Structure determination of CdS and ZnS nanoparticles: Direct modelling of synchrotron radiation diffraction data

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We introduce a modified method of powder diffraction data analysis to obtain precise structural information on freestanding ZnS- and CdS-nanoparticles with diameters well below 5 nm, i.e., in a range where common bulk-derived approaches fail. The method is based on the Debye-equation and allows to access the crystal structure and the size of the particles with high precision. Detailed information on strain, relaxation effects, stacking faults, and the shape of the particles becomes available. We find significant size differences between our new results and those obtained by established methods, and conclude that a mixed zincblende/wurtzite stacking and significant lattice distortions occur in our CdS nanoparticles. Our approach should have direct impact on the understanding and modelling of quantum size effects in nanoparticles.

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I. INTRODUCTION

Semiconductor nanoparticles are of increasing interest for both applied and fundamental research. In material science, for example, they are used for fabricating thin film light-emitting diodes and solar cells. In biology and bio-chemistry they are used as marker particles [1]. In fundamental research, particles with a diameter of 1-5 nm are of particular interest since they represent the transition regime between solid state physics and molecular or cluster physics. Quantum size effects play an important role in this regime.[2] However, for very small particles the effective-mass approach, which is common in solid state physics, is not applicable any more. Significant deviations from bulk properties are expected for particles with diameters below 5 nm, and were observed in many cases [1-4] as well as also in this study.

Of course, the determination of geometrical particle parameters like size, shape, and crystallinity is a very important issue. However, it is very difficult to obtain precise data. Often local probes like transmission electron microscopy or atomic force microscopy are used, but in most cases they cannot provide representative conclusions on the *average* particle size or shape, or on the internal structure. Other more indirect approaches, which make use of quantum size effects like, e.g., the position of the exciton-like optical absorption peaks [5], contain

the risk of large systematic errors since they rely on effective mass or tight-binding models. As indicated by often very largely differing sizes obtained by different methods in the literature [3-8], no general consensus could be obtained so far about the most suitable method for the size-determination for small nanoparticles. Moreover it is difficult to obtain a good estimate for the precision of the obtained parameters. Potentially, diffraction methods yield precise structural information, provided that special care is applied to the measurement and – in particular – to the numerical method used for analyzing the data.

Powder diffraction is a well-established method for structural and analytic examinations of micro-crystalline materials. For example, the Scherrer-equation [9] represents a very simple way of grain size evaluation which provides sufficient precision in the μm -range. Until today this approach is also frequently used for nanoparticles (see, e.g., [4, 8]) and often combined with fit-routines like, e.g., a Rietveld-refinement, which analyzes the peak profile and its dependence on the Bragg-angle. This method considers the peak broadening due to a finite grain size in a somewhat artificial way, since the diffraction pattern of an idealized infinite periodic structure is convoluted with a peak shape function. Its width is fitted to the data and interpreted as a finite-particle peak broadening. *Per se* this bulk-like approach lacks a direct correlation between the particle size and the peak broadening. Nevertheless, quite reliable results can be obtained for larger particles (above a diameter of approx. 5-10 nm). However, for smaller particles this approach yields only a coarse extrapolation of bulk-properties towards the nano-regime,

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and hence often yields questionable results.

One alternative, more direct way of calculating the powder pattern of finite structures is the use of the Debye-formula [9], which is the explicit sum of all scattered partial waves from all atoms of the nanocrystal (see below). This approach was already used before and sporadic publications can be found in the literature [3, 10, 11]. A rather detailed investigation of experimental data was published by Bawendi et al. in 1989 [12]. Even though this method is in principle well understood, it is rather rarely used in the community. Its application is more complex compared to the Rietfeld / Scherrer-equation approach due to the necessity to model the diffraction data from an explicit list of all atomic positions. It represents the superior method for a structural analysis of small nanoparticles (below 5 nm in diameter), since all structural parameters like size, shape, crystal structure, stress, relaxation effects, stacking faults and other inhomogeneities, etc., are intrinsic parameters of the atomic models of the particles and hence are directly accessible by a modelling approach. Ensemble averaging also enables the consideration of distributions of these parameters.

In this paper we present a Debye-formula based method for the structure determination of nanoparticles with diameters of 2-5 nm. The experimental data is obtained from scattering of high-brilliance synchrotron radiation using an experimental approach similar to standard powder diffraction. The power of this technique is demonstrated by results obtained from ZnS and CdS nanoparticles. This method can also be applied to the small crystalline core of a nanoparticle which is embedded in a much larger amorphous shell. Anomalous diffraction can be used to separate the bulk-signal from the background of the amorphous shell, even if the latter is dominant. Results obtained for core-shell particles will be presented in a forthcoming publication.

II. EXPERIMENTAL METHODS

A. Synthesis of the Particles

The samples presented here as examples have been employed in other investigations before and thus their synthesis is described only very briefly. Thioglycerol-stabilized ZnS (CdS) particles were prepared using zinc acetate (cadmium acetate dihydrate) as starting material together with dry sodium sulfide. Thioglycerol in different concentrations was added as organic stabilizer molecule ("capping agent") in order to control the size of the nanoparticles (diameters between 1 and 4 nm) [13]. The synthesis of glutathion-stabilized CdS particles is described in detail in Ref. [7].

B. X-ray Diffraction

All X-ray diffraction experiments were performed using the high-flux wiggler beamline BW2 at the DORIS storage ring of the Hamburger Synchrotronstrahlungslabor HASYLAB in Hamburg, Germany. For nanoparticles in the size range of only a few nanometers special care has to be taken in order to reduce the scattering background sufficiently. In particular, parasitic scattering from amorphous compounds in the beam path must be avoided, since the particle-size broadening of Bragg-reflections of the nanocrystals already reaches the width of the scattering form factor of amorphous materials. In our case a Silicon wafer was used as a substrate for the nanoparticle powder. Since the experimental conditions ensured that no Si-bulk reflection was hit during the measurements, this substrate choice eliminates significant scattering background. Furthermore, air scattering was avoided by either evacuating or Helium-flooding the entire beam path. The diffraction experiment was performed in a modified z-axis geometry [14]. The angles of incidence and excidence (with respect to the Si-wafer) were kept constant at 0.2° . Apart from these very small angles, the scattering vector $\mathbf{q} = \mathbf{k}_{out} - \mathbf{k}_{in}$ was always oriented parallel to the surface of the Si wafer. $\mathbf{k}_{in}$ and $\mathbf{k}_{out}$ is the incoming and scattered wave vector, respectively. The Bragg angle θ is correlated to the scattering vector via $|\mathbf{q}| = 4\pi \sin(\theta)/\lambda$, where λ is the wavelength of the X-rays. This reflection geometry ensures that the length of the beam path within the sample, which is relevant for absorption, is constant during the measurement. Radial $\mathbf{q}$ -scans (i.e., ω - 2θ -scans) in the range of $q = |\mathbf{q}| = 0.1...7.0 \text{ \AA}^{-1}$ were performed, corresponding to a Bragg angle of $\theta \approx 0.5...45^\circ$ at a photon energy of 9.6 keV ($\lambda \approx 1.3 \text{ \AA}$).

III. RESULTS AND DISCUSSION

A. Modelling

As described in the introduction we present a modelling approach based on the Debye-formula in order to investigate the structural properties of very small nanoparticles with diameters below 2-5 nm. The particles were simulated by creating an explicit list of all atomic coordinates using the program DISCUS [15]. The structure was assembled from zincblende- or wurtzite-like atomic layers. Initially the crystals were shaped in a columnar fashion of several stacks and subsequently all atoms outside a desired radius were removed in order to generate nanoparticles of approximately spherical shape. In order to study the effect of local strain, the lattice constants were adjusted. The powder diffraction intensities were calculated using the Debye formula [9]

$$I(q) = \sum_m \sum_n f_m f_n \frac{\sin(qr_{mn})}{qr_{mn}}, \quad (1)$$

where f_n is the atomic form-factor of the n -th atom. Note that this equation only involves the magnitudes of the distances r_{mn} of each atom from every other atom. Hall & Menot [10] developed a faster algorithm for particles consisting of one atomic species only. They used a histogram of interatomic distances and applied a fast Fourier transform which was finally multiplied by the atomic form factor. This results in the same diffraction pattern as equation 1. We extended this algorithm to particles consisting of several different atomic species.

The effective widths of the diffraction peaks are an intrinsic feature of this algorithm and depend entirely on the size and defect concentration of the simulated nanoparticles. In contrast to a Rietveld refinement or the Scherrer equation, no convolution is necessary to modify the peak widths; the resulting simulation can be directly compared to the experimental diffraction pattern. Furthermore, in contrast to the Scherrer equation approach, we calculate the intensity separately at each q -value, i.e., we take into account that the structure factor changes within the broad q -range of the diffraction maxima. This effect is neglected when the Scherrer equation is used, which convolutes the structure factor of a given Bragg reflection with a peak profile function to describe the broad diffraction peak. Moreover, the small size and high defect concentration within the nanoparticles renders the concept of Bragg reflections meaningless, since “Bragg planes” no longer exist.

Background subtraction is a crucial aspect of the data analysis. As described above, parasitic scattering from amorphous materials and air was effectively avoided in the experiment. Thus, the dominating part of the background was caused by the tails of the direct beam, which was properly subtracted by fitting one Lorentzian profile fixed at $q = 0$, i.e., at the position of the direct beam. Only in a few cases an additional linear or parabolic background had to be subtracted. The resulting, background-corrected powder pattern was simulated as described above. All essential structural features like size, shape, atomic structure, atomic displacement parameters, stress and relaxation, stacking faults, and vacancies are explicitly taken into account since they are intrinsic parameters of the nanoparticle model.

B. Data Analysis: Several examples for different nanoparticles

We performed measurements on organically stabilized ZnS and CdS particles with diameters between 1.5 and 4 nm. The diffraction data were modelled by atomic clusters with 50-300 atoms for which only the Zn or Cd atoms and the bulk-sulfur atoms were considered. Except for their sulfur atoms which bond to the particle surface the organic stabilizer molecules were neglected in the atomic models since they consist of disordered low- Z compounds and thus do not contribute significantly to the powder diffraction pattern.

The principle modelling procedure was performed as follows: At first spherical models with pure Zincblende or pure Wurtzite structure of different sizes were tested. In some cases (e.g. for the ZnS particles described in the next section) a good agreement of experimental and calculated data could already be obtained at this stage. If that was not the case the lattice parameters were varied, next the effect of stacking faults were tested. In the case of those thioglycerol-stabilized nanoparticles shown in sec. IIIB 2 a lattice distortion in the particles was sufficient to fit the experimental data well, for the glutathione-stabilized particles described in the same section stacking faults and even an anisotropic shape had to be considered to obtain a reasonable fit. This modelling procedure was applied to all particles presented in this paper.

1. ZnS nanoparticles

Figure 1a shows a measurement on thioglycerol-stabilized ZnS-particles together with calculated patterns for both the zincblende and the wurtzite structure, the inset shows the corresponding atomic models. The region between $q = 2.5 \text{ \AA}^{-1}$ and $4.5 \text{ \AA}^{-1}$, in particular, can only be reproduced by the zincblende model, whereas the wurtzite structure exhibits additional peaks at $q \approx 2.7 \text{ \AA}^{-1}$ and $3.5 \text{ \AA}^{-1}$ which were not observed in the experiment. Thus, the structure can be clearly identified as zincblende, having a stacking sequence of the ABC...-type, whereas the wurtzite-like stacking AB'... can be excluded.[17] This indicates that even below a diameter of 3 nm the bulk structure is conserved in our ZnS nanoparticles.

In Fig. 1b several calculated patterns for different particle diameters are shown. It is clearly visible that the peaks at $q \approx 2.0 \text{ \AA}^{-1}$ and $3.3 \text{ \AA}^{-1}$ are best reproduced by the atomic model with a diameter of 2.6 nm, for the third peak at $q \approx 3.9 \text{ \AA}^{-1}$ the 2.1 nm model fits slightly better. Since the peaks at higher q -values are more strongly influenced by a possibly slightly incorrect temperature factor and since they are caused by several overlapping Bragg reflections, the reliability of a size determination decreases at higher q , and hence we conclude that the particle diameter is $2.6 \pm 0.3 \text{ nm}$. (The error was estimated from different model calculations judging the peak widths.) In cases with strongly varying peak widths it might also be possible to conclude a non-spherical shape of the nanoparticles from the different widths of the peaks, since their (hkl)-vectors indicate the crystallographic direction in which the peak profile is sensitive to the particle dimensions (see below). However, in this case the width difference between the first and the third peak (corresponding to the (111) and (311) Bragg-reflection, respectively) is very small and hence a significant deviation from the spherical shape can be ruled out. The determined size is surprising, because a determination from the excitonic absorption line at 280 nm using a tight-binding model [5] results in a diameter of 1.65 nm,

a value which is smaller by more than 35%. In contrast, the effective mass approach gives 2.9 nm [5]. A size determination from the diffraction peak broadening using the Scherrer-equation yields a diameter of 3.5 nm. All these values deviate significantly from our result. They clearly demonstrate that a dedicated method for size determination and structural analysis is urgently needed.

2. CdS nanoparticles

The XRD data for smaller thioglycerol-stabilized CdS particles are shown in Fig. 2, together with three different calculated patterns. As indicated by the blue dotted line a zincblende model cannot fit the region between $q = 2.5 \text{ \AA}^{-1}$ and $4.0 \text{ \AA}^{-1}$. The situation improves when a wurtzite structure (corresponding to the CdS bulk structure; red dashed line) is used. However, there is still a significant shift of the first peak at $q \approx 2 \text{ \AA}^{-1}$, indicating a distorted unit cell, and additional discrepancies at higher q -values can be seen. We thus tested a large number of models with different sizes (0.9-2.0 nm in diameter) and distorted unit cells (up to 15% difference to bulk-values), and obtained the solid line in Fig. 2 as presently best fit. The agreement is still not perfect, but can be considered satisfactory if one takes into account that the low intensity region above $q = 4 \text{ \AA}^{-1}$ is of minor significance due to the occurrence of many weak Bragg reflections in that region. The shoulder at $q = 1.4 \text{ \AA}^{-1}$ is due to scattering from amorphous material and hence must not be considered. The remaining deviation between calculated and measured data is the small peak at $q = 3.8 \text{ \AA}^{-1}$ in the calculated data. This part of the pattern is expected to be better described when a distortion gradient is included in the modelling procedure (see discussion below).

The diameter found for the CdS particles by our modelling is $(1.4 \pm 0.2) \text{ nm}$, while the use of the Scherrer-equation yields 1.8 nm, and the UV/VIS absorption line analysis (line at 310 nm) via a tight-binding and an effective mass model gives 1.2 nm and 2.5 nm, respectively. Compared to a bulk crystal, the distortion was determined to be a 8% reduction in the lattice parameter **a** (in both directions parallel to the hexagonal stacking layer) and a 3% extension in the lattice parameter **c** (corresponding to the layer-to-layer distance). These values indicate a strongly distorted unit cell, however, nanoparticles of this size exhibit an exceptionally high surface-to-volume ratio: 47 of 77 atoms, i.e., approx. 2/3 of the atoms, are surface atoms. Therefore the hexagonal distortion of the hcp-structure and, in particular, the reduction of the unit-cell size are not surprising. An inward relaxation of surface atoms was reported before for small nanoparticles [12] and is very often found in structural investigations of surfaces (see, e.g., Ref. [16] and references therein).

In Fig. 3 measurements on glutathion-stabilized CdS particles are shown, the diffraction pattern of which can

neither be described by a pure zincblende nor by a pure wurtzite structure, not even with strongly distorted unit cells. A large series of models with different sizes (1.0-3.0 nm) and distortion parameters (up to 15%) was tested. The blue dashed and red dotted lines in Fig. 3 represent two examples from this test series for spherical particles with pure zincblende and pure wurtzite structure, respectively. They both cannot fit the measured data well enough. The situation improves when stacking faults are considered: The black solid line corresponds to an atomic model of a spherical particle which consists of a zincblende-like sequence in the upper half and a wurtzite-like stacking sequence in the lower half of the particle (stacking sequence ABCAB'AB'). We also tested other stacking sequences which partly resulted in quite similar diffraction patterns, however, it turned out that the number of Zincblende- and wurtzite-like stacked layers has to be very similar in the present case. Our best result for a spherical model (black solid line in Fig. 3) reproduces the measured intensity quite well, apart from the peak at $q = 3.9 \text{ \AA}^{-1}$. This can be improved further by considering a non-spherical shape. The magenta dash-dotted line represents our best fit to the data and corresponds to the atomic model shown in the inset. It has a cylindrical shape with a height of 2.1 nm and a diameter of 1.3 nm, i.e., an aspect ratio of 1.6:1, and consists of an equal volume of zincblende and wurtzite. Again, we tested particle sizes in the range of 1.0-3.0 nm, height and diameter independently. This result demonstrates that CdS nanoparticles tend to form stacking faults, particularly particles smaller than $\approx 2 \text{ nm}$, and that non-spherical shapes cannot be neglected. Note that such information is not accessible with other methods like UV/VIS absorption analysis or the Scherrer equation. In our case a UV/VIS line at 365 nm is detected, [7] which corresponds to diameters of 1.8 nm and 3.0 nm for a tight-binding and an effective mass model, respectively. The use of the Scherrer-equation yields 1.3 nm, but this can only be a very crude estimate since a mixture of zincblende and wurtzite principally cannot be modelled by this approach. Based on our results, we propose a structural transition in this interesting region of particle sizes which now becomes accessible for further structural investigations. We emphasize that stacking faults appear to occur in the majority of the particles.

IV. OUTLOOK

So far, our modelling only considers a homogenous relaxation of the structure for the entire nanoparticle, i.e., a distortion of its unit cell. However, since it can be expected that the finite size does have a different impact on the atomic structure in the inner part of the particle as compared to its surface, a gradient-like relaxation of the particle will be considered in the future. This aspect will be combined with stochastic growth models for the particles to allow a more statistical treatment of

the formation of atomic structure models. Furthermore, an ensemble-average will be included in the modelling, which will also allow a finite size distribution analysis of the nanoparticles.

V. CONCLUSION

We have demonstrated that it is possible to obtain precise structural information on nanoparticles from X-ray diffraction data, even for diameters well below 5 nm. Superior to simple, bulk-like approaches a much more detailed structural analysis is possible in a more direct way. Elementary properties like crystal structure, size and shape of the particles are accessible with relatively high precision as well as more intricate properties like stress, relaxation effects, and stacking faults. Our results differ significantly and (in part) systematically from results obtained by the Scherrer-equation or a Rietveld refinement. Since they are obtained in a direct way, using a specific atomic model for the entire nanoparticle, they

are more precise than indirect approaches such as, e.g., the size determination via UV/VIS absorption combined with tight binding or effective mass models. Thus, these results are expected to have significant impact on the understanding of quantum size effects and to contribute to an improvement of models to describe the optical and electronic properties of nanoparticles.

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 - [17] While the difference between A-, B-, and C-layers in zincblende is only a transversal shift of the layers, in the wurtzite structure the B'-layers are shifted *and* mirrored with respect to the A-layers. Thus, the B-layer in zincblende and the B'-layer in wurtzite are *not* identical. This additional difference between zincblende and wurtzite structure is due to the fact that each layer consists of two atomic species (Zn and S in this case) and does not occur in a cubic or hexagonal closed packed structure, where only one species is present.

FIG. 1: (Color online). Powder diffraction pattern of thioglycerol-stabilized ZnS-nanoparticles and calculated patterns for (a) zincblende and wurtzite structural models and (b) zincblende models for three different sizes. Atomic models and their layer stacking sequences (ABC... for zincblende and AB'... for wurtzite, respectively) are also shown.

FIG. 2: (Color online). Powder diffraction pattern of thioglycerol-stabilized CdS nanoparticles and calculated patterns for zincblende and wurtzite structural models. The best agreement between measured and calculated data can be obtained using a model with a distorted wurtzite unit cell.

FIG. 3: (Color online). Powder diffraction pattern of glutathion-stabilized CdS nanoparticles and calculated patterns for pure wurtzite and zincblende structural models of spherical particles (red dotted and blue dashed line, respectively) as well as two models including stacking faults. The latter models consist of equal volume fractions of zincblende and wurtzite structure and have a layer-stacking sequence of ABCAB'AB'. One represents a spherical particle with a diameter of 1.9 nm (solid black line), the other one a cylindrical particle (diameter 1.3 nm, height 2.1 nm; magenta dash-dotted line) which is shown in the inset. In all cases a lattice distortion of -10% in **a** and +2% in **c** was included.