IN SEARCH FOR A REFINABLE MODEL OF NANOCRYSTALS

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ABSTRACT

When presenting a diffraction pattern of the material under study, it is a good practice to list the parameters that characterize its structure. The appropriate technique for structural analysis of nanocrystals is powder diffraction. Parameters that are derived from routine diffraction studies (crystal phase, lattice parameters, size, strain, etc.) do not necessarily contain any information that reflects unique physical properties of the material. Although some structural parameters of nanocrystalline materials can be routinely derived from diffraction, those that are published are used by nano-researchers only occasionally. The reason for that is that the parameters obtained routinely from a diffraction experiment are derived assuming that the structure of the nanocrystal is the same as that of a single crystal and, therefore, is does not provide any specific information about material in the nano-state. The assumption of uniform structure is a common practice although it is generally agreed that the structure of a few nm nanocrystal is not the same as that of a “real single crystal”. Obviously no progress will be made in exploration of the atomic structure of nanocrystals unless a reliable and refinable model of a single nano-particle is elaborated. Such a model is urgently needed for establishing standards for description of nanocrystalline structures. We suggest that, for the time being, to overcome the limitations of not having an atomistic model for nanocrystals, a practical and temporary solution might be building (and databasing) projections of nanocrystals in real and/or reciprocal spaces. Those projections could have a form of specific plots of experimentally derivable and reproducible parameters from Bragg and/or PDF data. Tentative solution based on the concept of the apparent lattice parameters is presented.

INTRODUCTION

Up to now crystallography does not have much to offer to support nanoscience by providing reliable information on the atomic structure of nanocrystals. Unfortunately, due to that very reason, crystallography (and crystallographers) play only a marginal role in development of nanotechnologies. Definitely there is a need to provide a model for description of nanocrystal structures. To achieve this goal one needs to have appropriate tools and methodology for structural analysis of nanocrystals.

When elaborating a diffraction data of polycrystalline sample one has already in mind a model of the material’s structure to which one refers to. In a routine procedure of diffraction data analysis of crystalline materials the model which one “has in mind” is a single crystal. Due to different environment of the atoms in the grain interior and that at the surface, the atoms at the grain boundary show different specific arrangement than that in the bulk crystal lattice. In other words, a crystallite of any size definitely does not show a perfect crystal lattice in the whole sample volume. Obviously a more complex atomic model of a nanocrystal is needed, a model that accounts for a unique atomic architecture of the crystal surface, since that comprises a large
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fraction of the sample. Although this is "common knowledge", standard crystallographic tools are routinely used for characterization of nanocrystals. From a crystallographer-experimentalist point of view one can indeed disregard the presence of surface atoms for the materials for which the number of surface atoms is small compared to the total number of atoms in the sample volume. This follows from the fact that there is always a detection limit of any diffraction experiment and the effect of a presence of different atomic architecture at the grain surface on the diffraction profile must be strong enough to be measured and evaluated. Assuming the thickness of the surface layer of about 10 Å, for the grain size of 100 nm about 6% of all atoms are located in the surface layer. This is close to the detection limit of crystal phases examined with powder diffraction techniques. Since it is generally agreed that materials with dimensions below 100 nm belong to nano-class, structural analysis for them should account for a presence of a surface layer with the structure varying from that in the grain interior.

CONDITIONS FOR A SUCCESSFUL DIFFRACTION EXPERIMENT ON A NANOMATERIAL

There are three (key) conditions for a sucessfull analysis of nanocrystals: (i), selection/design of an appropriate model of the nanocrystal which, in the course of the structural analysis, will be described by a set of reproducible structural parameters, (ii), doing the right experiment, which is sensitive to diffraction signals from the grain surface, and (iii), application of the appropriate data elaboration technique.

![Fig.1 Tentative models of a nanocrystalline grain](image)

(i) A realistic "universal" model of a nanocrystal that could be described by a set of “refinable” parameters does not exist. A tentative core-shell model, which is often recalled in the literature, is a kind of a “substitute” that might help in deriving some parameters characterizing a presence of internal strains in nanograins. Some tentative models of a nanocrystal are shown in Fig. 1. The first model, which is just a small single crystal, is definitely incorrect, the second accounts for different structure of the interior and of the surface of the grain, the third one indicates that there can be a complex distribution of strains in the grain volume; presence of strains means that corresponding interatomic distances \( r \) in core and shells differ. Obviously, when building a model of a real material, one should account for anisotropy of the crystal lattice, i.e. for its specific shape, distribution of internal strains in the grain volume, and that at the surface layer (the shell).
The appropriate experimental technique applicable to nanocrystals is powder diffraction. Reliable information on the atomic arrangements in nanograins requires collection of data including large magnitudes of the diffraction vector, much larger than that available from standard laboratory diffractometers. Definitely “hot neutrons” or hard X-rays available at synchrotron sources are preferable choices to perform structural analysis of nano-materials. Among laboratory diffractometers, the only meaningful choice is powder diffractometer equipped with Ag radiation. The requirement of collecting the data up to a large diffraction vector is true for any material under study, and follows from the obvious goal of determining structural parameters with possibly high resolution and accuracy. For nanocrystals, large Q diffraction measurements are not only desired but, plainly, necessary to observe and evaluate deviation(s) of the atomic structure of a nanocrystal from that of the corresponding single crystal lattice, see below.

Any software developed so far for elaborating the structure of crystalline materials and applied to nanocrystals might serve only for evaluation of “how poorly” single crystal lattice represents the actual structure of nano-samples. Definitely, for nanocrystals one needs specific software dedicated to such materials. Recently a variety of computer programs were developed for modeling atomic structure of nanocrystals and accounting for specific grain shape and size distribution (Neder, 2010; Cervellino and Guagliaroi, 2010; Thomas, 2010). Most of these programs are still based on the assumption that, "in principle", the structure of a nanocrystal can be satisfactorily approximated by a crystal lattice, i.e. it is represented by a unit cell. This is a practical approach, which, unfortunately, has an internal self-limitation due to the applied crystal model with its structure described by a strictly periodic crystal lattice. Definitely, software for data elaboration that would account for deviations of the atomic architecture of a nanocrystal from a fully periodic crystal lattice is required.

ELABORATION OF DIFFRACTION DATA OF A NANOCRYSTAL USING RECIPROCAL AND REAL SPACE APPROACHES

Not knowing a real model of a nanocrystal, one needs to take into account that, in addition to the crystalline part of the nanograin, there are atoms belonging to the grain volume that show only a short (limited) range order. Those atoms do not contribute to Bragg scattering. Thus, if we use only Bragg reflections, we definitely miss information on non-crystalline part of the sample volume. If this is the case the lattice parameters of the nanocrystal, even if derived correctly, describe only the crystalline part of the sample volume. For this reason alone structural analysis of nanocrystals should not be limited to examination of Bragg reflections. The obvious alternative is the real space analysis, PDF, which provides information on all interatomic distances in the sample volume including coherently and incoherently scattering atoms. When choosing this way of structural analysis one faces similar problems to those encountered with reciprocal space analysis: (1), resolution, and (2), interpretation of the experimentally derived interatomic distances which need to be referred to a certain model of the materials structure (Palosz et al., 2007, 2010). An important difference between reciprocal and real space analyses is, that while resolution of Bragg diffraction patterns depends mostly on the mechanics and optics of the instrument used, resolution of PDF is a function of the maximum Q-range applied (Egami and Billinge, 2003).

APPLICATION OF RECIPROCAL AND REAL SPACE ANALYSES TO
NANOCRYSTALS WITH A PERFECT CRYSTAL LATTICE

Application of both Bragg and PDF methods to interpretation of a powder diffraction pattern of a small crystallite is demonstrated in Figs. 2 and 3. Fig. 2 shows a theoretical diffraction pattern calculated for 5 nm diameter spherical grains with a perfect diamond lattice, for which the Bragg equation is applied to every individual reflection and serves for calculation of the values named the apparent lattice parameters, \( a_p \). The last plot in Fig. 2 shows relative \( a_p \) values, \( a_p(Q)/a_0 \) (\( a_0 \) being the real lattice parameter of the model), calculated for different diffraction vectors \( Q \) of the corresponding Bragg reflections. This plot demonstrates, that due to a small dimension of the grain the \( d \)-distances calculated from the Bragg equation are larger than the real values in the model; this difference gets smaller as the \( Q \) increases and tends to reach the real values for very large-\( Q \) reflections. This shows that if a nanocrystal was a small single crystal, to measure its lattice parameters one should use only the largest \( Q \) reflections. Fig. 3 shows again the calculated apparent lattice parameters of the same model, but this time obtained using the interatomic Pair Distribution Function, PDF. The \( g(r) \) function presents interatomic distances which are volumetric averages of the examined sample, in our case of an individual nanocrystal. The \( a_p(r)/a_0 \) plot shows very clearly, that the real space analysis, PDF, is definitely more appropriate/better suited for structural analysis of nanocrystals.

Fig. 2 (a), theoretical diffraction pattern of 5 nm diamond nanocrystal with a perfect crystal lattice; (b), individual apparent lattice parameters calculated from the Bragg reflections; (c), the corresponding plot of \( a_p(Q)/a_0 \) values vs. diffraction vector \( Q \).

Fig. 3 (a), theoretical PDF function \( g(r) \) of 5 nm diamond nanocrystal with a perfect crystal lattice; (b), individual apparent lattice parameters calculated for individual interatomic distances; (c), the corresponding plot of individual values of \( a_p(r)/a_0 \), vs. interatomic distances \( r \).
APPLICATION OF RECIPROCAL AND REAL SPACE ANALYSES TO NANOCRYSTALS WITH A NON-UNIFORM STRUCTURE

Introduction of strains into a crystalline model of a nanocrystal (e.g. by adding compressed or expanded surface shell surrounding the crystalline core) always results in changes of the original diffraction pattern. At the first sight such changes can be easily overlooked, since the "general view" of the pattern remains unchanged. However, taking into account that a given structure might be non-uniform, one needs to verify the meaning of the structural parameters that are derived with a standard data elaboration procedure. In a routine reciprocal space analysis based on the Bragg equation, one tacitly assumes that the sample structure is represented by a unit cell and calculates the lattice parameters of that assumed cell. For a material with a non-uniform structure, one can still apply the Bragg equation, but one must remember that the derived values might have not a unique meaning and that they describe neither the crystalline interior of the grain nor its strained surface. In the real space analysis, the interatomic distances observed in the $g(r)$ plots are volumetric averages, i.e. they correspond neither to the grain interior nor to its surface shell. The individual $r_i$-values observed in the $g(r)$ are then not strictly related to each other, as opposed to the structure with a uniform crystal lattice represented by a unit cell. In other words, the set of $<r_i>$ values measured from the $g(r)$ function does not represent a uniform atomic lattice and, therefore, there is no unique model of a crystal (i.e. with defined lattice parameters) which would correspond to $<r_i>$ values determined from the $g(r)$ function. One can still ask about the lattice parameter corresponding to the measured $<r_i>$ values and apply the usual procedures, like the PDFgui refinement program, to derive the lattice parameters of the "tentative unit cell" (Proffen and Billinge, 1999; Peterson et al., 2000; Farrow et al., 2007; Le Roux and Petkov, 2010). However, instead of searching for one value of the lattice parameter describing the structure of a nanocrystal, we suggest an alternate method of characterization of nanograin structures (Palosz et al., 2008, 2010).

Appearance of strain in a nanograin, in particular in the surface shell, always leads to changes of all $r$-values in the interatomic Pair Distribution Function, and to changes of positions of Bragg reflections on the diffraction pattern relative to those corresponding to the perfect crystal. Fig. 4 presents examples of apparent lattice parameters calculated from Bragg reflections, $alp(Q)$ plots, and those calculated from the $g(r)$ function, $alp(r)$, which are derived for tentative models of nanocrystals in which the crystalline core is surrounded by a surface shell(s) with the same arrangement of atoms as that in the core but with smaller or larger interatomic distances. A presence of tensile strain in the surface shell of Model I results in elongation of all average values of the interatomic distances. Relative changes of the shortest and the longest (grain diameter) distances are the largest, while the $r$-distance equal to the grain diameter is elongated the least. In the case of Model II with five shells, the character of changes in interatomic distances is more complex but here, again, the changes of the shortest and the longest distances are the largest. A comparison of $alp(Q)$ with $alp(r)$ plots in Fig. 4 shows, that real space analysis reflects differences between the two models much better than the results derived from reciprocal space analysis.
Fig. 4  \( \Delta p \) plots of 5 nm diameter diamond grain with, (a), tensile strain in a single surface shell, (b), four shells with compressive followed by tensile strains surrounding the crystalline core; 
\[
\Delta p(r_i)/\Delta p_0 = 1 + (r_i - r_0)/r_0.
\]

Fig. 4 shows very clearly that the apparent lattice parameters derived from a diffraction experiment for a nanocrystal with internal strains, whether using reciprocal or real space approaches, have no physical meaning, since there are no real objects that the \( \Delta p \) values correspond to. The only way to determine meaningful numbers/parameters that can characterize quantitatively the atomic structure of a nanocrystal is by developing an appropriate model, which reproduces the diffraction images of the examined material.

**SUMMARY AND CONCLUSIONS**

Without a reference model and an appropriate and positively verified method of interpretation of the diffraction data, it is practically impossible to present a unique quantitative description of the structure of a nanocrystal. In our opinion it is definitely better to avoid publication of structural parameters than publicize data that might (and quite likely will) be misinterpreted.

We suggest that a practical, although a temporary solution for overcoming the limitations resulting from the lack of a proper atomistic model of nanocrystals, could be achieved by presenting \( \Delta p-r \) and/or \( \Delta p-Q \) plots derived from experimental diffraction patterns and PDFs, respectively. This way we could build a database of the experimental data that would serve for a meaningful comparison of nanomaterials examined by different researchers using different radiation sources and different instruments. Once the tools needed for interpretation of those data
are developed, they could retroactively be used to derive sets of nanocrystal parameters of the materials.

Fig. 5. Example of diffraction representation of a model of nanocrystal with a core shell structure through \( a\rho \)-r and/or \( a\rho \)-Q plots.

REFERENCES


