, Fig. 2. The centre position is at 2.9 eV indicating that the first transition of the quantum confined states of the nanocrystals is shifted about 500 meV to higher energies compared to the CdS bulk value. The energy position corresponds to an average diameter of the nanocrystals of 3.2 nm.

In order to prove that Mn^{2+} is responsible for this effect we performed ODMR experiments. The spectrum taken at high microwave powers (100 mW, 24 GHz) is shown in Fig. 3. The lineshape of the MCD as a function of the magnetic field follows a Brillouin function behaviour with $S = 5/2$. At the magnetic field position corresponding to $g \approx 2.0$ a strong resonance is observed reducing the MCD about 70%, at half field position an additional weaker resonance can be noticed, typical for high spin systems. To observe structure in the $g \approx 2.0$ resonance the microwave power has to be reduced considerably. Figure 4(a) shows the spectrum of the sample doped with three Mn per nanocrystal at -30 dB microwave power.

The structure of Mn^{2+} with the large hyperfine (HF) splitting of 9.5 mT is visible. For the sample doped with only one Mn per dot (Fig. 4(b)) we find Mn^{2+} with 6.9 mT hyperfine splitting, but also Mn^{2+} with HF = 9.5 mT is also present, however, in lower intensity. These results show directly that Mn^{2+} either located in the centre of the nanocrystals or near the surface create the large polarisation of the excitonic levels of the quantum dots.

Switching the microwave power on/off and monitoring the recovery of the MCD signals allows to get information on the spin lattice relaxation times. We found for both cases of high and low Mn doping that the spin lattice relaxation is faster than 10 ms, which is the time resolution of the experimental setup due to the Lock-In technique. However, the ODMR signal intensity is usually weaker in the highly doped samples which may indicate a faster

spin relaxation due to Mn-Mn interactions.

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