Magnetic circular dichroism of CdTe nanoparticles

A.V. Malakhovskii [a],[*], A.E. Sokolov [a], A.S. Tsipotan [b], S.M. Zharkov [a],[b], V.N. Zabluda [a]

[a] *Kirensky Institute of Physics, Federal Research Center KSC SB RAS, 660036 Krasnoyarsk, Russian Federation*
[b] *Siberian Federal University, Krasnoyarsk, 660041, Russian Federation*

A R T I C L E   I N F O

A B S T R A C T

Magnetic circular dichroism (MCD) of water-soluble CdTe nanoparticles was observed in the visible spectral range for the first time. Diameter of nanoparticles varied from 2.3 to 4.5 nm. Absorption and photoluminescence spectra were also recorded. Absorption line at 19400 cm^{-1} and luminescent line at 18200 cm^{-1} were observed. Splitting of value 960 cm^{-1} was revealed in the MCD spectrum. Approximately the same splitting was extracted from the absorption spectrum. The MCD was identified as the temperature independent paramagnetic mixing effect. Nature of the absorption line and of its splitting are discussed.

1. Introduction

Colloidal semiconductor nanoparticles, usually called quantum dots (QDs), show the onset of quantum confinement effects. The latter determines their unique electronic and optical properties, and a range of potential applications. QDs are ideal candidates for application as the emitting layer in light emitting diodes (LEDs) [1,2] because of their tunable colors, bright emission etc. Another promising applications of QDs are light emitted displays (QD-LED) [3] and solar energy harvesting [4,5]. Moreover colloidal QDs are widely used as labels and contrast agents for in vitro and in vivo bioimaging [6,7].

Magnetic [8,9] and Faraday rotation measurements [10] have shown that bulk CdTe is a diamagnetic. Optical properties of the bulk CdTe were studied in Ref. [11]. In particular, it was found that the band gap energy was 1.534 eV (12373 cm^{-1}). Thereby, the pure CdTe is the narrow band gap dielectric. Optical properties of the thiol-capped CdTe nanocrystals were measured in Refs. [12, 13]. Absorption and emission lines were observed in the region of 450–600 nm (22200–16600 cm^{-1}), depending on the particle sizes. The present work is devoted to the first study of the magnetic circular dichroism (MCD) of the CdTe nanoparticles.

2. Results and discussions

Water-soluble CdTe nanoparticles under study were produced by the PlasmaChem company. They were initially stabilized by
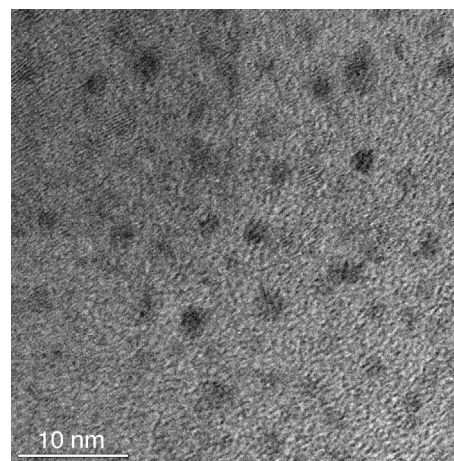
* Corresponding author.
E-mail address: malakha@iph.krasn.ru (A.V. Malakhovskii).

Fig. 1. High-resolution transmission electron microscope image of the CdTe nanoparticles taken at 200 kV.

thioglycolic acid. Molar concentration of nanoparticles in the solution was $C = 3 \cdot 10^{-6}$ M. The morphological structure and local elemental composition were determined by the high-resolution transmission electron microscope JEOL JEM-2100 (LaB$_6$) equipped by the energy dispersive spectrometer Oxford Inca x-sight (Fig. 1). The nanoparticles' diameter, as extracted from Fig. 1, varied from 2.3 to 4.5 nm.

The absorption spectrum (Fig. 2) of 0.9 cm thick CdTe solution was measured by Perkin-Elmer Lambda 35 spectrometer, and the luminescence spectrum (Fig. 2) excited at 480 nm was measured by the HoribaJobinIvon Fluorolog3. The MCD spectra were recorded
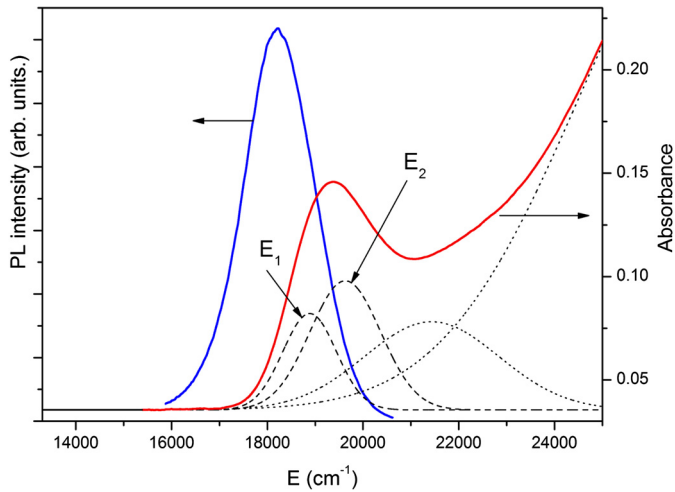
Fig. 2. Absorption and photoluminescence (PL) spectra of the CdTe nanoparticles and the least-squares method decomposition of the absorption spectrum (dashed and dotted lines).
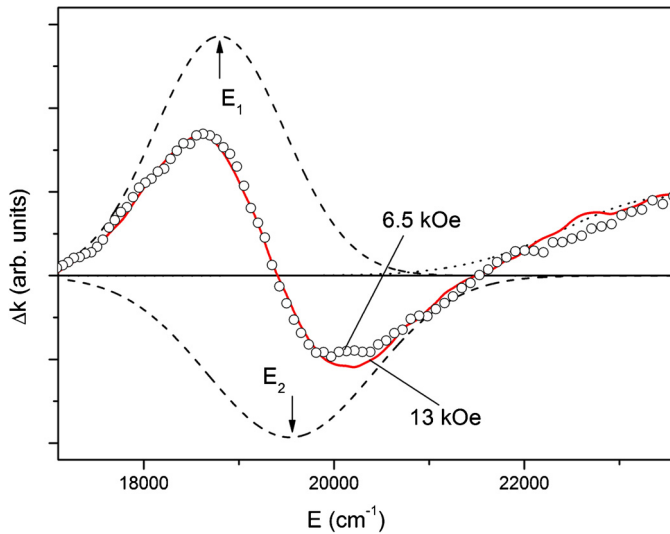

Fig. 3. The MCD spectra of the CdTe nanoparticles (solid line and points) and the least-squares method decomposition of the spectrum at 13 kOe (dashed lines).

using modulation of the light wave polarization with piezoelectric modulator (details see in Ref. [14]). The MCD measurements were performed in the magnetic field up to 13 kOe at room temperature. The MCD spectra obtained in magnetic fields 6.5 and 13 kOe and normalized on positive amplitudes are presented in Fig. 3. They are totally identical. The decomposition of the MCD spectrum at 13 kOe on the Gauss shape components is also given in Fig. 3. The decomposition of several independent spectra was fulfilled and they gave average splitting 960 ± 100 cm^{-1}, which did not depend on the magnetic field at least up to 13 kOe. The decomposition of the absorption spectrum (Fig. 2) gave energies E_1 and E_2 close to those obtained from the MCD spectra. The rest features in the absorption spectrum probably refer to the scattering of light. The spectra are good described by the Gauss functions, testifying to the inhomogeneous broadening.

As mentioned above, strong optical absorption of the bulk CdTe begins from 12373 cm^{-1} [11], i.e., observed resonance (Figs. 2, 3) is already in the conduction band of the material. Consequently, at these conditions the CdTe nanoparticles can be considered in a first approximation as the conducting nanoparticles. Strong optical absorption at the electron transitions into the conduction band is due to dissipation of the electrons energy as a result of their collisions

with atoms. However, when size of the particle becomes smaller than the mean free path of the electron, the metal absorption disappears, and the particle becomes transparent, but the surface plasmon resonance (SPR) can appear. Additionally, presented above experimental data qualitatively coincide with those for Au [15,16] and Ag [17,18] nanoparticles. Therefore, for the beginning we shall discuss the studied properties of Au and Ag nanoparticles.

There are three specific properties of the metal nanoparticles: magnetic ordering, SPR and splitting of the SPR, observed in the MCD spectra. The SPR is the resonance absorption of free electrons, and therefore it exists both in capped [19] and uncapped [20] nanoparticles, while magnetic order occurs only in the capped nanoparticles [21]. Consequently, magnetic order is connected with the localized electrons on the surface. The MCD was observed in Au [15,16] and Ag [17,18] nanoparticles. The splitting in these spectra were referred to the cyclotron resonance in Refs. [22,17,18]. However the cyclotron frequency is too small as compared to the observed splitting and this frequency is proportional to the magnetic field that contradicts to the experimental observations.

LaShell et al. [23] measured experimentally the energy difference between two spin orientations of the surface state bands on the Au (111) surface. It was equal to 887 cm^{-1}. This difference actually means magnetic ordering of the surface states. So large splitting can explain existence of the magnetic ordering in the gold nanoparticles even at the room temperature [24]. It is worth noting that the splitting in the MCD spectra has the same order of value. Hernando et al. [25] associated this splitting with the giant magnetic anisotropy on the surface of nanoparticles. The MCD in gold nanoparticles did not change from 5.5 K up to the room temperature [15]. All these mean that both initial and final states of transitions are singlet, and the observed MCD is the temperature independent effect of the *B*-type (mixing effect). Taking into account all observations mentioned above, it is possible to propose the following model.

Conduction electrons of the gold (for the certainty) are in the 6*s* states. Odd components of the crystal field, certainly existed on the surface of the capped metal, admix 6*p* states of the localized electron to its 6*s* state, which remains orbital singlet. The spin double degeneration is removed by the exchange interaction and we obtain two totally not degenerated states with the opposite spin orientations for the localized electrons:

$$\Psi_L(\uparrow\downarrow) = S(\uparrow\downarrow) + aP_{1/2} + bP_{3/2}. \qquad (1)$$

There are actually two slightly bound electron systems in the metal nanoparticle: localized electrons on the surface and free electrons. Wave function of the whole particle can be presented as the product of wave functions of these two systems: $\Psi = \Psi_L\Psi_F$, where Ψ_L and Ψ_F are wave functions of the localized and free electrons, respectively. The wave functions $\Psi_F(\uparrow\downarrow)$ of the free electrons correspond to the wave functions $\Psi_L(\uparrow\downarrow)$ of the localized electrons and they also can differ a little, depending on the spin orientation of the localized states. Taking into account some coupling between the two systems, it is possible to create the energy (state) diagram, presented in Fig. 4. ΔE_2 and ΔE_1 are the exchange splitting of the localized states with excited and not excited plasmon resonances, respectively. They can differ a little. According to the mentioned above observations, the exchange splitting is of the order of several hundreds of cm^{-1}. Consequently, the level $\Psi 1(\downarrow)$ is not populated up to the room temperature, and only two transitions can be observed: ω_1 and ω_2 (Fig. 4). Thus, we observe the exchange splitting of the surface localized state, when the surface plasmon is excited. The electric dipole transitions between states of type (1) are partially parity allowed due to admixture of the *P*-states by the odd crystal field and are partially spin-allowed due to the spin-orbit interaction. However, parameters of transitions
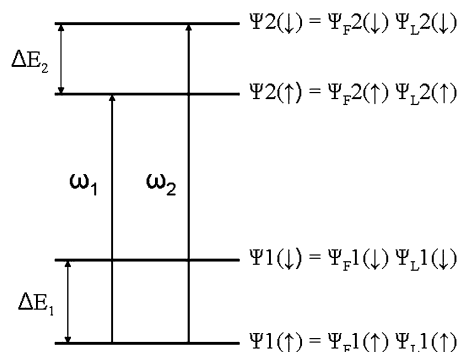
Fig. 4. Diagram of states of conducting nanoparticles. ΔE_2 and ΔE_1 are the exchange splitting of the localized states with excited and not excited plasmon resonances, respectively. ω_1 and ω_2 – are resonances observed in the MCD spectra.

$\Psi 1(\uparrow) \rightarrow \Psi 2(\uparrow)$ and $\Psi 1(\uparrow) \rightarrow \Psi 2(\downarrow)$ (Fig. 4) can be, evidently, different that is in agreement with the experiments. The ground and excited states are not degenerated. Therefore, both diamagnetic and temperature dependent paramagnetic circular dichroisms should not exist. Only independent of temperature B-term of MCD, which is due to the mixing of states by magnetic field, should exist. This is the very thing observed in the experiments on the metal nanoparticles.

Returning to the CdTe nanoparticles, we can suppose that at least the excited state of the nanoparticle is split according to the spin states. Indeed, in the ground state of the CdTe two $5s$ electrons of Cd move to $5p$ orbitals of Te, and electron shells of the both atoms become filled and the crystal is dielectric. If we suppose that in the excited state one electron from the Te^{-2} ion moves to $5s$ orbital of Cd, and that it is the conduction electron, then situation becomes to some extent similar to that in Au. Both the free electron and the hole in CdTe have spin 1/2. Consequently the nanoparticle as a whole has in the excited state two spin-states with different energies due to the exchange interaction between the hole and the free electron. Energies of these states and the splitting between them are increased with the particle size decrease because of the space confinement. The energy of the SPR in metal nanoparticles reveals opposite dependence on the nanoparticle size. Thus, in spite of the qualitative identity of the absorption and the MCD spectra of the metal and the semiconductor nanoparticles, nature of the spectra is substantially different in these objects.

The ground state of the CdTe particle is singlet. Therefore the temperature dependent paramagnetic MCD (C-term) does not exist. The excited states are degenerated and the MCD of the diamagnetic type exists. However, due to the space inhomogeneity of absorption, the summation of the individual diamagnetic MCD lines along the absorption band gives zero. Only the temperature independent paramagnetic mixing effect (B-term) remains.

The splitting of the photoluminescence [26] and absorption [27] spectra, similar to that discussed above, were observed in CdSe nanoparticles. Prado et al. [28] calculated theoretically absorption spectrum of the spherical CdTe nanoparticles, considering them as the quantum dots. In particular, the authors obtained for the particle with the radius $R = 3$ nm three strong absorption lines at 16700, 19040 and 19920 cm^{-1}. It is necessary to emphasize, that the first line is not observed in the spectrum of our nanoparticles (Fig. 2), however positions of the second and the third lines and especially the splitting between them (880 cm^{-1}) are close to the experimental ones. In the luminescence spectra of CdSe nanoparticles of 3–6 nm in radius the splitting $\sim$200 cm^{-1} was observed [29]. The existence of the exchange splitting in the ground state of the capped CdTe nanoparticles, similar to that of the capped Au nanoparticles, is doubtful. Indeed, attempts to measure the parti-

cles magnetic moments did not reveal a spontaneous magnetization.

3. Summary

The MCD, absorption and photo luminescence spectra of the water-soluble CdTe nanoparticles with diameter varied from 2.3 to 4.5 nm were measured. The absorption line at 19400 cm^{-1} and the luminescent line at 18200 cm^{-1} were observed. The splitting of value 960 cm^{-1} was revealed in the MCD spectrum. Approximately the same splitting was extracted from the absorption spectrum. The splitting can be accounted for as a consequence of the exchange interaction of the free electron and the hole in the excited state of the nanoparticle. The absorption and MCD spectra of the metal and semiconductor nanoparticles are similar, but their nature is different. In the ground state CdTe is diamagnetic. Therefore the temperature dependent paramagnetic MCD (C-term) does not exist. Due to the space inhomogeneity of the absorption, the summation of the individual diamagnetic MCD lines along the absorption band gives zero. Only the temperature independent paramagnetic mixing effect (B-term) remains.

References

[1] Y. Yang, Y. Zheng, W. Cao, A. Titov, J. Hyvonen, J.R. Manders, J. Xue, P.H. Holloway, L. Qian, High-efficiency light-emitting devices based on quantum dots with tailored nanostructures, Nat. Photonics 9 (2015) 259–266.

[2] D.Y. Wang, I.S. Wang, I.S. Huang, Y.C. Yeh, S.S. Li, K.H. Tu, C.C. Chen, C.W. Chen, Quantum dot light-emitting diode using solution-processable graphene oxide as the anode interfacial layer, J. Phys. Chem. C 116 (2012) 10181–10185.

[3] T.H. Kim, K.S. Cho, E.K. Lee, S.J. Lee, J. Chae, J.W. Kim, D.H. Kim, J.Y. Kwon, G. Amaratunga, S.Y. Lee, B.Y. Choi, Y. Kuk, J.M. Kim, K. Kim, Full-colour quantum dot displays fabricated by transfer printing, Nat. Photonics 5 (2011) 176–182.

[4] D. Zhao, C.F. Yang, Recent advances in the TiO2/CdS nanocomposite used for photocatalytic hydrogen production and quantum-dot-sensitized solar cells, Renew. Sustain. Energy Rev. 54 (2016) 1048–1059.

[5] A.N. Jumabekov, F. Deschler, D. Böhm, L.M. Peter, J. Feldmann, T.J. Bein, Quantum-dot-sensitized solar cells with water-soluble and air-stable PbS quantum dots, Phys. Chem. C 118 (2014) 5142–5149.

[6] B.A. Kairdolf, A.M. Smith, T.H. Stokes, M.D. Wang, A.N. Young, S. Nie, Semiconductor quantum dots for bioimaging and biodiagnostic applications, Annu. Rev. Anal. Chem. 6 (2013) 143–162.

[7] Q. Le Trequesser, H. Seznec, M.-H. Delville, Functionalized nanomaterials: their use as contrast agents in bioimaging: mono- and multimodal approaches, Nanotechn. Rev. 2 (2013) 125–169.

[8] M.R. Begam, N.M. Rao, G.M. Joshi, S. Kaleemulla, M. Shobana, N.S. Krishna, M. Kuppan, Structural, optical and magnetic properties of Co doped CdTe alloy powders prepared by solid-state reaction method, Adv. Condens. Matter Phys. 2013 (2013) 218659.

[9] Yu.V. Shaldin, Magnetic properties of high-resistivity CdTe(In) and CdTe(Cl) crystals, Inorg. Mater. 37 (2001) 560–563.

[10] P.I. Nikitin, A.I. Savchuk, The Faraday effect in semimagnetic semiconductors, Sov. Phys. Usp. 33 (1990) 974–1005.

[11] S. Lalitha, S.Zh. Karazhanov, P. Ravindran, S. Senthilarasu, R. Sathyamoorthy, J. Janabergenov, Electronic structure, structural and optical properties of thermally evaporated CdTe thin films, Physica B 387 (2007) 227–238.

[12] N. Gaponik, D.V. Talapin, A.L. Rogach, K. Hoppe, E.V. Shevchenko, A. Kornowski, A. Eychmüller, H. Weller, Thiol-capping of CdTe nanocrystals: an alternative to organometallic synthetic routes, J. Phys. Chem. B 106 (2002) 7177–7185.

[13] A. Eychmüller, A.L. Rogach, Chemistry and photophysics of thiol-stabilized II–VI semiconductor nanocrystals, Pure Appl. Chem. 72 (2000) 179–188.

[14] A.V. Malakhovskii, S.L. Gnatchenko, I.S. Kachur, V.G. Piryatinskaya, A.L. Sukhachev, I.A. Gudim, Optical and magneto-optical properties of Nd$_{0.5}$Gd$_{0.5}$Fe$_3$(BO$_3$)$_4$ single crystal in the near IR spectral region, J. Alloys Compd. 542 (2012) 157–163.

[15] M.A. Zaitoun, W. Roy Mason, C.T. Lin, Magnetic circular dichroism spectra for colloidal gold nanoparticles in xerogels at 5.5 K, J. Phys. Chem. B 105 (2001) 6780–6784.

[16] A.E. Sokolov, S.G. Ovchinnikov, V.N. Zabluda, A.M. Kal'sin, Ya.V. Zubavichus, Magnetic circular dichroism and the nature of ferromagnetism in colloidal gold nanoparticles, JETP Lett. 97 (2013) 98–101.

[17] H. Yao, T. Shiratsu, Individual and collective modes of surface magnetoplasmon in thiolate-protected silver nanoparticles studied by MCD spectroscopy, Nanoscale 8 (2016) 11264–11274.

[18] Y. Ishikawa, H. Yao, Surface magnetoplasmons in silver nanoparticles: apparent magnetic-field enhancement manifested by simultaneous deconvolution of UV–vis absorption and MCD spectra, Chem. Phys. Lett. 609 (2014) 93–97.

[19] M.A. Garcia, J. de la Venta, P. Crespo, J. Llopis, S. Penadés, A. Fernández, A. Hernando, Surface plasmon resonance of capped Au nanoparticles, Phys. Rev. B 72 (2005), 241403(R).

[20] C. Bréchignac, P. Cahuzac, J. Leygnier, A. Sarfati, Optical response of large lithium clusters: evolution toward the bulk, Phys. Rev. Lett. 70 (1993) 2036–2039.

[21] S. Trudel, Unexpected magnetism in gold nanostructures: making gold even more attractive, Gold Bull. 44 (2011) 3–13.

[22] F. Pineider, G. Campo, V. Bonanni, C. de Julián Fernández, G. Mattei, A. Caneschi, D. Gatteschi, C. Sangregorio, Circular magnetoplasmonic modes in gold nanoparticles, Nano Lett. 13 (2013) 4785–4789.

[23] S. LaShell, B.A. McDougall, E. Jensen, Spin splitting of an Au (111) surface state band observed with angle resolved photoelectron spectroscopy, Phys. Rev. Lett. 77 (1996) 3419–3422.

[24] P. Crespo, R. Litrán, T.C. Rojas, M. Multigner, J.M. de la Fuente, J.C. Sánchez-López, M.A. García, A. Hernando, S. Penadés, A. Fernández, Permanent magnetism, magnetic anisotropy, and hysteresis of thiol-capped gold nanoparticles, Phys. Rev. Lett. 93 (2004) 087204.

[25] A. Hernando, P. Crespo, M.A. García, E.F. Pinel, J. de la Venta, A. Fernández, S. Penadés, Giant magnetic anisotropy at the nanoscale: overcoming the superparamagnetic limit, Phys. Rev. Lett. 96 (2006) 057206.

[26] S.A. Empedocles, D.J. Norris, M.G. Bawendi, Photoluminescence spectroscopy of single CdSe nanocrystallite quantum dots, Phys. Rev. Lett. 77 (1996) 3873–3876.

[27] D.J. Norris, M.G. Bawendi, Measurement and assignment of the size-dependent optical spectrum in CdSe quantum dots, Phys. Rev. B 53 (1996) 16338–16346.

[28] S.J. Prado, C. Trallero-Giner, A.M. Alcalde, V. López-Richard, G.E. Marques, Optical transitions in a single CdTe spherical quantum dot, Phys. Rev. B 68 (2003) 235327.

[29] Al.L. Efros, M. Rosen, M. Kuno, M. Nirmal, D.J. Norris, M. Bawendi, Band-edge exciton in quantum dots of semiconductors with a degenerate valence band: dark and bright exciton states, Phys. Rev. B 54 (1996) 4843–4856.