

## ATOMIC AND ELECTRONIC STRUCTURE OF CdS-BASED QUANTUM DOTS

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The *ab initio* computer design of the CdS-based quantum dots and the cobalt doped CdS quantum dots is carried out. The characteristics features of the atomic and electronic structures of semiconductor colloidal quantum dots on CdS of different sizes are studied, and the effect of cobalt impurity atoms is estimated. We have proved the sensitivity of the X-ray absorption near-edge structure (XANES) method for the verification of the nanosized atomic structural parameters calculated by the methods of computer modeling for small-scale quantum dots of the CdS family, and for the determination of the local environment parameters of the cobalt atom in the quantum dot.

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### INTRODUCTION

In recent years, quantum nanostructures have been playing more and more important role in high-tech economic sectors, thus, in particular, semiconductor colloidal quantum dots can be used for new generation LED displays [1], as sensor elements for environment protection, and as elements in biomedical diagnostics [2]. There is extensive research for the application of quantum dots having magnetic properties [3, 4]. Quantum dots are also promising materials for new generation photovoltaics [5, 6]. A major part of the unique physicochemical properties of new quantum nanostructures depend on their local atomic ordering and electronic structure. However, at present, in the world there are no universal nondestructive methods for the accurate determination of the parameters of nanosized atomic and electronic structures of quantum nanostructures. Therefore, there is an important problem of developing a combined nondestructive technique for the X-ray spectral accurate nanodiagnosics of the parameters of 3D atomic and electronic structures of colloidal semiconductor quantum dots.

Recently, the outlook for the application of extended X-ray absorption fine structure (EXAFS) has been demonstrated for the investigation of impurities in semiconductor quantum dots [7]. There have been made attempts to study quantum size effects in the quantum dots using also X-ray absorption near-edge structure (XANES) methods [8]. The computer nanodesign of the nanosized atomic and electronic structures of quantum nanoobjects of the type of colloidal semiconductor quantum dots, based on the multiscale computer modeling also seems to be important [9]. *In silico* experiments using supercomputer technologies are one of the new trends in developing modern instruments for the materials science [10-12]. However, for the verification of the results of the computer modeling it is desirable to use also experimental

techniques [13-15]. It is of prime importance to use them for quantum dot based heterostructures [16, 17] or in taking into account the effects of different types of ligands [18].

To this end, in the present work we have carried out a combined study involving two different theoretical methods of computer modeling of the atomic and electronic structure of CdS-based semiconductor quantum dots and the modeling of XANES spectra, which at present becomes an important instrument to investigate fine features of the nanosized atomic structure of small-scale quantum nanoparticles [19, 20].

## CALCULATION PROCEDURE

The optimization of the atomic geometry of quantum dots based on CdS nanoparticles was carried out by density functional theory (DFT) using the ADF 2014 and VASP5.3 program packages.

The atomic structure of smaller CdS nanoparticles was optimized using the ADF program package [21], which is based on Kohn-Sham DFT. The spherical fragments of the cubic phase of CdS were used as the initial structures preceding the optimization [22]. The ADF complex allows the user to calculate the exchange-correlation potential within various approximations. In the present work, the calculations were carried out with the generalized gradient approximation (GGA) using the BP exchange-correlation potential. The geometric optimization was carried out using the DZ basis set. The atomic structures of CdS particles consisting of 29 atoms ( $\text{Cd}_{13}\text{S}_{16}$ ) and 123 atoms ( $\text{Cd}_{55}\text{S}_{68}$ ) were optimized. Previously, the ADF program package has been successfully used to analyze the atomic structure and electronic features of the compounds (e.g. see [23, 24]).

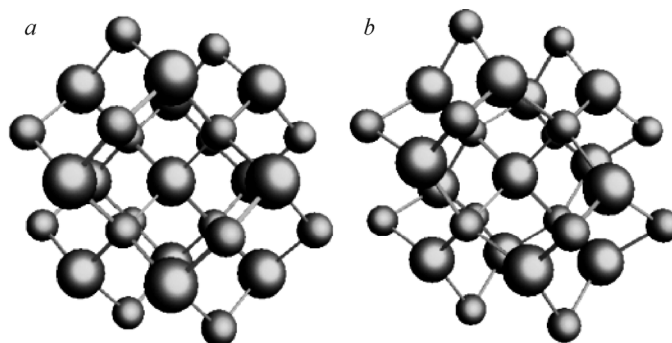
The optimization of the atomic geometry of larger clusters was carried out using the VASP5.3 program package [25-29] within DFT with regard to periodic boundary conditions. Pseudopotentials [30] used in the VASP5.3 program package enable the sufficient reduction of resource consumption for solving computational problems, thus allowing to carry out calculations for a larger CdS particle containing 174 atoms. The spherical fragment of the hexagonal crystal phase of the wurtzite type CdS was taken as the initial structure for the optimization [31]. The CdS particle with a diameter of  $\sim 2$  nm (174 atoms) was put into a hexagonal cell with the parameters  $a = b = 3.2$  nm,  $c = 3.9$  nm, in such a way that to eliminate the effects of nanoparticles of the neighboring cells. The Perdew–Burke–Ernzerhof (PBE) exchange-correlation potential and the plane wave basis set with the upper energy boundary at 340 eV was chosen for the optimization.

The XANES spectra were calculated for the initial and optimized structures of the studied CdS-based quantum dots. The XANES spectra above the cadmium *K*-edge of the CdS particle were calculated based on the real-space full multiple scattering method implemented within the FEFF9.6.4 program package [32, 33] and by the finite-difference method implemented within the FDMNES program package [34]. The FEFF program uses already the *muffin-tin* approximation [35] for the potential shape. The advantage of the FDMNES program package is a possibility to perform the full potential calculations (beyond the *muffin-tin* approximation for a potential shape). The Cd *K* XANES spectra were calculated using the model of the Hedin-Lundqvist exchange-correlation potential. The calculations were carried out with regard to the core vacancy created due to the electron transition.

## RESULTS AND DISCUSSION

In the present work, we have studied the atomic and electronic structure of the quantum dots based on the CdS particles of different sizes using the computer modeling.

At the first stage, we have studied the small-scale CdS particles. We have calculated the electronic structures and carried out the optimization of the atomic geometry of CdS particles consisting of 29 atoms ( $\text{Cd}_{13}\text{S}_{16}$ ) and 123 atoms ( $\text{Cd}_{55}\text{S}_{68}$ ) based on DFT implemented within the ADF program package (see Calculation Procedure). The spherical fragments of the cubic phase of CdS were used as the initial structure for the optimization [22]. Fig. 1 shows a schematic representation of the initial and optimized structures of the CdS particle (29 atoms). The optimization of the atomic structure of  $\text{Cd}_{13}\text{S}_{16}$  has demonstrated the following changes in the interatomic distances: an 0.15 Å increase (from 2.52 Å to 2.67 Å) for Cd–S and an 0.25 Å increase (from 4.11 Å to 4.36 Å) for S–S, and an 0.08 Å decrease (from 4.11 Å to 4.03 Å) for Cd–Cd.



**Fig. 1.** Schematic representation of the CdS nanoparticle structure (29 atoms) before the optimization of the atomic structure (a) and after the optimization of the atomic structure obtained with the ADF program package (b). Cd atoms are shown as large balls; S atoms are shown as smaller balls.

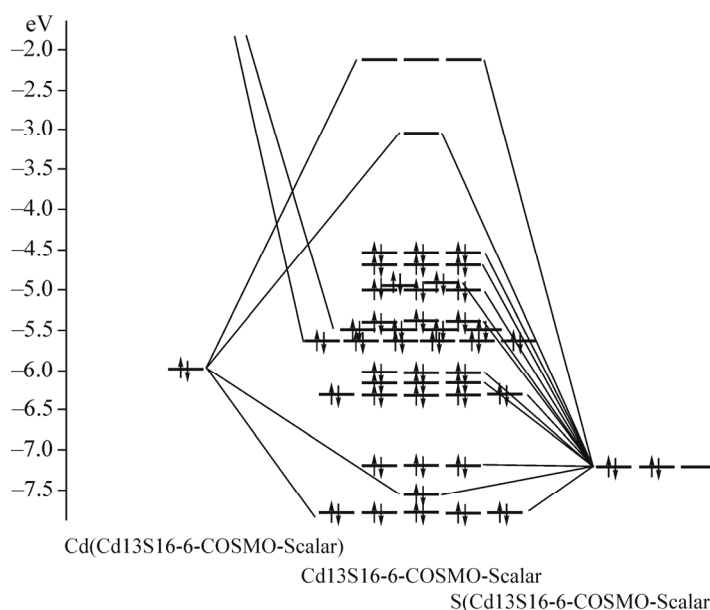
Fig. 2 shows a scheme of the energy levels of the CdS nanoparticle consisting of 29 atoms ( $\text{Cd}_{13}\text{S}_{16}$ ). The energy difference between the highest occupied and lowest unoccupied molecular orbitals (the HOMO-LUMO gap) for the  $\text{Cd}_{13}\text{S}_{16}$  cluster was 1.49 eV. However, it must be taken into account that the DFT method, as a rule, underestimates the Homo-Lumo gap [36].

Fig. 3 gives a schematic representation of the initial structure of the CdS particle consisting of 123 atoms ( $\text{Cd}_{55}\text{S}_{68}$ ), and of the structure obtained as a result of the optimization of the atomic geometry.

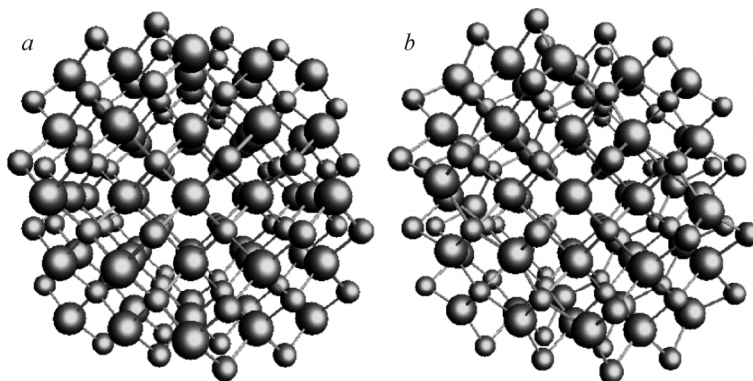
At the next stage, we have studied larger CdS nanoparticles. We have carried out the calculation of the electronic structure and the optimization of the atomic geometry of the CdS nanoparticle consisting of 174 atoms using the VASP5.3 program package within DFT with regard to periodic boundary conditions.

Fig. 4 shows a schematic representation of the initial structure of the CdS nanoparticle before the optimization of the atomic geometry (a) and of the structure of the CdS particle obtained as a result of the optimization (b).

XANES [37] is an efficient modern method allowing to obtain, with a high degree of accuracy, information about the electronic subsystem and the local atomic structure (bond lengths and bond angles) around the atoms of the studied type



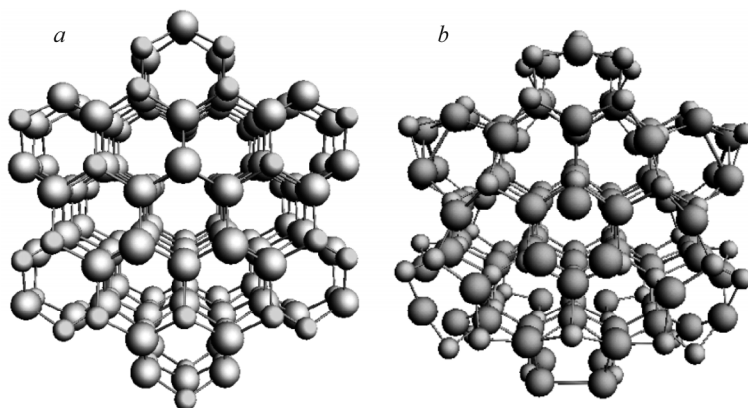
**Fig. 2.** Scheme of the energy levels of the CdS nanoparticle consisting of 29 atoms ( $\text{Cd}_{13}\text{S}_{16}$ ) and the spatial distribution of electron states at HOMO and LUMO orbitals



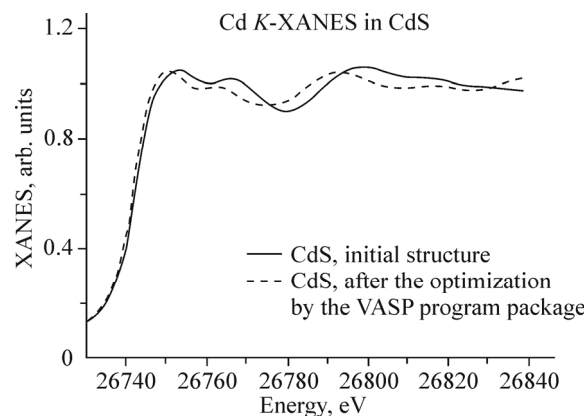
**Fig. 3.** Schematic representation of the CdS nanoparticle structure (123 atoms) before the optimization of the atomic structure (*a*) and after the optimization of the atomic structure by the ADF program package (*b*). Cd atoms are shown as large balls; S atoms are shown as smaller balls.

in materials in the condensed state, including also atoms without the long-range ordering. Thus, the bond lengths can be determined by the XANES spectroscopy with the accuracy to 0.01 Å, and the bond angles can be determined with the accuracy up to several degrees [38]. One of the main advantages of the X-ray spectroscopy method is the possibility to study the environment of atoms of various types in the material. XANES spectroscopy can be applied to materials of any type, including crystalline, amorphous solids, liquids, and nanostructures. However, the method to obtain structural information from the XANES spectra is indirect and requires to carry out complicated theoretical calculations, often with the use of supercomputers and high performance computing clusters. Nevertheless, recently, XANES spectroscopy was successfully used to investigate the atomic and electronic structure of nanosized objects [39, 40].

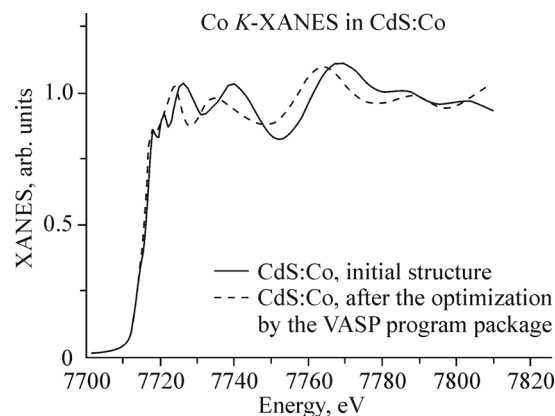
In the present work, the calculations of the XANES spectra above the cadmium *K*-edge in the CdS particle are presented. The calculations were based on the method of full multiple scattering in free-space implemented within the FEFF program package. The theoretical Cd*K* XANES spectra of the structures of the CdS particle before the optimization of the atomic geometry and after the optimization are compared in Fig. 5; Fig. 6 shows the Co*K* XANES spectra calculated for the initial and optimized structures of the CdS particle, where one of the central cadmium atoms is replaced by a cobalt atom. In



**Fig. 4.** Schematic representation of the CdS nanoparticle structure (174 atoms) before the optimization of the atomic structure (*a*) and after the optimization of the atomic structure by the VASP5.3 program package (*b*). Cd atoms are shown as large balls; S atoms are shown as smaller balls.



**Fig. 5.** Theoretical CdK XANES spectra of the CdS nanoparticle (174 atoms) calculated with the real-space full multiple scattering method using the FEFF program package. The solid line corresponds to the XANES spectrum calculated for the initial structure; the dashed line shows the XANES spectrum calculated for the CdS structure obtained as a result of the optimization using the VASP5.3 program.



**Fig. 6.** Theoretical CoK XANES spectra of the CdS quantum dot doped with Co. The spectra are calculated based on the real-space full multiple scattering method using the FEFF program package. The solid line corresponds to the XANES spectrum calculated for the initial structure of CdS, where the central absorbing atom is replaced by the Co atom. The dashed line shows the XANES spectrum calculated for the optimized (VASP5.3) structure of CdS.

Figs. 5 and 6, one can see that the XANES spectra of the CdS and CdS particles doped with Co are sensitive to minor changes in the atomic structure of the particles. Thus, at the subsequent stages of the investigation this makes relevant the measurements the XANES spectra of synthesized quantum nanoobjects of the type of colloidal semiconductor quantum dots with the aim to obtain information about their atomic structure.

## CONCLUSIONS

In the present work, we have carried out the *ab initio* computer design of the CdS-based quantum dots and CdS quantum dots doped with cobalt atoms using two approaches. We have studied the features of the atomic and electronic structure of the semiconductor colloidal quantum dots based on CdS of different sizes, and we have estimated the effects of the cobalt impurity atom. We have proved the sensitivity of XANES spectroscopy for the verification of the nanosized atomic structural parameters determined by the methods of computer modeling for small-scale quantum dots of the CdS family, and for determining the parameters of the local environment of the cobalt atom in the quantum dot.

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