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Doped CdTe-Based Quantum Dots

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Abstract—Colloidal semiconductor CdTe-based quantum dots are investigated. An ab initio computer design of quantum dots based on nanoparticles of CdTe and CdTe doped with atoms of transition elements (Co, Mn) is executed. Partial densities of the electron states of the investigated quantum dots are calculated. The sensitivity of X-ray absorption near edge structure (XANES) spectroscopy for verifying the parameters of the nanoscale atomic structure of small quantum dots based on CdTe, and for determining the parameters of the local environment around cadmium atoms and doping atoms in quantum dots was proved.

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INTRODUCTION

Quantum dots based on cadmium telluride continue to attract attention from researchers owing to their unique characteristics [1]. These nanoparticles find wide application in different fields [2, 3]. The effectiveness of CdTe-based quantum dots in the femtosecond range was demonstrated in [4]. Systematic theoretical analysis of the electronic structure must be performed in order to understand the fundamental patterns in the characteristics of quantum dots, including their nonlinear optical characteristics [5]. Density functional theory (DFT) techniques are accurate theoretical methods that allow to obtain important results for small CdTe-based quantum objects [6]. The more approximate but less resource-intensive pseudopotential method was used in [7] to optimize the atomic structure of large nanoparticles containing up to 83 pairs of Cd and Te atoms, and to determine the details of their electronic structures. Quantum-chemical methods (particularly those used in the Gaussian 03 computer package) were also used to investigate charge-transfer effects in a quantum dot–ligand system [8]. In some cases, semi-empirical schemes can also be used to study features of the electronic structure and characteristics of optical excitation in CdTe quantum dots [9, 10].

Nonlinear optical effects in small nanoclusters (2–20 atoms) can be investigated using more accurate ab initio schemes [11]. The use of band methods (the Wien2k package) for theoretical investigations of patterns in dependences of the electronic structure parameters of CdTe-based quantum dots would also seem to be promising [12]. The DFT approach in the GGA approximation (VASP code) was used in [13] to analyze the HOMO-LUMO-gap in the electronic structure of CdTe-type quantum dots.

Modern quantum-chemical approaches (e.g., those used in the Gaussian 09 software package) allow to study features of the electronic structure of CdTe quantum dots coated with stabilizing compounds [14]. In all the above studies, however, only defect-free ("pure") CdTe quantum dots were considered. In this work, we studied features of the atomic and electronic structures of doped quantum dots, and the possibility of verifying the information obtained on the basis of computer simulation by experimental methods (e.g., X-ray absorption near edge structure spectroscopy, XANES) was examined.

CALCULATION PROCEDURE

The atomic structure of colloidal semiconductor quantum dots based on the nanoparticles of CdTe and CdTe doped with atoms of transition elements (CdTe:Co, and CdTe:Mn) was optimized using the ADF 2014 code [15] which is based on Kohn–Sham DFT.

A spherical fragment of crystalline CdTe [16] containing 123 atoms was used as the initial structure of the CdTe particle. Spherical CdTe fragments (123 atoms) in which the central cadmium atom was replaced with Co or Mn atoms, respectively, were used as the initial structures for optimizing CdTe particles doped with Co and Mn.

The ADF program allows to perform calculations using different approximations for the exchange-correlation potential. In this work, calculations were performed in the generalized gradient approximation (GGA) using the model of the BLYP exchange-correlation functional with Stefan Grimme's D3-BJ dispersion correction [17]. Geometry optimization was done using the DZ basis set. The ADF program code was recently used successfully for analyzing the atomic and electronic structures of compounds [18, 19].

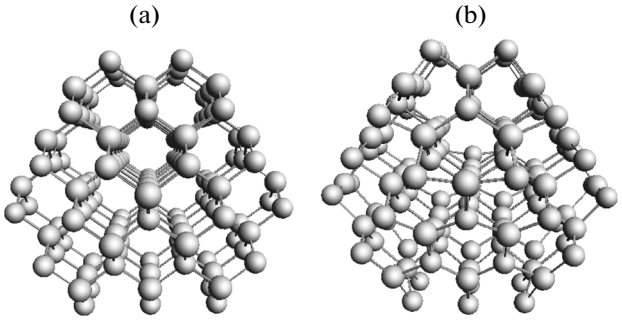

Fig. 1. Schematic representations of the structures of a CdTe nanoparticle (123 atoms) (a) before optimization of the atomic structure, and (b) after optimization of the atomic structure using the ADF program.

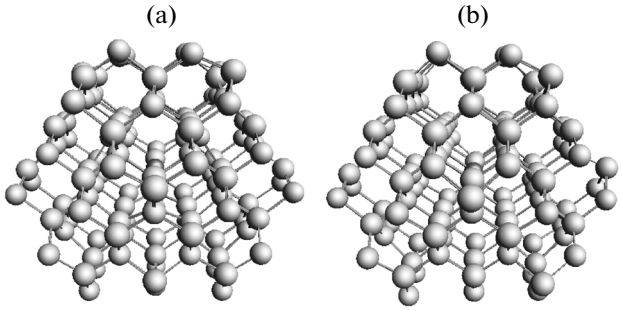

Fig. 2. Representations of the structures of (a) CdTe:Co, and (b) CdTe:Mn, obtained as a result of optimization using the ADF program.

Calculations of the XANES spectra were performed for the initial and optimized structures of the investigated CdTe-based quantum dots. The XANES spectra near the Cd *K*-edge in CdTe particles, near the Co *K*-edge in CdTe:Co, and near the Mn *K*-edge in CdTe:Mn were calculated on the basis of the full multiple scattering theory in the real space realized in the FEFF9.6.4 code [20, 21]. The FEFF9.6.4 program uses the muffin-tin approximation [22] for the potential shape. The XANES spectra were calculated using the Hedin–Lundqvist type of the exchange-correlation potential. The calculations were performed taking into account the core hole created by the electronic transition.

RESULTS AND DISCUSSION

At the first stage of the study, the atomic structures of quantum dots based on CdTe nanoparticles were optimized using the density functional theory implemented in the ADF code (see above). A spherical CdTe particle consisting of 123 atoms, taken as a fragment of solid-state CdTe with structural parameters from [16], was used as the initial structure for optimization. Figure 1 shows a schematic representation of the initial structure of the CdTe nanoparticle (a) before atomic geometry optimization and (b) after geometry optimization.

The structures of quantum dots based on CdTe nanoparticles doped with atoms of transition elements were studied next. The atomic structures of CdTe particles doped with Co and Mn atoms were optimized on the basis of the density functional theory (ADF program). Structures obtained as CdTe fragments [16] in which the central cadmium atom was replaced with Co or Mn atoms, respectively, were used as the initial structures for the optimization. Figure 2 shows representations of the structures of the (a) CdTe:Co nanoparticles and (b) CdTe:Mn nanoparticles obtained as a result of optimization.

Calculations of the partial electronic densities of states (DOS) (FEFF9.6.4 program) near the top of the valence band and the bottom of the conduction band were performed for the optimized structures of our CdTe:Co and CdTe:Mn nanoparticles. The calculations were performed in the ground-state of the electron system. Figure 3 shows the resulting partial DOS of CdTe:Mn nanoparticles.

XANES spectroscopy is currently becoming an important tool for investigating fine details of the nanosized atomic structure of small quantum particles. XANES spectroscopy allows us to obtain information on the electronic structure and three-dimensional atomic structure around the investigated types of atoms in materials with a high degree of precision, including materials without long-range order in the arrangement of atoms. On the basis of XANES spectroscopy, bond lengths can be determined with an accuracy of ~0.002 nm; bond angles, with an accuracy of several degrees. However, XANES spectroscopy is an indirect method of investigation. In order to extract structural information, calculations of the spectra for structural models are needed that require the use of supercomputers and computer clusters. Successful investigations of the atomic and electronic structures of some nanoscale objects have recently been conducted using XANES spectroscopy [23, 24].

In this work, we performed calculations of the XANES spectra near the Cd *K*-edge in CdTe nanoparticles. Cd *K*-XANES spectra were calculated on the basis of full multiple scattering using the FEFF9.6.4 program. The calculations were performed for an excited state of the electron system (a core hole created by the electronic transition was considered). Theoretical Cd *K*-XANES spectra of the initial and optimized structures of the CdTe nanoparticle (123 atoms) are compared in Fig. 4.

Calculations of the XANES spectra of doped CdTe-based quantum dots were performed next. Calculations of the Co *K*- and Mn *K*-XANES spectra were performed for the initial and optimized structures

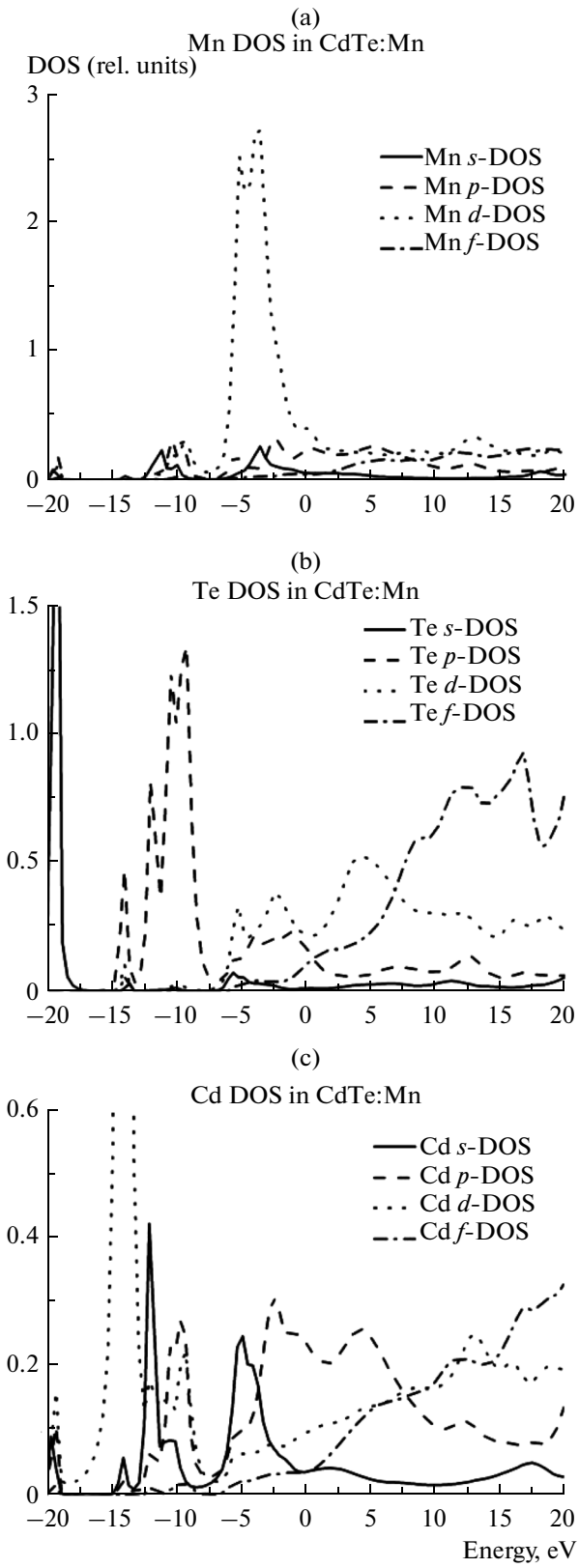

Fig. 3. Partial densities of electron states of (a) Mn, (b) Te, and (c) Cd in the CdTe:Mn nanoparticle. The Fermi energy is −3.3 eV.

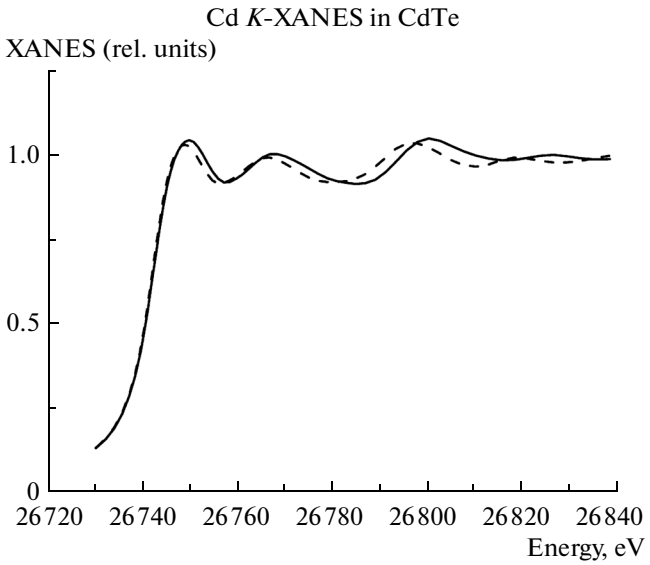

Fig. 4. Theoretical Cd *K*-XANES spectra of the CdTe nanoparticle. The solid line corresponds to the XANES spectrum calculated for the initial (non-optimized) structure. The dashed line shows the XANES spectrum calculated for the CdTe structure obtained as a result of geometry optimization using the ADF program.

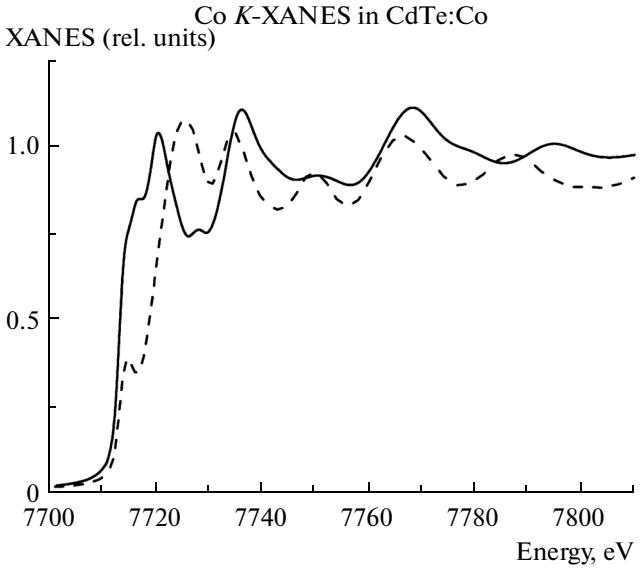

Fig. 5. Theoretical Co *K*-XANES spectra of a CdTe quantum dot doped with Co. The solid line corresponds to the XANES spectrum calculated for the initial (non-optimized) structure. The dashed line shows the XANES spectrum calculated for the CdTe:Co structure obtained as a result of geometry optimization using the ADF program.

of CdTe:Co and CdTe:Mn nanoparticles. The Co *K*-XANES spectra of CdTe:Co and the Mn *K*-XANES spectra of CdTe:Mn are shown in Figs. 5 and 6, respectively.

From Figs. 4–6, one can see that the XANES spectra of the particles of CdTe, and CdTe doped with atoms of transition elements are sensitive to small

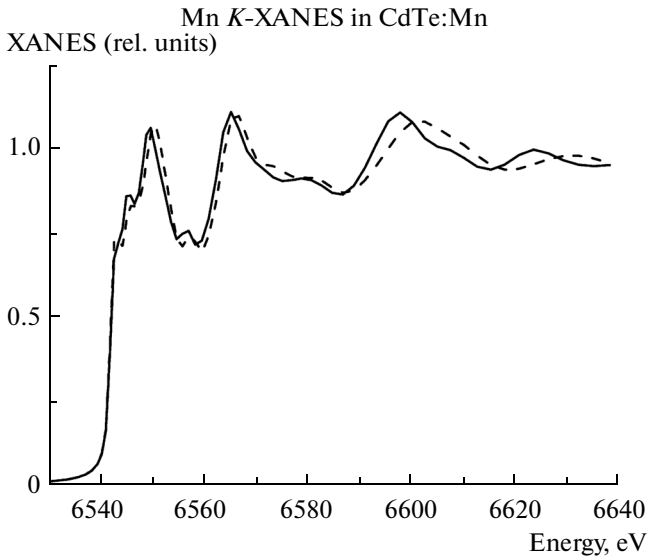

Fig. 6. Theoretical Mn *K*-XANES spectra of the CdTe nanoparticle doped with Mn. The solid line corresponds to the XANES spectrum calculated for the initial (non-optimized) structure. The dashed line shows the XANES spectrum calculated for the CdTe:Mn structure obtained as a result of geometry optimization using the ADF program.

changes in the atomic structure of the particles. Thus, XANES spectroscopy may be used to verify the parameters of the nanoscale atomic structure (determined by computer simulation methods) of small CdTe-based quantum dots, and to determine the parameters of the local environment of cadmium atoms and doping transition elements in quantum dots.

CONCLUSIONS

An ab initio computer design of quantum dots based on nanoparticles of CdTe and CdTe doped with atoms of transition elements (Co, Mn) was done on the basis of the density functional theory (ADF code). Features of the atomic structure of semiconductor CdTe-based quantum dots were studied, and the influence of doping atoms was evaluated. Calculations of the partial electronic densities of states near the top of the valence band and the bottom of the conduction band of the investigated quantum dots were performed. The sensitivity of XANES spectroscopy for verifying the parameters of nanoscale atomic structure (determined by computer simulations) of small CdTe-based quantum dots, and for determining the parameters of the local environment of cadmium atoms and doping atoms in a quantum dot was demonstrated.

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