

Structural Disorder in Colloidal InAs and CdSe Nanocrystals Observed by X-Ray Absorption Near-Edge Spectroscopy

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We report the observation of size dependent structural disorder by x-ray absorption near-edge spectroscopy (XANES) in InAs and CdSe nanocrystals 17–80 Å in diameter. XANES of the In and Cd $M_{4,5}$ edges yields features that are sharp for the bulk solid but broaden considerably as the size of the particle decreases. FEFF7 multiple-scattering simulations reproduce the size dependent broadening of the spectra if a bulklike surface reconstruction of a spherical nanocrystal model is included. This illustrates that XANES is sensitive to the structure of the entire nanocrystal including the surface.

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The advent of colloidal methods to prepare high quality inorganic nanocrystals has led to an increasing number of studies of size dependent scaling laws [1]. Because of the finite size of nanocrystals, the structure and composition of their surface may have particular importance for their chemical and physical properties. For instance, nanocrystal growth and manipulation relies heavily on their surface chemistry [2]. The thermodynamic phase diagrams of nanocrystals are strongly modified from those of the bulk materials by the surface energies [3]. The electronic structure of semiconductor nanocrystals is influenced by surface states which lie within the band gap but are thought to be eliminated by surface reconstruction [4]. Thus, for any picture of the physical properties of nanocrystals to be complete, the structure of the surface must be determined.

For bulk solids, surface reconstructions have been well characterized by various techniques. Therefore, the surface structure is known for several types of bulk solids for different crystallographic faces and adsorbate systems [5]. However, determination of nanocrystal surface structure has proven to be particularly difficult. In nanocrystals, the surface consists of a combination of low and high index planes as well as edges and corners. In consequence, long-range mechanical restoring forces, which can play a determining role in bulk surface reconstructions, will be markedly different in nanocrystals. The presence of surface reconstructions on a nanocrystal is plausible, yet it is believed that the surface structure is quite complex in that it influences the crystal lattice throughout the entire particle. Thus, how surface atoms reconstruct to accommodate large surface area in a finite sized, organic surfactant capped particle cannot easily be anticipated [6].

Techniques such as transmission electron microscopy (TEM) and powder x-ray diffraction (XRD) yield much information about the shape of the nanocrystal and the long-range order of the atoms [7–9]. They show that the interior of the noncrystals is crystalline and defect-free, manifesting itself as single nucleation events observed in

structural phase transitions [10]. Furthermore, TEM indicates that CdSe nanocrystals are faceted [8]. However, the structural rearrangements at those faces are still unknown. Powder x-ray diffraction has been used extensively to model the structure of the nanocrystals, and it is possible to obtain fits of XRD patterns by assuming bulk lattice parameters [9]. However, the information content in XRD patterns is limited, particularly with respect to aperiodic parts of the nanocrystal such as the surface. Consequently, apart from a few cases in which single crystal x-ray diffraction patterns of small nanocrystals could be recorded [11], almost no information about the surface structure of nanocrystals is available.

A technique with the potential to measure structural disorder including surface atom configurations in nanocrystals is x-ray absorption spectroscopy (XAS). The cross section of an absorbing atom in XAS depends on the scattering of the generated photoelectron wave from neighboring atoms, thereby including information about the local structure around the absorber [12]. Because of the local nature of this process, XAS does not rely on any long-range order in a sample, in contrast to diffraction techniques. It has been used extensively to investigate the local structure in the interior and at the surface of a variety of solid-state materials, in liquids, gases, and molecular beam clusters [13]. Also, EXAFS (extended x-ray absorption fine structure) has proven to be a valuable tool to investigate surface induced changes in nanocrystals [14].

Whereas EXAFS mainly probes the radial arrangement of neighboring atoms with respect to the absorbing atom, the spectrum within 50 eV above the absorption edge (x-ray absorption near-edge structure, XANES) is sensitive to the relative arrangement of multiple atoms due to the increased contribution of multiple-scattering effects. In principle, one can extract from XANES spectra more complex information such as bond angles instead of an averaged pair distribution function [12]. Therefore, it is in theory more amenable to the modeling of complex

structural rearrangements in nanocrystals than EXAFS. Here we report the measurement of XANES spectra at the In and Cd $M_{4,5}$ edges of InAs and CdSe nanocrystals which exhibit a size dependent broadening that can be explained by surface reconstructions in the nanocrystals.

CdSe and InAs nanocrystals with a mean diameter ranging from 17–80 Å were synthesized according to literature methods [2,15]. The particles are capped with tri-*n*-octylphosphine oxide (TOPO) and tri-*n*-octylphosphine (TOP) in the case of CdSe and InAs, respectively. High-resolution TEM show crystalline, well separated CdSe and InAs particles with wurtzite and zinc blende lattice fringes, respectively, in agreement with corresponding XRD patterns. Submonolayers of particles were deposited onto HF etched Si wafers from toluene solutions. The XANES spectra of the $M_{4,5}$ edge at 405 eV (Cd) and 445 eV (In) were measured in total current yield at the Advanced Light Source Synchrotron, Berkeley, on Beamline 6.3.2. The photon energy was calibrated to the F 1s line in MgF₂ (690 eV). The linewidth for the 3d core level of both In and Cd is estimated at ~300 meV [16] which is the limiting factor in the resolution of the experiment. Note that since we are exciting 3d core electrons we are mapping the local partial density of states with *p* character in the spectra. Therefore, we are *not* exciting into states located at the conduction band edge which are mainly derived from the metal 5s states, but into higher *p* bands that are 2–6 eV above the conduction band minimum.

Figure 1 shows the absorption onset at the (a) Cd and (b) In $M_{4,5}$ edges as a function of size of CdSe and InAs nanocrystals as well as the respective bulk spectrum (bottom). The 3d core in both atoms is spin orbit split by 6.76 and 7.6 eV, respectively, leading to a superposition of the M_4 and M_5 edge spectra. The bulk solids show relatively sharp spectral features. As the size of the particle decreases, the features broaden significantly to the point that for the smallest particle (17 Å for InAs) no splitting within the M_4 or M_5 edge spectra is visible anymore. X-ray photoelectron spectroscopy (XPS) of the In 3d core levels show a slight size dependent shift to higher binding energies and an increase of the spectral linewidth resulting from a decreased core-hole screening in nanocrystals [Fig. 1(c)] [17]. However, the magnitude of this effect (0.5 eV) is negligible compared to the effects seen in the XANES spectra. Therefore, the smearing of the XANES spectrum is not due to the core level from which the electron is ejected (initial state) but the environment of the photoelectron in the crystal (final state).

To gain a qualitative understanding of these data, we have undertaken simulations of the In $M_{4,5}$ edge absorption spectra using a multiple-scattering model recently extended for XANES spectra, FEFF7 [18]. The InAs nanoparticles are modeled as roughly spherical with an excess of In atoms at the surface, in accordance with results from XPS [19]. In the simulations, the two outer-

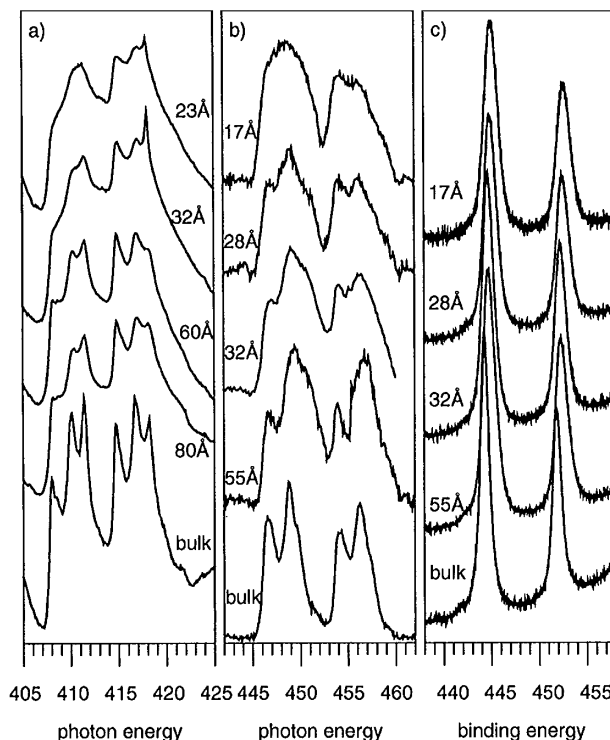


FIG. 1. (a) Cd and (b) In $M_{4,5}$ edge spectra for bulk and a series of particles of CdSe and InAs, respectively. A polynomial background is subtracted. (c) In 3d XPS spectra of InAs nanocrystals and bulk (referenced to Fermi energy).

most layers of In and As atoms are distinguished from those in the interior of the particle by calculation of their muffin-tin potential separately [20]. The absolute energy of the simulated spectra was shifted to match the data at the first spectral feature of bulk (446.5 eV). The calculation included a broadening of 100 meV to account for the experimental resolution and a factor of 300 meV for core-hole broadening. Figure 2 shows simulations (lines) and spectra (dots) of (a) InAs bulk, as well as (b) 28 Å (441 atoms) and (c) 17 Å (99 atoms) diameter InAs nanocrystals with the same lattice parameters as in bulk. In agreement with experiment, the simulated bulk spectrum shows features at 446.5 and 449 eV, though it introduces a broad peak around 460 eV that is not seen in the experiment. For the nanocrystals, the simulation predicts similar results with a slight broadening of the features at 446.5 and 449 eV. However, this broadening is much smaller than observed in the experimental data. Apparently, if the nanocrystal has uniform bulk bond lengths throughout, then the broadening of the spectra in smaller particles is not reproduced. Thus, the observed broadening does not arise simply from the finite number of coherent scatterers, as it does in the case of XRD.

However, by introducing a reconstruction of the surface in spherical 17 and 28 Å InAs nanocrystals (Fig. 3) we observe a broadening of the simulated spectrum comparable to the experiment. We assume a relaxation of the outermost In layer by -0.85 Å (inwards) and

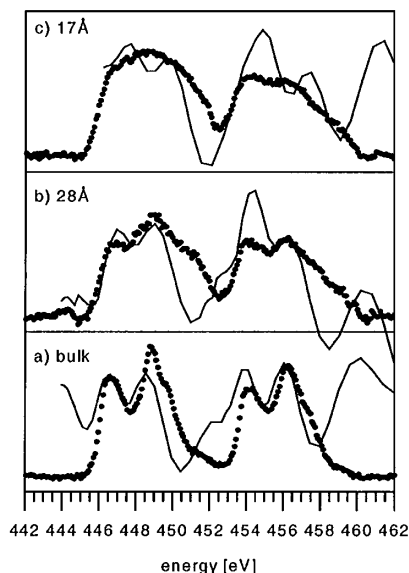


FIG. 2. FEFF7 simulations (lines) of the In $M_{4,5}$ edge XANES spectra for (a) InAs bulk and spherical InAs nanocrystals with bulk lattice parameters with (b) 28 Å (441 atoms), and (c) 17 Å (99 atoms) diameters. The dots are experimental data.

the As layer just beneath it by +0.39 Å (outwards). This is similar to calculations by Wang and Duke for III-V bulk semiconductors [21]. For the (110) surface of zinc blende III-V and (10 $\bar{1}$ 0) surface of (II-VI) wurtzite semiconductors this type of reconstructions conserves the nearest neighbor bond length but changes angles [22]. Note that in nanocrystals this surface relaxation changes the bond lengths at the outermost surface layers.

Including a surface reconstruction in the models for the XANES simulations introduces a broadening of the bond

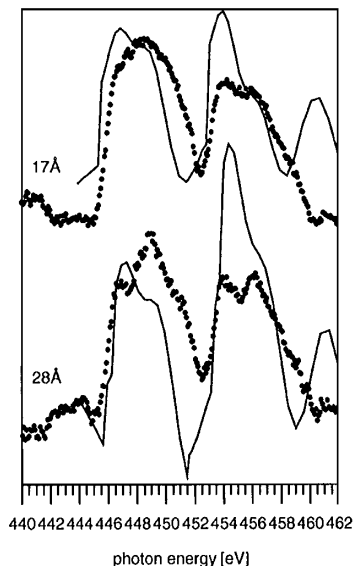


FIG. 3. Simulated In $M_{4,5}$ edge spectra (lines) of 17 Å and 28 Å InAs particles with a surface reconstruction. The dots are experimental data.

length distribution within a nanocrystal with respect to the bulk material. This in turn increases the number of distinct photoelectron scattering paths in a nanocrystal, yielding a broadening of the XANES spectra in the simulations, as observed in experiment.

However, the experimental broadening may not be due only to a structural rearrangement of exclusively the two outermost layers as assumed in the simulations. It is very probable that bond lengths and angles deviate from the idealized bulk values throughout the whole particle, with the largest displacements occurring at the surface. However, lacking an appropriate model to account for internal rearrangements, we state here only that the observed broadening of XANES spectra can be related to structural disorder within the nanocrystals, which is believed to be largely due to atomic displacements at the surface.

Other possible structural sources for the broadening effects have been systematically studied and excluded. We simulated spectra (not shown) for an unreconstructed 17 Å nanocrystal with (a) a capping of the outermost In layer with P atoms and (b) a slightly elliptical shape. The surface capped with P atoms models the experimental situation that the outermost In layer is covered by a disordered layer of ligands (TOP) as confirmed by XPS [19]. Since the scattering scales as Z^2 , where Z is the atomic number, the P atoms at the surface contribute weakly to the spectrum compared to As or In atoms. A slightly elliptical particle shape (aspect ratio 1.1) which is evident from TEM and XRD results [8,23] increases the number of scattering paths due to the symmetry reduction from a sphere, and should in principle lead to a broadening of the XANES spectra. However, this contribution is negligible compared to the experimental result.

Quantum size effects convoluted with the finite size distribution of the nanocrystal sample can also be excluded. We simulated the effects of a size distribution with 10% width on the x-ray absorption spectrum of 17 Å InAs nanocrystals. For this purpose, the bulk spectrum was convoluted with a Gaussian of a width of 100 meV representing the conduction band shifts (ΔE_{CB}) corresponding to the size distribution [24,25]. The result shows a minor amount of broadening of the spectrum relative to the experiment. In order to reproduce the experimental broadening of the 17 Å InAs nanocrystal, the bulk spectrum must be convoluted with a Gaussian of at least 1.7 eV in width.

Therefore, we conclude that structural disorder in InAs and CdSe nanocrystals is the major factor in the broadening of the XANES spectra at the In and Cd $M_{4,5}$ edge as seen from the simulations including a bulklike surface reconstruction in Fig. 3.

Yet, as may be expected for a single bulk-derived reconstruction of the outermost surface layers, it is still not in quantitative agreement with the experiment. The FEFF7 multiple scattering model relies on muffin-tin potentials which are too simplistic. Also, approximations used by FEFF7 have only been thoroughly tested for bulk

materials which might have to be altered for nanocrystals. For instance, deviations of the mean-free path in nanocrystals from the bulk value have been discussed for Al nanoparticles [26]. Also, the presence of multiple faces with different reconstructions and, in particular, deviations from bulklike surface reconstructions must be accounted for in the models. Comparison between the XANES spectra of nanocrystals of different sizes and surface stabilizations might provide more information. For example, the nanocrystals can be stripped of their surfactant, and epitaxial shells of related semiconductors can be grown onto the cores (e.g., InAs coated with CdS). These surface modifications will provide additional checks on the complex surface reconstructions of semiconductor nanocrystals.

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- [1] H. Weller, *Angew. Chem., Int. Ed. Engl.* **35**, 1079 (1996); S. Empedocles and M. Bawendi, *Science* **278**, 2114 (1997); T.G. Schaaff *et al.*, *J. Phys. Chem. B* **101**, 7885 (1997); J.R. Heath and J.J. Shiang, *Chem. Soc. Rev.* **27**, 65 (1998).
- [2] X. Peng, J. Wickham, and A.P. Alivisatos, *J. Am. Chem. Soc.* **120**, 5343 (1998).
- [3] J.M. McHale *et al.*, *Science* **277**, 788 (1997); S.H. Tolbert and A.P. Alivisatos, *J. Chem. Phys.* **102**, 4642 (1995).
- [4] N.A. Hill and K.B. Whaley, *J. Chem. Phys.* **100**, 2831 (1994).
- [5] C. B. Duke, *Chem. Rev.* **96**, 1237 (1996).
- [6] However, the growth of quantum dots by molecular beam epitaxy and metal-organic chemical vapor deposition is determined by long-range mechanical forces. In this case, surface effects are well understood to the point where a high degree of growth control is possible. D. Bimberg, M. Grundmann, and N.N. Ledentsov, *Mater. Res. Bull.* **23**, 31 (1998).
- [7] A.R. Kortan *et al.*, *J. Am. Chem. Soc.* **112**, 1327 (1990); X. Peng *et al.*, *J. Am. Chem. Soc.* **119**, 7019 (1997); C.L. Cleveland *et al.*, *Phys. Rev. Lett.* **79**, 1873 (1997).
- [8] J.J. Shiang *et al.*, *J. Phys. Chem.* **99**, 17417 (1995).
- [9] C.B. Murray, D.J. Norris, and M.G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993).
- [10] C.-C. Chen *et al.*, *Science* **276**, 398 (1997).
- [11] H. Krautscheid *et al.*, *Angew. Chem., Int. Ed. Engl.* **32**, 1303 (1993); N. Herron *et al.*, *Science* **259**, 1426 (1993); T. Vossmeier *et al.*, *Science* **267**, 1476 (1995); T. Vossmeier *et al.*, *J. Am. Chem. Soc.* **117**, 12881 (1995).
- [12] A. Bianconi, in *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, XANES*, edited by D.C. Koningsberger and R. Prins (Wiley, New York, 1988), p. 573.
- [13] *Proceedings of the 9th International Conference on X-Ray Absorption Fine Structure in Grenoble, France, 1996* [*J. Phys. IV (France)* **7** (1997)].
- [14] J. Rockenberger *et al.*, *J. Phys. Chem. B* **101**, 2691 (1997); J. Rockenberger *et al.*, *J. Chem. Phys.* **108**, 7807 (1998); T. Shido and R. Prins, *J. Phys. Chem. B* **102**, 8426 (1998).
- [15] A. A. Guzelian *et al.*, *Appl. Phys. Lett.* **69**, 1432 (1996).
- [16] N. Mårtensson and R. Nyholm, *Phys. Rev. B* **24**, 7121 (1981).
- [17] S. B. Diczko and G. K. Wertheim, *Comments Solid State Phys.* **11**, 203 (1985).
- [18] S. I. Zabinsky *et al.*, *Phys. Rev. B* **52**, 2995 (1995).
- [19] J.E. Bowen Katari, V.L. Colvin, and A.P. Alivisatos, *J. Phys. Chem.* **98**, 4109 (1994); A. A. Guzelian *et al.*, *J. Phys. Chem.* **100**, 7212 (1996).
- [20] D. Bazin *et al.*, *J. Phys. Chem. B* **101**, 5332 (1997).
- [21] C.B. Duke, *J. Vac. Sci. Technol. B* **1**, 732 (1993).
- [22] T.N. Horsky *et al.*, *Phys. Rev. B* **46**, 7011 (1992).
- [23] D.J. Norris *et al.*, *Phys. Rev. B* **53**, 16347 (1996).
- [24] T. van Buuren *et al.*, *Appl. Phys. Lett.* **60**, 3013 (1992).
- [25] Since the $M_{4,5}$ transition is into higher energy p bands, ΔE_{CB} is not known. It is approximated by using the shifts for the lowest energy band (s bands), obtained from the optical excitation energy ΔE_{opt} . ΔE_{opt} measured by UV-vis is fit to a $1/R$ polynomial describing the size dependence. As the effective masses of the hole and electron in InAs bulk are identical ($m_e = m_h = 0.026$), we assume ΔE_{CB} and the valence band shift (ΔE_{VB}) contribute equally to ΔE_{opt} in InAs nanocrystals. From the particle size distribution determined by TEM (10%), a width in ΔE_{CB} of 100 meV is calculated for 17 Å InAs nanocrystals. Since the curvature of the p bands is lower than in the s bands, this overestimates the effects of quantum confinement and subsequently the size distribution effect on the x-ray spectra.
- [26] J. Zhao and P.A. Montano, *Phys. Rev. B* **40**, 3401 (1989).