

# Non-periodicity in nanoparticles with close-packed structures

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Experimentally it is observed that nanomaterials from II–VI compounds like CdS have a high density of stacking faults. It is argued that these are not crystal defects but rather that they represent a characteristic feature of nanomaterials.

## 1. Introduction

Close-packed planes with hexagonal symmetry are needed to fill space to the highest possible degree with equal spheres. To achieve the highest packing density in three dimensions, these close-packed planes may be stacked on each other in two different ways, usually referred to as *AB* or *ABC* stacking. In both cases each sphere (atom) has 12 neighbours. Indeed, the *nature* of most one-element substances is such that they crystallize in one of these two close-packed structures, *i.e.* face-centred cubic (f.c.c.) with *ABC* stacking or hexagonal close-packed (h.c.p.) with *AB* stacking. Many binary substances show a more complicated but again periodic close-packed structure built from two f.c.c. or two h.c.p. packings, one for each element. These are shifted relative to each other either in an octahedral or in a tetrahedral manner. Among binary close-packed arrangements, the most common are the rock salt (*B1*), zincblende (*B3*) and wurtzite (*B4*) structures. Neglecting point defects and for temperatures not too close to the melting point, it can be assumed that the minimum of the free energy is obtained when a completely ordered structure is formed in a binary system. In contrast, we report here on our finding that the principle of a regular stacking sequence becomes void in binary nanomaterials with a small number of close-packed planes and, in consequence, crystalline periodicity no longer exists.

As an example, we always find a non-periodic arrangement of layers for nanoparticles of the close-packed substance CdS. Thus, it appears that a critical number of stacking planes is needed to establish periodicity, and this number intrinsically correlates with the extent of long-range interactions. We expect that the bonding character plays a crucial role in the minimum size needed for an agglomerate to establish its final structure. An agglomerate with a metallic bonding with free conduction electrons may need a much larger particle size than an agglomerate with local covalent bonds where a particle size of the order of a few nanometres may suffice. This implies that for nanoscale crystals the disordered structure is more fundamental than a periodic arrangement for the layer stacking. Ordering in regular stacking sequences, *i.e.* with a well defined crystal structure, occurs exclusively after taking into account long-range interactions, and this can be seen like

the development of a long-range superstructure based on a disordered fundamental structure. We believe that our assay can serve as a novel starting point for future sophisticated measurements, for developments of new crystallographic approaches and for *ab initio* calculations of the free energy for substances of small particle size. Since the energy differences for modified sequences of close-packed planes are small, the close-packed structures will not be regular and in a classical approach they are named stacking faults or polytypes. Persistent efforts should be undertaken to understand the reasons for the stabilization of different periodic sequences in nano-sized crystals of close-packed planes with the aim of tailoring the structure of close-packed materials for fundamental research and for applications.

## 2. Polytypes of close-packed substances

For many years much effort has been devoted to the question of why close-packed substances adopt one out of several possible types of structure. Moreover, some materials take on different structures depending on slightly changed growth conditions. For example, the well known wide band gap semiconductor silicon carbide (SiC) has numerous polytypes such as *3C*, *2H*, *4H*, *6H* or *15R* to name just a few. Another wide band gap semiconductor cadmium sulfide (CdS) has at least two polytypes, *B3* and *B4* (Krumbiegel & Jost, 1955), and the narrow band gap semiconductor lead sulfide (PbS) crystallizes either in *B1* or *B3*. The one-dimensional disorder in the direction of the close-packing stacking was discussed by Jagodzinski (1949) for zinc sulfide (ZnS). This list of materials could be easily extended. It is still unclear why some substances form polytypes or isomorphous structures and others don't. However, it can be suggested that the substances forming polytypes have a hypothetical disordered structure with a symmetry that is higher than the symmetry of each polytype of that substance. This disordered structure, which could be stable at higher temperatures close to the melting point, is not observed in general. This is probably because high-temperature structural studies of the defect nature of materials are difficult and have, up to now, only been performed for very few selected substances. The possibility of observing such disordered phases at ambient temperature may

be brought into reach by reducing the size of a crystal to the nanoscale.

### 3. Structure of clusters

In 1962 Mackay published a paper about a dense non-crystallographic packing of equal spheres (Mackay, 1962) considering the space filling by an increasing number of shells with icosahedral symmetry. Recently his idea was extended for the stacking of tetragonal polyhedra using modern calculation techniques (Haji-Akbari *et al.*, 2009). The Mackay icosahedra consist of 20 close-packed trigonal pyramids sharing a single vertex. The point symmetry of an icosahedral structure with 120 symmetry operations (*International Tables for Crystallography*, 2002) is much higher than is the case for structures with cubic ( $\frac{4}{m}\bar{3}\frac{2}{m}$ ) or hexagonal point symmetry ( $\frac{6}{m}\frac{2}{m}\frac{2}{m}$ ), which have 48 and 24 symmetry operations, respectively. Mackay found that a non-crystallographic packing has a slightly lower space filling than an h.c.p. or an f.c.c. packing which is  $\pi/[3(2)^{1/2}] \simeq 0.7405$ . He considered the option that small crystals have a non-periodic, *i.e.* a non-translational, structure, which can easily transform into a crystallographic structure when the size of the agglomerate increases. He further speculated about mechanisms for a transformation into close-packed structures by considering that an icosahedral cluster can serve as a nucleus for crystalline growth in a classical sense.

In 1981 the ‘magic numbers’  $m$  for sphere packing (no tight binding between atoms) were experimentally verified in free xenon (Xe) clusters (Echt *et al.*, 1981). The observed values of  $m = 13, 55$  and 147 coincide with the numbers of spheres required for complete-shell icosahedra. The structure of the Xe clusters was thus in agreement with hard-sphere packing as proposed by Mackay. Calculations with a Lennard–Jones potential made in Echt *et al.* (1981) support these experimental findings.

A calculation of magic numbers and of the stability of small clusters (tight binding between atoms) was performed by Tománek & Schlüter (1986). The cohesive energy for Si clusters up to size  $m = 14$  derived from a tight-binding Hamiltonian shows no open and no diamond-like fragments. Particularly stable clusters found for  $m = 6$  and 10 coincide with experimentally observed magic numbers.

Magic numbers were found by Douglas *et al.* (1992) for the magnetic properties of gadolinium (Gd) clusters. Clusters with  $m = 11–92$  in a molecular beam were shown to exhibit a dramatic size dependence in their magnetic properties which provides further evidence that the structural issues of nanoparticles are size dependent.

Sodium (Na) clusters also show magic numbers (Brack, 1998). These are  $m = 8, 20, 40, 58, 92, 138, 198, 264, 344, 442, 554$  for hot clusters, which show no distinct shape and have an amorphous (liquid) structure. In contrast, cold clusters show well defined polyhedral shapes and they come with different magic numbers, which may be taken as an indication of an ordered structure. The shapes of cold clusters coincide with one of the five ideal polyhedra already described by the Greek

philosopher Plato (Platonic polyhedra). It should be pointed out that, to date, one can only speculate about the inner structure of clusters.

Up to now, the studies of magic-number clusters do not include a precise measurement of atomic configurations. The models promoted are based on several speculations. First, the existence of magic numbers is interpreted as a criterion for the stability of an agglomerate of a specific size. These magic numbers in general coincide with completely filled shells for simple icosahedral, cuboctahedral or decahedral structures (Forschungszentrum Jülich, 1997; Kawazoe *et al.*, 2002). Second, the calculation of the electronic structure of clusters does not take into account the structure of the clusters; it merely uses the size and number of atoms. Third, characteristic bond lengths in a cluster can be deduced from spectroscopic measurements, from which a structure model is then proposed.

Nevertheless, there have been some attempts to access the atomic structure of atomic clusters. In a first approach a superstructure of clusters is grown, in a similar manner as for proteins and other organic or biological substances. Assuming that the structure does not change upon agglomeration, the structure of nanoclusters can be resolved, similar to the case of agglomerated  $C_{60}$  molecules (fullerene), named fullerite, which has an f.c.c. structure. Nevertheless, it cannot be excluded that the coalescence or cross linking of  $C_{60}$  molecules induces modifications as compared to the structure of isolated clusters.

To the best of our knowledge, there is no experiment in the literature which accesses the cluster structure. Max von Laue in 1940 (von Laue, 1960) referred to the inherent difficulties in resolving the structure of amorphous materials or of materials with a small number of unit cells, which he termed ‘paracrystals’. Since then, formidable progress has been made in experimental techniques and computing, but it remains an enormous task for the future to determine the structure of objects with dimensions on the nanoscale.

There are examples from the past where crystalline structures of some substances were correctly predicted without direct measurements. For example, the structure of NaCl was described by Sohncke (1879) and the diamond structure of carbon was predicted before 1912 when the first X-ray diffraction measurement was performed on crystalline matter. However, not in every case was the structure predicted correctly and graphite can serve as an example (Ubbelohde & Lewis, 1960). Only through experiments could the structure of this substance be determined correctly.

### 4. Close-packed structures and disorder

As already mentioned, a close packing is needed to fill a plane densely with spheres of equal size, and the resulting honeycomb pattern has hexagonal symmetry (plane group  $p6mm$ ). Such planes need to be stacked to form a close-packed structure in three-dimensional space. Each sphere/atom has 12 nearest neighbours, while each atom from one plane together with three atoms from an adjacent plane form a regular

tetrahedron. Two possibilities exist for the stacking of the planes. If one marks the bottom plane as an *A* plane corresponding to the *x, y* coordinates of the atoms, then one can put either a *B* plane or a *C* plane on its top, depending on whether the in-plane translation vector is  $(1/3, 2/3)$  or  $(2/3, 1/3)$ , respectively. Such an *AB* stacking sequence creates a hexagonal close-packed structure (h.c.p.), although the sixfold rotational axis of the layer is destroyed. An *ABC* stacking sequence results in a cubic f.c.c. structure. Both structures have identical atomic densities. More generally, any stacking of *A, B* and *C* planes like *ABACBAC* is a close-packed arrangement with an identical space filling (Fig. 1). The development of a space-group theory for two-dimensional order–disorder (OD) structures which are disordered in one dimension but fill the three-dimensional space infinitely was initiated by Dornberger-Schiff (1956). However, it is generally accepted that Nature prefers periodic stacking sequences. Is it like this, and if so, why is it like this?

We note for completeness that an *AA* stacking has an in-plane translation vector of  $(0, 0)$ . This sequence results in a low packing density [ $\pi(3)^{1/2}/9 \approx 0.6046$ ] and thus it is not realized for elements or simple compounds.

The short-range order is the same for any close-packed stacking sequence with first and second coordination numbers of 12 and 6. If the interactions between the atoms in a substance are central or pairwise and short-ranged (up to the second coordination sphere) like van der Waals, covalent *etc.* then the enthalpy will be independent of the sequence. However, the entropy term for disordered layer sequences is higher than for a truly periodic stacking and will thus reduce the free energy of the solid. Still, for large crystals Nature chooses ordered structures.

The reason may be that the interactions between atoms are anisotropic and/or long-ranged. The first argument holds in particular in the case of covalent bonds, while the second argument is relevant for metallic or ionic interactions. How can anisotropy and the range of interactions be accessed? An anisotropic interaction may originate from many-body correlations in contrast to isotropic interactions which are called pair correlations. Using quantum mechanical *ab initio* calculations, it is possible to estimate the anisotropy and the range of interactions. But many existing approaches for solving Schrödinger's equation may still be too crude for the fine

details that need to be considered in the present context. It is the experiment which can test *ab initio* calculations and which can access the anisotropy term and the range of interactions.

## 5. Thermodynamical approach

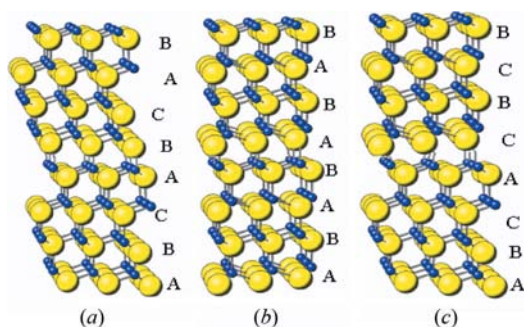
The contributions from anisotropy and from the range of the interactions become experimentally accessible when nanoparticles of different size can be synthesized. By solving their structure in dependence of their size it should become possible to give a critical size  $D_c$  and hence a critical number of stacked planes  $n$  at which the structure changes from disordered to ordered. The configurational entropy of a particle  $S_{\text{dis}}$  multiplied by the temperature of the synthesis  $T$  is equal to the enthalpy of the disordered sequence of planes  $H_{\text{ord}} = TS_{\text{dis}}$  (diffraction studies should be done *in situ* at the temperature of synthesis). Indeed, the free energy of the disordered particle is equal to  $G_{\text{dis}} = H - T(S + S_{\text{dis}})$  and the free energy of an ordered particle is equal to  $G_{\text{ord}} = H - H_{\text{ord}} - TS$ , where  $H$  and  $S$  are the enthalpy and the entropy of the particle without taking into account an anisotropy term and long-range-order interactions. The configurational entropy of the disordered particle  $S_{\text{dis}}$  is proportional to the number of non-equivalent sequences  $Z$  in which the planes can be assembled, and this can easily be calculated for a given number of stacking planes. In our case  $Z = 2^{n-2}$ . Multiplying the entropy  $S = k_B \ln Z$  by the temperature of the experiment, it thus becomes possible to estimate the anisotropic and/or long-range-order contribution to the main term of enthalpy  $H$ . In these considerations it is assumed that phononic contributions to the free energy can be neglected. This reasoning is justified by the fact that the vast majority of phonon modes are independent of the stacking of the densely packed planes.

## 6. Cadmium sulfide

In the following we concentrate on CdS as an example. It is a wide band gap semiconductor used for optical applications such as solar cells, lasers, quantum dots, or as a biological label (Bruchez *et al.*, 1998). It is well known that the semiconductor properties of CdS such as the width of the band gap can be tailored through the size of particles at the nanometre scale (Katsikas *et al.*, 1990). These properties are inherently linked to the atomic structure which we will focus on in the following.

Bulk CdS possesses either the hexagonal wurtzite structure with *AB* layering (*B4* type, *i.e.*  $E + 00\frac{3}{8}E$ ) or cubic zincblende structure with *ABC* sequencing (*B3* type, *i.e.*  $F + \frac{11}{44}F$ ) depending on the method of synthesis. For both structures a tetrahedral surrounding is established for both elements. If upper- and lower-case characters are used to distinguish the two elements Cd and S, respectively, the full record of the plane sequence for example for the hexagonal *B4* phase is given by *AaBb*...

According to the literature (Wu *et al.*, 2004; Li *et al.*, 2006; Chen *et al.*, 2004), the X-ray diffraction (XRD) patterns of nanostructured CdS films and powders synthesized by different methods show the same features. However, the



**Figure 1**

The close-packed stacking sequence of atomic planes in (a) cubic zincblende, (b) hexagonal wurtzite and (c) disordered structures.

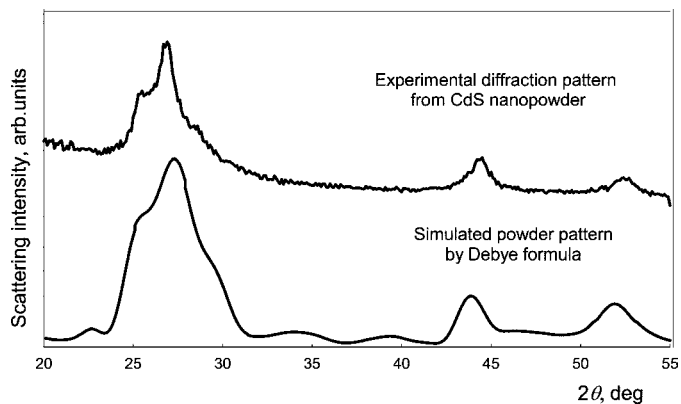
**Table 1**  
Manifold structure for nanoparticles with close-packed planes.

No. of planes	Type of stacked planes	No. of structures
1	A	1
2	B C	2
3	C A B	4
4	A B B A C B A C A B C A B C	8
5	B C A C A C A B A C A B B C A B	16
...	...	...
<i>n</i>		$2^{n-1}$

atomic structure of nanoparticles differs from the crystalline structure of bulk CdS.

We prepared CdS nanoparticles by wet chemical synthesis (for the experimental details see Appendix A). The particle size was varied from 2 to 8 nm with about 1 nm size dispersion. *Ab initio* calculations of X-ray powder diffractograms using the Debye equation (Vorokh *et al.*, 2007) and a comparison with the experimental spectra show that the atomic structure of CdS nanoparticles smaller than a critical size  $D_c = 5$  nm is disordered. The crystal structure is close packed with tetrahedral coordination for both elements, but there is a non-periodic sequence of planes of types A, B and C. For larger particles an ordered B4 structure is found. An XRD pattern of CdS nanoparticles with a size smaller than  $D_c$  is shown in Fig. 2. The best fit of the simulated pattern was obtained when the CdS nanoparticles were modelled as hexagonal prisms with an aspect ratio of 1.6 and with a disordered stacking. The height of the nanoparticles is about 3 nm, the axis of prism coincides with the direction of the stacking of the close-packed planes, and the total number of cadmium and sulfur planes equals 10.

To simplify the calculations for the anisotropy term and for the range of interactions, we take the data for ambient temperature. It is noted that both synthesis and data collection were performed at a temperature of 295 K. Further, possible stackings of close-packed planes result in either AB or AC, in BC or BA, or in CA or CB sequences (see Table 1). Since the total number of stacking planes is equal to 10, there is a total of  $Z = 2^{10-2} = 256$  entropic different sequences. In consequence, the entropy term gives 140 meV per pair of Cd and S



**Figure 2**  
Comparison of experiment and simulation. The simulation is for a powder of nanoparticles each containing 3380 atoms arranged in ten CdS layers.

atoms. This entropic energy is significant as it represents 50% of the thermal energy at the condition of synthesis. It should be comparable to the energy difference between the disordered and the ordered phase, and it should also be close to the energy difference between the two ordered phases B3 and B4. However, these values are not known for CdS. SiC is probably the most famous system with different stacking sequences. From the heat of formation of the different polytypes 3C, 6H, 15R, 4H (Fissel, 2000) it appears that the difference in enthalpy is about 16 meV per pair of Si and C atoms. This value is one order of magnitude less, corresponding to the difference in dominant long-range ionic character of the bonding in CdS in contrast to the strong short-ranged covalent bonding in SiC. The significant difference in entropy between the ordered and the disordered state of a CdS nanoparticle smaller than the critical size and the differences between the enthalpies of SiC polytypes confirms that the above description predicts reasonably well the values of the anisotropy and of the range of interactions.

## 7. Conclusion

In the present paper we show that nanoparticles made from materials with close-packed structures have an intrinsic lowest energetic state with a non-crystalline disordered stacking sequence of close-packed hexagonal planes. In bulk material the number of stacked planes is large and the correlation between planes of different types (A, B, C) develops on an extended length scale. Therefore the crystalline structures of bulk materials show periodicity in their stacking sequence. In contrast, in nanoparticles the number of stacking planes is reduced to a few planes and long-range correlations become less important. Since there are many possibilities of stacking even a few planes in a non-periodic manner, different nanoparticles may have different sequences. In consequence, the electronic structure will be different in spite of the same size and morphological shape. This leads to differing properties between the particles and this may be important for fundamental science as well as for applications. In the natural composites it is already proven that mechanically highly stable biomaterials consist of building blocks on the nanometre length scale (Gao *et al.*, 2003).

## APPENDIX A Sample preparation

The wet synthesis of CdS nanoparticles used in this work was based on a chemical reaction between a cadmium salt ( $\text{CdCl}_2$ ) and a sulfur-containing compound [thiourea,  $(\text{NH}_2)_2\text{CS}$ ] in an aqueous solution. The chemical deposition of CdS nanoparticles in the  $\text{CdCl}_2\text{-NH}_3\text{-NaOH-(NH}_2)_2\text{CS-H}_2\text{O}$  bath is described elsewhere (Rempel *et al.*, 2005). In the present work all baths had the same composition and were prepared from solutions of cadmium chloride  $\text{CdCl}_2$  ( $0.005 \text{ mol l}^{-1}$ ), ammonia  $\text{NH}_3\text{-H}_2\text{O}$  ( $1.5 \text{ mol l}^{-1}$ ), sodium hydroxide  $\text{NaOH}$  ( $0.074 \text{ mol l}^{-1}$ ) and thiourea  $(\text{NH}_2)_2\text{CS}$  ( $0.025 \text{ mol l}^{-1}$ ) using

distilled water. The synthesis was carried out at ambient temperature. The primary concentrations of the precursors were chosen according to a thermodynamical analysis (Kitaev *et al.*, 1965).

## APPENDIX B Measurements

X-ray Bragg–Brentano powder diffraction was used to investigate the atomic structure of CdS nanoparticles. The diffraction pattern was measured on a Philips X'Pert diffractometer using a 2.2 kW copper tube driven at 40 kV and 35 mA. A secondary graphite monochromator reduced the background to 0.3 counts s<sup>-1</sup>. The diffracted beam was recorded in the 2θ range 15–135° with 40 s counting time per 0.02° step width (in 2θ). All measurements were performed at ambient temperature. The resolution of the diffractometer (full width at half-maximum) for the experimental set-up in the angular range of interest was much better than the measured widths of CdS reflections caused by the small size of the nanoparticles.

## APPENDIX C Fitting procedure

To simulate XRD powder patterns, an approach based on the Debye function (Debye, 1915) was chosen among the methods available for an *ab initio* structure determination of nanomaterials (Debye, 1915; Juhás *et al.*, 2006). Alternative options such as the LIGA method, an efficient algorithm where large clusters are grown by adding atoms to a population of high-quality subclusters (Juhás *et al.*, 2006), are normally restricted to smaller particles not exceeding about 100 atoms, while the Debye-function approach allows simulation of powder patterns of nanoparticles in excess of 3000 atoms including defects and disordering and arranged in any morphological shape. For the simulation of *N* atomic particles and within the frame of an ideal powder averaging a slightly modified Debye formula was used:

$$I(q) = \sum_{\nu} N_{\nu} f_{\nu}^2(q) + 2 \sum_{j=1}^N \sum_{k>j}^N f_j(q) f_k(q) \frac{\sin(2\pi q R_{jk})}{2\pi q R_{jk}},$$

where  $\nu$  denotes the Cd and S atoms,  $N_{\nu}$  is the number of atoms of the element type  $\nu$ ,  $R_{jk}$  is the interatomic distance between atoms  $j$  and  $k$ ,  $q$  is the length of the wavevector, and  $f_j(k)$  is the atomic scattering factor for the  $j$ th atom. For the simulation a nanoparticle was constructed by a disordered sequence of close-packed Cd planes. Next to each Cd plane a close-packed plane of S atoms was placed according to the tetrahedral environment. Fig. 2 shows the comparison of an experimental spectrum and a simulation of a disordered CdS nanoparticle featuring 3380 atoms and ten CdS planes. All possible stacking sequences (2<sup>9</sup>) were taken into account. The *R* value was less than 0.10, while a model with ordered

structures like *B3* or *B4* always resulted in an *R* value in excess of 0.18.

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