

Internal structure of CdSe quantum dots as derived from total scattering analysis

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Material

Colloidal Quantum Dots (QD) were synthesized using a typical route in non-polar environment [1]. Samples of CdSe nanocrystals (2.5-3 nm in diameter) coated with up to 5 molecular layers of CdS or ZnS were examined.

Diffraction experiment

Structural analysis was based on diffraction patterns collected up to Q_{\max} of 22 \AA^{-1} using Bruker D8 Advance diffractometer equipped with Ag sealed tube.

Photoluminescence

CdSe quantum dots are of interest because of their intense photoluminescence. Fig.2 shows PL spectra of CdSe/ZnS QDs and the dependence of the positions of the PL lines on the number of molecular layers of ZnS covering CdSe core. The PL lines shift towards longer wavelength, which is believed to be caused by the increase of the grain size. The present work shows that the covering material, either ZnS or CdS, does not show up in diffraction. Therefore it is not the size of CdSe but, rather, the overall size of the CdSe/CdS, CdSe/ZnS particles decides on the PL wavelength, without regard to the specific atomic structure of the material covering the CdSe core.

X-Ray data elaboration

A new methodology of elaboration of experimental inter-atomic Pair Distribution Function (PDF) was applied. It is based on the assumption that in actual nanocrystals there exists some modulation of atomic density extending from the surface towards the bulk [2]. Such modulation changes average interatomic distances in a nanocrystal and, therefore, affects the positions of the peaks in PDF. That results in differences between lattice parameters calculated at different r -intervals. We examined the experimental PDFs in search for relative displacement of the r -peaks from the positions they would have had if the crystal structure of QD-s were perfectly periodic.

Simulations and data analysis was performed using computer program NanoPDF developed specifically for those tasks [3]. Tentative models of real atomic architecture of CdSe QD-s. are proposed based on comparison of values of lattice parameters calculated for different parts of experimental $G(r)$ functions, Fig.3. Results of the calculations are presented in a form of $\delta(r)$ -functions:

Experiment: $\delta(r) = [1 - \alpha p(r)]/a_0$, where

$\alpha p(r)$ is the lattice parameter calculated from $G(r)$ for a given r -interval with the average value of r_i

a_0 is the lattice parameter of a reference structure with the perfect crystal lattice,

x is the length of the r -distances for which $\alpha p(r)$ values are calculated.

The experimental $\delta(r)$ functions were compared to theoretical $\delta(r)$ plots derived for atomistic models of CdSe nanograins with a given diameter:

Theory (model): $\delta(r) = \langle r_i \rangle / r_{i,0} - r_i / r_{i,0}$, where

$\langle r_i \rangle$ is the average interatomic distance r_i calculated for a model with density modulation, $r_{i,0}$ is the corresponding inter-atomic distance in the reference crystal lattice.

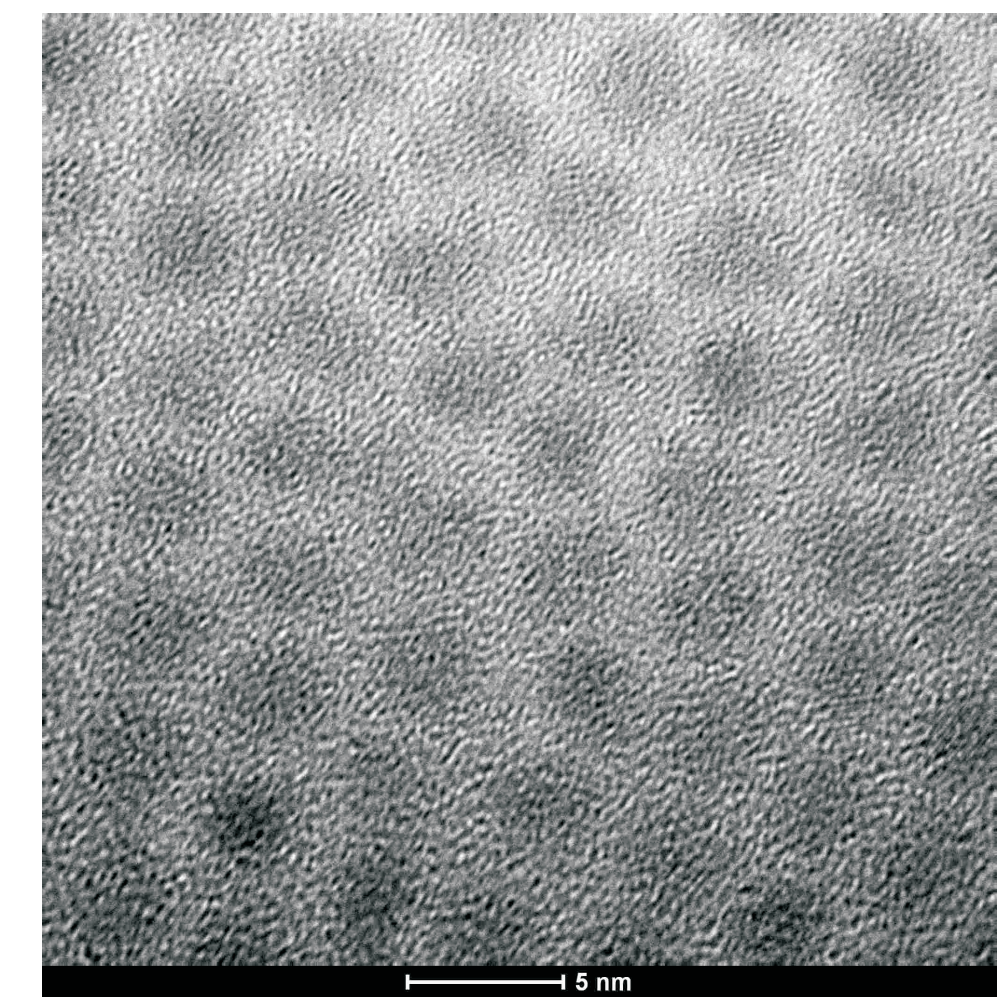


Fig.1. TEM image of CdSe QDs covered by 5 molecular layers of CdS

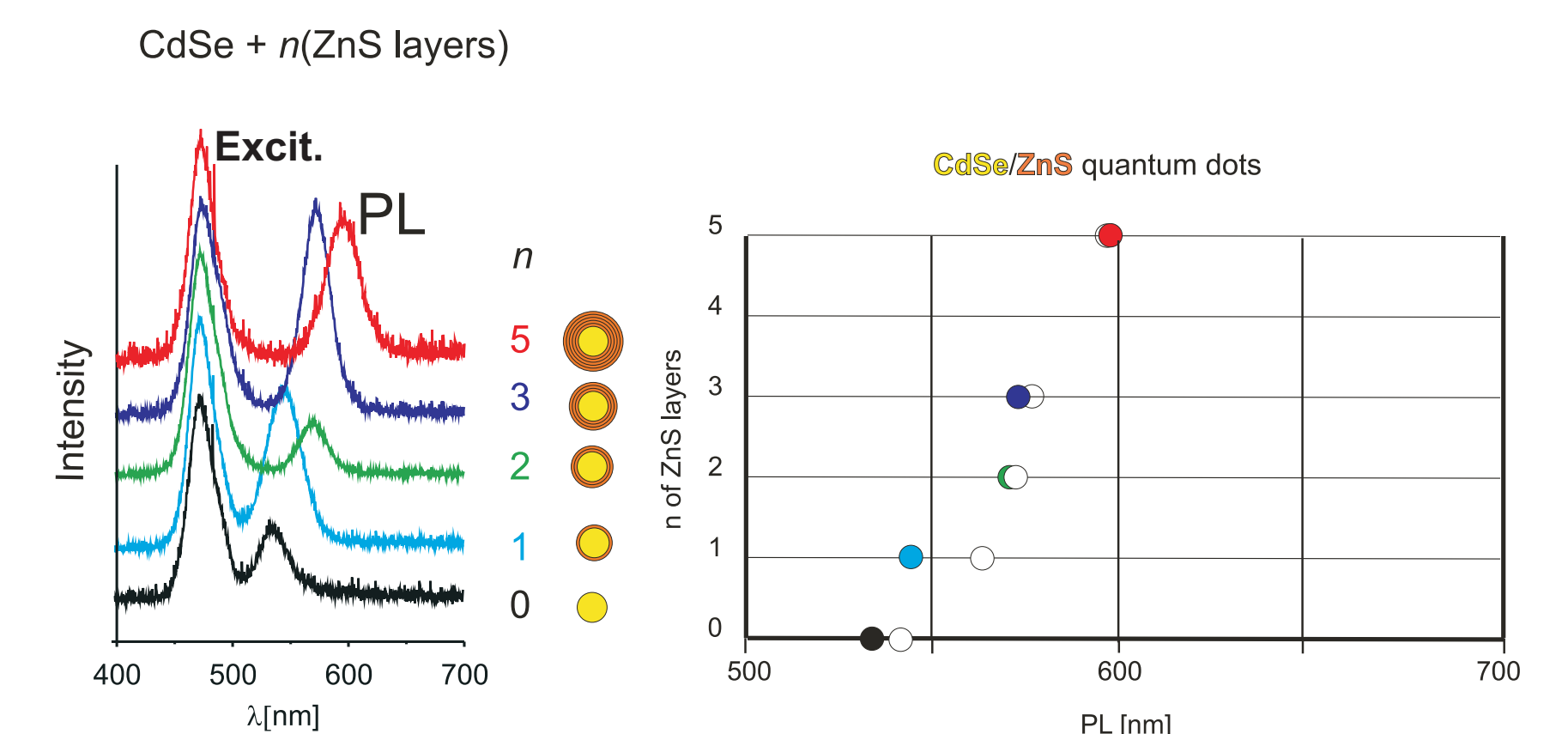


Fig.2. Positions of PL peaks of CdSe/ZnS QDs measured just after synthesis (open circles) and several months later (colored circles).

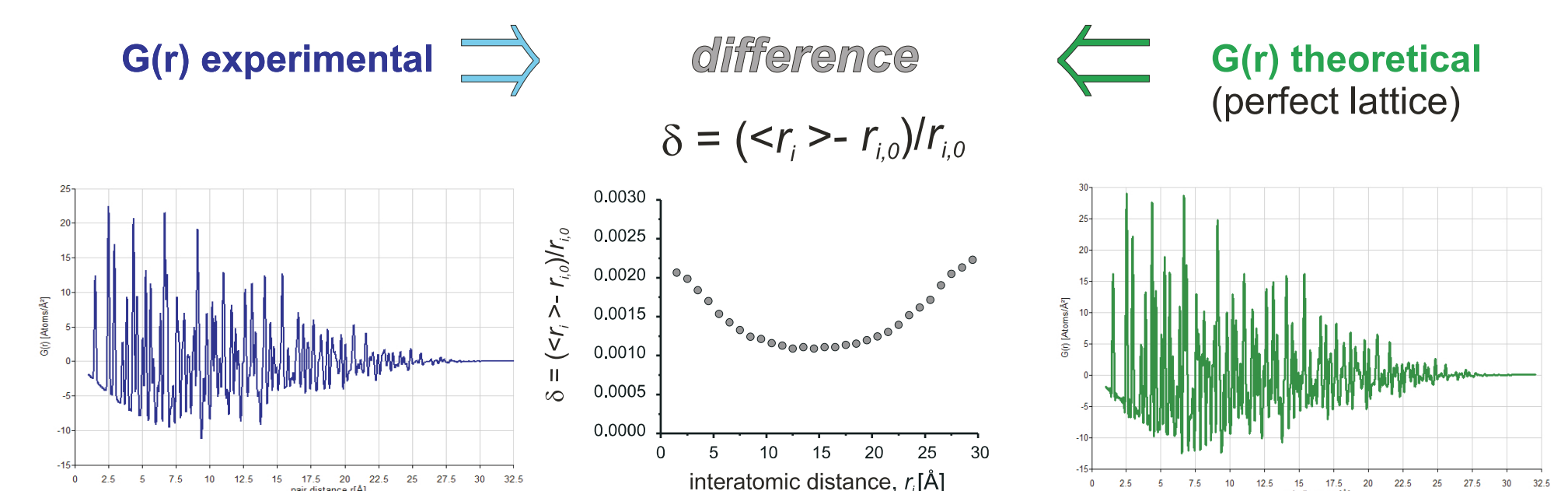


Fig.3. Procedure of derivation of $\delta(r)$ function from inter-atomic Pair Distribution Function (PDF); Note: theoretical $\delta(r)$ function can be derived in the same way by comparison of $G(r)$ of a model to $G(r)$ of a perfect crystal lattice

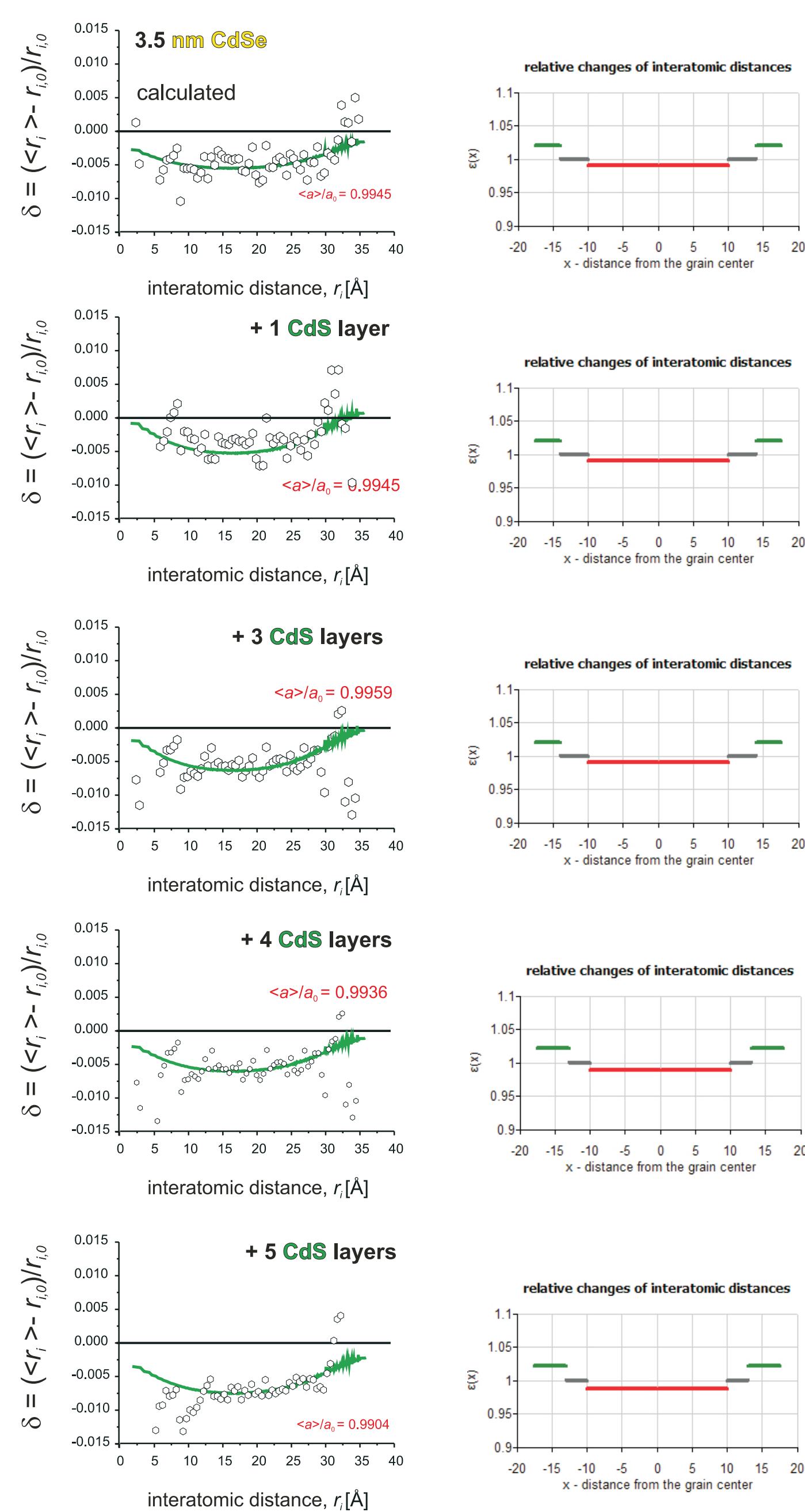


Fig.8. Experimental $\delta(x)$ plots of CdSe/CdS QDs with up to 5 molecular layers and corresponding model of the internal structure of CdSe core.

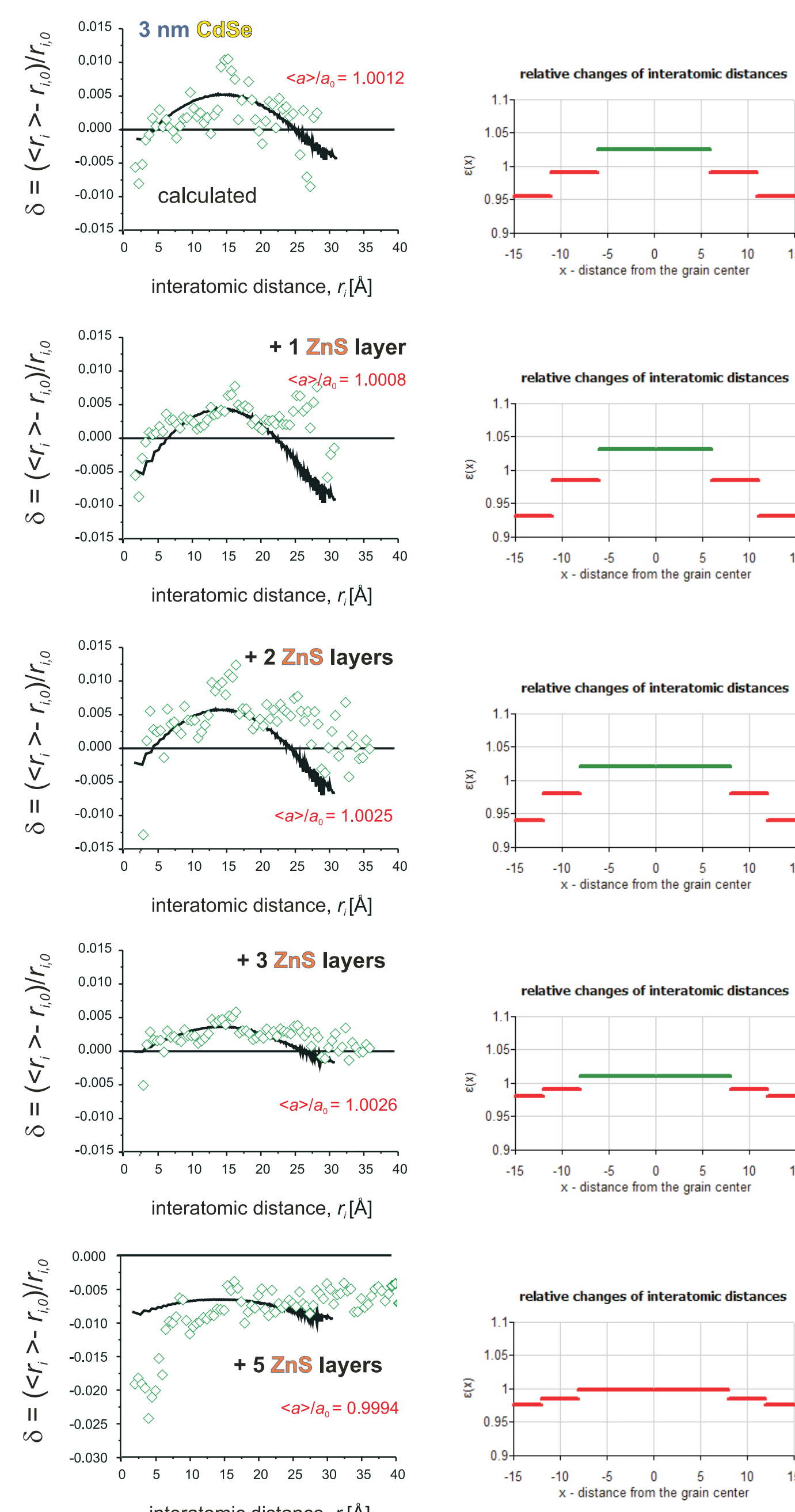


Fig.9. Experimental $\delta(x)$ plots of CdSe/ZnS QDs with up to 5 molecular layers and corresponding model of the internal structure of CdSe core.

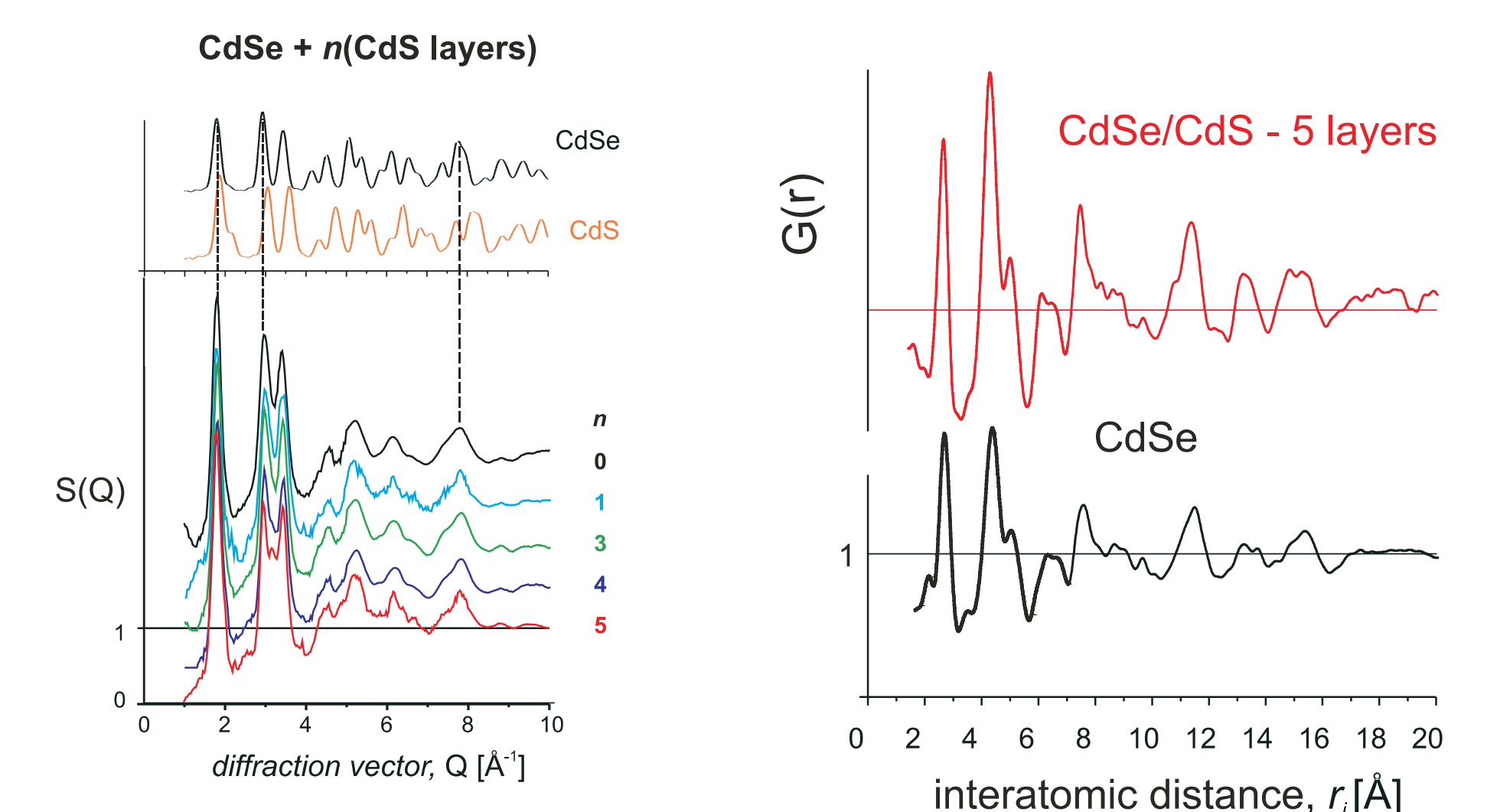


Fig.4. Experimental structure factor $S(Q)$ of CdSe samples covered with up to 5 molecular layers of CdS.

Fig.5. Experimental $G(r)$ plots of CdSe covered with 5 molecular layers of CdS.

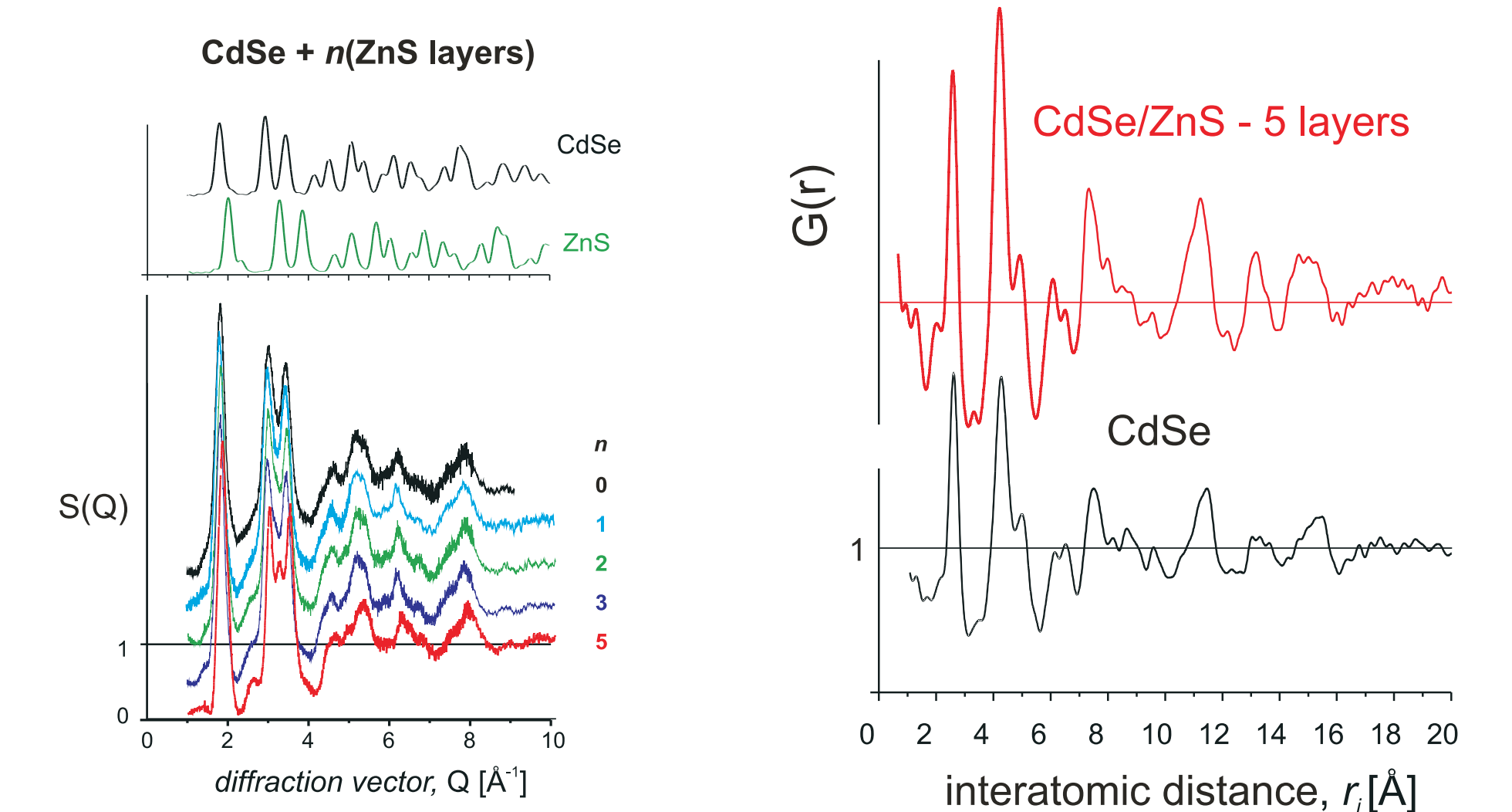


Fig.6. Experimental structure factor $S(Q)$ of CdSe samples covered with up to 5 molecular layers of ZnS.

Fig.7. Experimental $G(r)$ plots of CdSe covered with 5 molecular layers of ZnS.

Results - Internal structure of QDs

The structure of CdSe core is intermediate between cubic and hexagonal; it contains between 40 and 50% of the hexagonal layers.

On diffraction patterns of the examined CdSe samples Fig.4 and Fig.6 covered with up to 5 molecular layers of CdS or ZnS, the Bragg peaks of these materials do not show. This means that the CdSe quantum dots are covered by non-crystalline CdS and ZnS shells. Similarly, there is no indication of a presence of crystalline CdS and ZnS on corresponding $G(r)$ plots, Fig.5 and Fig.7.

Based on the comparison of experimental and theoretical $\delta(x)$ functions here we propose models describing the internal structure of CdSe, Fig.8 and Fig.9.

Note: on the plots presented in Fig.8 and Fig.9 a strong dispersion of inter-atomic distances is observed, particularly in the small r -values range. This comes from a presence of ligands and coverage materials. Since they show only a short range order, additional r -distances appear mostly at the low r -values range. Their appearance makes interpretation of the experimental $\delta(x)$ functions troublesome and not fully unique. However, since overall shape of the $\delta(x)$ plots is apparently reproduced for all samples of the CdS and ZnS series, we are convinced that they reflect their internal structure properly.

The internal structure of CdSe core is different in the CdSe/CdS than in CdSe/ZnS samples. (We have no explanation for this observation since in both cases similar synthesis conditions were applied.) The CdSe core in the CdSe/CdS sample shows average lattice parameter smaller than that in a perfect CdSe crystal lattice, while it is larger in the sample covered by ZnS layers. This obviously is related to the presence of strains at the surface. An appearance of tensile-type strain at the surface of CdSe (CdSe/CdS samples) leads to the appearance of compressive strain in the grain core. And, similarly, an appearance of compressive strain at the surface of CdSe in CdSe/ZnS samples leads to expansion of CdSe lattice in the grain core.

Presence of external shell of CdS or ZnS has only a small effect on the internal structure of the CdSe core; it does not change relative strains in the CdSe grain volume; it only leads to a small decrease of the average lattice parameters of CdSe.

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