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PbSe quantum dots: Finite, off-stoichiometric, and structurally distorted

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PbSe quantum dots with sizes of 2.8(1), 3.7(1), and 6.2(1) nm, freely suspended in solution, have been studied by high-energy x-ray diffraction coupled to atomic pair-distribution-function analysis and computer simulations. The atomic-scale structure of the quantum dots is best described by 371-, 763-, and 4084-atom configurations, respectively, that are substantially off-stoichiometric and structurally distorted. It is argued that such finite-size, "large-molecule-type" structure models and not quasi-infinite ones based on periodic crystalline lattices are better to be used when the properties of a few nanometer-sized materials, in particular, those of PbSe quantum dots, are to be explained in full detail.

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Nanosized materials are, with their limited physical dimensions, often off-stoichiometric[1–3] and structurally distorted.[4] This is, however, barely taken into account when their properties are considered in terms of atomic-scale structure models since those usually feature nearly perfect crystalline lattices with the stoichiometry and unlimited periodicity of the corresponding bulk materials. Not surprisingly, many aspects of the physicochemical and optoelectronic properties of nanosized materials cannot be explained on the basis of such a simplistic approximation.

A typical example is semiconductors, in particular, PbSe, quantum dots (QDs). Spatial confinement of charge carriers in a few nanometer-sized QDs renders their electronic properties QD-size dependent, offering very good potential for various applications, ranging from solar cells to quantum computing and biomedical imaging (Refs. 5–7 and references therein). Bulk PbSe is a cubic, rocksalt-type structure IV-VI semiconductor material and has a narrow band gap of ~280 meV at room temperature. The band gap of PbSe QDs can be tuned continuously from the bulk value to more than 1 eV when their size is reduced from a few tens of nanometers down to 1–2 nm.[1,8,9] This has inspired numerous theoretical and experimental studies aimed at understanding and, hence, gaining control of the optical properties of PbSe QDs. Despite the extensive research effort, prominent features in the optical absorption spectra of PbSe QDs, e.g., the second absorption peak, remains a mystery that contradicts basic quantum-mechanical principles. It has been suggested[6] that this contradiction may be explained only if the selection rules imposed by the PbSe cubic lattice symmetry are broken in a few nanometer-sized QDs to allow forbidden optical transitions, though the rationale for such a symmetry breaking has remained unclear. By using high-energy x-ray diffraction (XRD) coupled to atomic pair-distribution-function (PDF) data analysis and computer modeling we show that, at the atomic scale, PbSe QDs are substantially off-stoichiometric and structurally distorted. We argue that these intrinsic characteristics of PbSe QDs, together with their finite size, can and should be explicitly incorporated in their structure models so that the QD properties are understood in full detail.

PbSe QDs were obtained as follows: 0.38 g of lead acetate, 1.3–2.6 mL of oleic acid and 6.3 mL of diphenyl ether (DPE) were mixed in flask 1; 0.8 g of Se powder and 10 mL of tri-n-octyl phosphine-in flask 2. Both flasks were heated to 150 °C for one hour and then cooled down to room temperature. After that the contents of flasks 1 and 2 were mixed in due proportions and the mix injected into a third flask containing 10 mL of DPE at 175 °C. The temperature was then dropped to 135 °C and the reaction let to continue from 0.25 to 20 min to obtain PbSe QDs with sizes ranging from about 2 nm to 8 nm, respectively. The resulting spherical and almost monodisperse QDs were extracted via centrifugation and stored in toluene. More details of the preparation procedure, sample purity, composition, and QD-size determination may be found in Ref. 1.

High-energy XRD experiments on 2.8(1)-, 3.7(1)-, and 6.2(1)-nm PbSe QD suspended in toluene were performed at the beam line 11IDC, at the Advanced Photon Source, Argonne using x-rays of energy 115 keV ($\lambda = 0.1078$ Å). The diffraction data were reduced to the so-called structure factors, $S(q)$, and then Fourier transformed to the corresponding atomic PDFs $G(r)$, using the relationship

$$G(r) = \frac{2}{\pi}\int_{q=0}^{q_{\max}} q[S(q) - 1]\sin(qr)dq, \qquad (1)$$

where $q_{\max} = 25$ Å^{-1} in the present experiments. The wave vector q is defined as $q = 4\pi \sin(\theta)/\lambda$, where θ is half of the scattering angle and λ is the wavelength of the x-rays used. Note, as derived, atomic PDFs $G(r)$ are experimental quantities that oscillate around zero and show positive peaks at real space distances, r, where the local atomic density $\rho(r)$ exceeds the average one ρ_o. This behavior can be expressed by the equation $G(r) = 4\pi r\rho_o[\rho(r)/\rho_o - 1]$, which is the formal definition of the PDF $G(r)$. High-energy XRD and atomic PDFs have already proven to be very efficient in studying the atomic-scale structure of nanosized materials.[10]

As can be seen in Fig. 1(a) the experimental PDFs for PbSe QDs exhibit a series of well-defined peaks. The first PDF peak is located at approximately 3.02(2) Å and the second at 4.32(2) Å. These are the shortest Pb-Se and Pb-Pb distances, respectively, found in bulk PbSe. This indicates

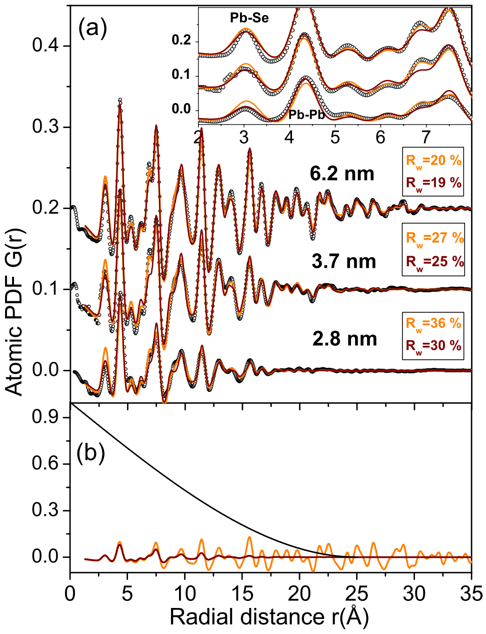

FIG. 1. (Color online) Experimental atomic PDFs (symbols) for PbSe QDs. Also shown are model PDFs for fully stoichiometric (orange/light gray line) and Se deficient (wine/dark gray line) PbSe cubic lattices with the respective agreement factors R_{wp}. The low-r part of the PDFs is given in the inset (a). The model PDFs (wine/dark gray line) are computed by multiplying a PDF for an infinite cubic lattice (orange/light gray line) by a QD-size and shape-dependent, rapidly decaying function (Ref. 13) as illustrated in (b).

that the atomic ordering in PbSe QDs and that in bulk PbSe are of a similar, rocksalt type. As it is to be expected the PDFs for the larger-size QDs exhibit peaks up to longer real-space distances. Yet, in all cases, the experimental PDFs decay to zero at distances much shorter than the respective QD size. This shows that the rocksalt-type ordering in PbSe QDs is substantially distorted. Note that structural distortions in nanosized materials are not uncommon. They may be understood in terms of the famous "uncertainty principle:" in this case it is an increase in the atomic positional disorder in physical systems of very limited dimensions.[4,11] Following the currently adopted approach[12] a structure model for PbSe QDs can be built and tested against the experimental PDF data by considering a small piece (usually the unit cell) of a crystalline, in our case rocksalt type, lattice, replicating it in all directions by applying of periodic boundary conditions and computing the respective PDF. The presence of both usual thermal disorder and extra structural distortions in nanosized QDs is taken into account by broadening the PDF peaks. The PDF for such a model of unlimited translational periodicity, however, shows peaks to very high, in theory unlimited, interatomic distances and cannot be directly compared to the experimental data. To take into account the finite QD size and their spherical shape, the model PDF is multiplied by a rapidly decaying function[13] which is essentially zero for distances exceeding the QD size, as exemplified in Fig. 1(b). Undoubtedly this modeling approach is a simplistic approximation to the structure of finite-size PbSe QDs, but is still useful since it allows determining their atomic-scale structure, including obtaining a set of structural parameters (e.g., lattice constants) that may be compared directly with those of the corresponding bulk material. In particular, results shown in Fig. 1(a) indicate that the atomic-scale structure of 2.8(1), 3.7(1), and 6.2(1) PbSe QDs may be described in terms of a cubic lattice with a constant a of 6.17(1) Å, 6.15(1) Å, and 6.14(1) Å, respectively. For reference the lattice constant of bulk PbSe is $a=6.12(1)$ Å. The results of this modeling approach (i) verify that the atomic ordering in PbSe QDs is of the cubic rocksalt type found in bulk PbSe and (ii) show that PbSe QD "lattice" constant differs from the bulk value and the difference increases with decreasing QD size (e.g., $\Delta a \sim 0.02$ Å for 6.2-nm QDs vs $\Delta a \sim 0.05$ Å for 2.8-nm QDs). The agreement between this quasi-infinite, lattice-type model and the experimental PDFs, however, is not very good especially in the vicinity of the PDF peaks (e.g., the first PDF peak) reflecting correlations involving Se atoms. The overall agreement between the model and experimental PDFs improves somewhat [compare the corresponding goodness-of-fit factors R_w in Fig. 1(a)] when the positions of the Se atoms in the model cubic lattice are only "partially" occupied. Results from thus modified modeling indicate that the Pb/Se ratio in 2.8(1) nm, 3.7(1) nm, and 6.2(1) nm QDs is 1.7(1), 1.5(1), and 1.3(1) respectively, i.e., that (iii) PbSe QDs are substantially off-stoichiometric and the off-stoichiometry increases with decreasing QD size. The improved overall agreement, however, comes together with an increased misfit between several peaks in the model and experimental PDFs [e.g., the PDF peak at 7 Å in the inset in Fig. 1(a)] indicating that the Se deficiency of PbSe QDs does not relate to their atomic-scale structure in a uniform way.[14] As shown below, the way the

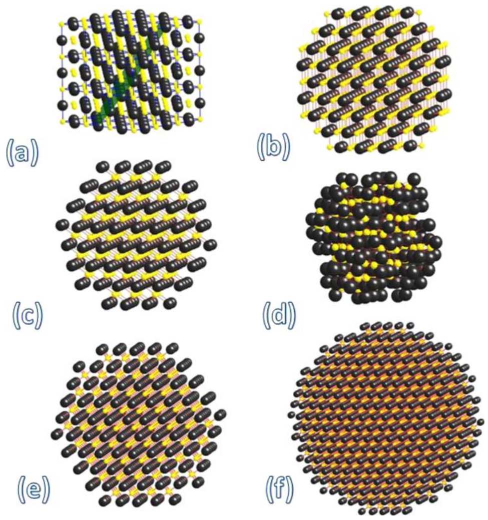

FIG. 2. (Color online) Fragment from the infinite cubic lattice (broken lines) of bulk PbSe terminated with {100} facets; (a) one of the {111} atomic planes is shown in green; (b) 2.8-nm PbSe QD terminated with {100} and {111} facets occupied by both Se and Pb atoms; (c) 2.8-nm PbSe QD terminated with {100} and {111} facets occupied by Pb atoms only; and (d) a snapshot of (c) with the atomic site specific disorder included. (e) 3.7- and (f) 6.2-nm PbSe QDs terminated with {100} and {111} facets occupied by Pb atoms only. Pb atoms are in black and Se atoms in yellow (light gray).

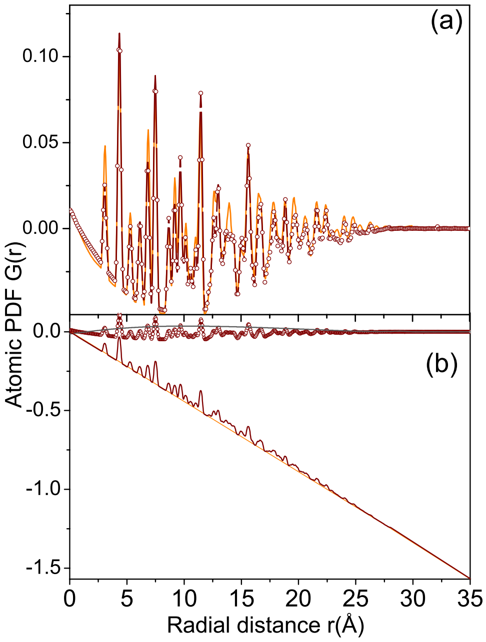

FIG. 3. (Color online) Model atomic PDFs $G(r)$ for finite size 2.8-nm PbSe QDs shown in Fig. 2(b) (orange/light gray line) and Fig. 2(c) (symbols). A model PDF for a single QD in vacuum (wine/dark gray line) does not oscillate around zero as demonstrated in (b). It does (symbols) when a base line$=-4\pi\rho_o^* r$ (orange/light gray line) and a bumplike correction (thin black line) are added to it following a procedure (Ref. 15) described in the text.

PbSe QDs small physical size, spherical shape, and essential structural characteristics (i)–(iii) coexist together becomes much clearer when nonlattice-type models are considered.

Finite-size structure models for PbSe QDs were built following an approach suggested in Ref. 15 and illustrated in Fig. 3. As a first step 2.8-, 3.7-, and 6.2-nm configurations of Pb and Se atoms, arranged according to the rules of a rocksalt-type lattice, were generated. In each of the cases the respective lattice constant a was used. To achieve the experimentally observed spherical shape of PbSe QDs, the model atomic configurations had to be terminated by at least two families of atomic planes, in particular, {100} and {111}, from the rocksalt-type lattice. A termination with only {100} or {111} atomic planes results in QDs with a highly asymmetric shape which is not observed with our samples.[1] In line with experimental observations[16] the ratio of {100} to {111} facets was found to increase with the size of the QD being modeled. Note, as built, the initial atomic configurations reflect the Pb/Se=1 stoichiometry of an ideal rocksalt lattice. Accordingly, their surface is occupied both by Pb and Se atoms [see Fig. 2(b)]. The substantial off-stoichiometry of PbSe QDs suggested by the present and previous studies[1] cannot be accommodated by introducing a corresponding number of Se vacancies (e.g., 43 % in the case of 2.8-nm QDs) inside the model atomic configurations. This would result in a very pronounced "swiss-cheese-type" morphology which is not seen in real QDs.[1] Besides, the lattice-type modeling already indicated that the Se deficiency across PbSe QDs is not uniform. It can, however, be easily accommodated by stripping the model's surface of Se atoms as shown in Fig. 2(c).

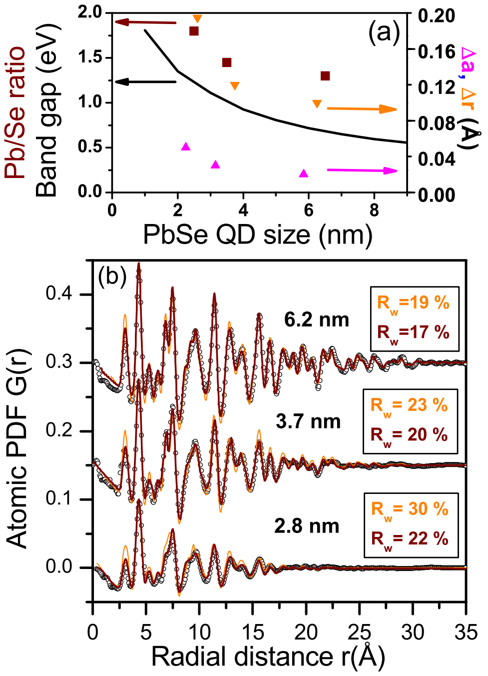

FIG. 4. (Color online) Experimentally observed change of the band gap of PbSe QDs with their size (full line). (a) Also shown are the Pb/Se ratio (wine squares) and extra structural distortions expressed in terms of uniform lattice dilatation Δa (magenta up triangles) and individual atomic displacements Δr (orange down triangles) as determined by the present structure studies. Experimental (symbols) atomic PDFs for 2.8(1)-, 3.7(1)-, and 6.2(1)-nm PbSe QDs. (b) Also shown are model PDFs for fully stoichiometric (orange/light gray line) and off-stoichiometric (wine/dark gray line) finite-size models of PbSe QDs with the respective agreement factors, R_w. The model PDFs are computed from the atomic configurations shown in Figs. 2(c), 2(e), and 2(f) subjected to extra structural distortions as described in the text.

A model PDF for a finite-size atomic configuration, however, would not oscillate around zero and, hence, cannot be directly compared with the experimental PDF data. This is since the former features a single QD in vacuum while the latter shows the structural features of an "assembly averaged" QD suspended in a solution of many uncorrelated QDs all constituting an infinite but structureless medium of average nonzero density ρ_o. To take into account the nonzero-density, structureless environment of real QDs, a straight line with a slope $-4\pi\rho_o r$ and a smaller in magnitude but important bumplike correction[15] are added to the model PDF for a finite QD [see Fig. 3(b)]. Thus computed model PDF oscillates around zero [see Fig. 3(a)] and can be directly compared with the experimental PDF data, allowing testing and refinement of the respective structure model.

Figure 3(a) shows model atomic PDFs for fully stoichiometric [see Fig. 2(b)] and Se-deficient surface [see Fig. 2(c)] 2.8-nm QDs which, as constructed initially, show no extra structural but only the usual thermal disorder. The PDFs exhibit peaks up to a distance of 2.8 nm which is exactly the physical size of the model atomic configurations. As it can be expected, the two PDFs show systematic differences in the vicinity of peaks reflecting correlations involving Se atoms with the PDF of the configuration with a Se-deficient surface being much more in line with the experimental PDF data. Therefore, the atomic configuration with a Se-deficient surface was pursued as a model for 2.8(1)-nm QDs. Structure models with Se-deficient surfaces were pursued for 3.7(1)- and 6.2(1)-nm QDs as well [see Figs. 2(e) and 2(f)]. The number of Se vacancies on the model's surfaces and the atomic positions were refined against the respective experimental PDF data using a reverse Monte Carlo-type procedure; results are shown in Fig. 4(b). As can be seen in the figure the experimental PDF data for 2.8(1)-, 3.7(1)-, and 6.2(1)-nm PbSe QDs are very well reproduced by structure models with a nominal composition of $Pb_{236}Se_{135}$ (Pb/Se =1.75), $Pb_{466}Se_{297}$ (Pb/Se=1.56) and $Pb_{1155}Se_{887}$ (Pb/Se =1.30), respectively. The models possess a rocksalt-type structure but are "Se-deficient" since their surface is terminated by Pb atoms only. In this respect, the PbSe QDs studied here may be viewed as nanosized particles with a fully stoichiometric (Pb/Se=1) core, wrapped with a single atomic layer of Pb atoms. Both Se and Pb atoms in the refined finite-size models are substantially displaced from their positions in an ideal rocksalt-type structure [compare the initial and refined structure models for 2.8-nm PbSe QDs shown in Figs. 2(c) and 2(d), respectively]. The average amplitude of the individual atomic displacement in 2.8(1)-, 3.7(1)-, and 6.2(1)-nm PbSe QDs amounts to $\Delta r \sim 0.2$ Å, 0.12 Å, and 0.1 Å, respectively. It exceeds the usual atomic displacement in bulk PbSe due to thermal disorder (~0.02 Å) (Ref. 17) and is responsible for the substantially reduced length of structural coherence in all PbSe QDs studied here.

In summary, the results from the present structural study show that 2.8(1)-, 3.7(1)-, and 6.2(1)-nm PbSe QDs are substantially off-stoichiometric and structurally distorted. This, together with the finite QD size, will inevitable disturb the local cubic symmetry and break the translational periodicity of the underlying rocksalt, cubic-type structure and may be the reason why not all experimentally observed optical properties of PbSe QDs can be accounted for by theoretical calculations based on lattice-type structure models.[6] As a matter of fact, the degree of off-stoichiometry and the structural distortions, both uniform as measured by Δa and atom sites specific as measured by Δr, in a few-nanometer PbSe QDs are size-dependent, just as the optical band gap [Fig. 4(a)]. Obviously, they all coexist and should not be considered separately. A unifying approach would be to adopt finite-size structure models for QDs which can explicitly incorporate and not just approximate their essential structural features. Theoretical attempts along this line have just begun[18–20] but much more is to be done.

On a more general note: evidence is mounting that a few-nanometer-sized materials not only preserve many of the structural features of the corresponding bulk, e.g., its structure type, but also show distinctive ones such as substantial nonuniform stoichiometry and structural distortions, rendering them essentially nonperiodic, i.e., "moleculelike." The apparent duality of nanosized materials brings unusual and very useful properties in the case of semiconductor QDs. Another well-known example is gold which is completely inert in bulk, yet catalytically very active when nanosized.[21] Again, similar to the case of nanosized semiconductors, the unusual properties of nanosized gold are still a mystery. Many more examples could be listed. To improve the situation, the "bulk-molecule" duality of nanosized materials should be paid more attention than now. A step forward will be to start considering them in terms of more appropriate structure models that go beyond the limits of traditional, infinite periodic lattices-based crystallography. The present work shows that such models are within a reach.

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[14] Note a few-nanometer-sized materials may often end up being chemically inhomogeneous since their surface reconstructs, either by design or by self-relaxation, in a way ensuring overall structural and size stability. As a result the surface and bulk stoichiometry may differ substantially.
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