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Application of Powder Diffraction Methods to the Analysis of Short- and Long-range Atomic Order in Nanocrystalline Diamond and SiC: the Concept of the Apparent Lattice Parameter (alp)

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Abstract. Two methods of analysis of powder diffraction patterns of diamond and SiC nanocrystals of different grain size are presented: (1) examination of changes of the lattice parameters (*"apparent lattice parameter", alp*) with the diffraction vector Q, which refers to Bragg scattering, and (2), examination of inter-atomic distances based on the analysis of the atomic Pair Distribution Function, PDF. Application of these methods based on theoretical diffraction patterns computed for models of nanocrystals having either a perfect, uniform crystal lattice or a core-shell structure constituting a two-phase system was studied. The models are defined by the lattice parameter of the grain core, thickness of the surface shell and the magnitude and the strain field distribution in the shell. X-ray and neutron diffraction data of nanocrystalline SiC and diamond powders of grain diameters from 4 nm up to micrometer range were analyzed. The effects of the internal pressure and strain at the grain surface on the structure, based on the experimentally determined dependence of the *alp* values on the Q-vector, and changes of the inter-atomic distances with the grain size determined experimentally by the atomic Pair Distribution Function (PDF) analysis are discussed. The experimental results lend strong support to the concept of a two-phase, core and the surface shell structure of nanocrystalline diamond and SiC.

Introduction

In polycrystals with micrometer size grains, the surface contains an insignificant fraction of the total number of atoms and its effect on the overall properties of the material can be ignored. The situation is different for small, nano-size particles where, due to the size, a considerable fraction of the atoms is located at the surface, i.e. where some of their neighbors are missing. Such a situation always leads to changes in the lengths of inter-atomic bonds of the surface atoms relative to those in the bulk. To date, no specific experimental methods have been developed for the structural analysis of the surface of nanocrystals and therefore information on the arrangement of atoms at the surface of nanograins is very limited. This work presents analyses the applicability of powder diffraction techniques for elucidation of the atomic structure of nanocrystals, particularly at the surface shell.

In a number of publications detailing changes in the physical properties of nanocrystals related to their size [1 - 9] the dependencies reported are often related to the lattice parameters which, for very small crystals, appear to be a size dependent property of the material. A dependence of the lattice parameters on the grain size have been reported for a variety of nanomaterials, like metals (Au [10, 11], Al [12], Cu [13]), semiconductors (CdSe [14], GaN [15]), ionic crystals (NaCl, KCl, NaBr, LiF [16], Y_2O_3 [17]), and others (e.g. Se [18]). Those results are often attributed to the presence of an "internal pressure" caused by surface stresses [19 - 28]. The stresses are located at the surface and a quantitative evaluation and description of this property of nanocrystals would require precise determination of the inter-atomic distances in the grain interior and the surface.

A nanocrystalline sample constitutes a polycrystalline material, for which the appropriate technique for determination of the atomic structure is powder diffraction. Recently, with this technique, we showed that the structure of a nanocrystal is not uniform and can be approximated by a two-phase model in which the grain core and the shell have different structures and properties [29 - 31]. It is obvious that such a model cannot be adequately characterized by only one set of lattice parameters which is a sufficient description only for uniform crystal phases. Therefore, application of the lattice parameters concept to characterization of the structure of nanocrystals requires a special treatment. In this work we discuss inherent limitations of different methods of elaboration of experimental powder diffraction data. We use a simple, spherical core-shell model to describe the diffraction patterns and present the results on evaluation of the lattice parameters of nanocrystalline diamond and SiC based on this model.

Analysis of short- and long-range atomic order based on powder diffraction experiment

The analysis of powder diffraction data is routinely performed using the concept of the unit cell and the Bragg equation. This approach assumes an unambiguous relation between the Bragg reflections of a given diffractogram through the quadratic equation. Among the procedures used for elaboration of powder diffraction data, the most common is based on the Rietveld program [32, 33]. Although possible in principle, it is impossible in practice, to derive information on the local atomic arrangements in nanocrystals using the Rietveld or similar programs. An alternate method for elaborating powder diffraction data, developed for materials with a short range order (like liquids and glasses) is the PDF analysis (known also as *rdf* - radial distribution function) leading to determination of the atomic Pair Distribution Function, G(r) [34 - 37]. Both methods are shown in Fig. 1.

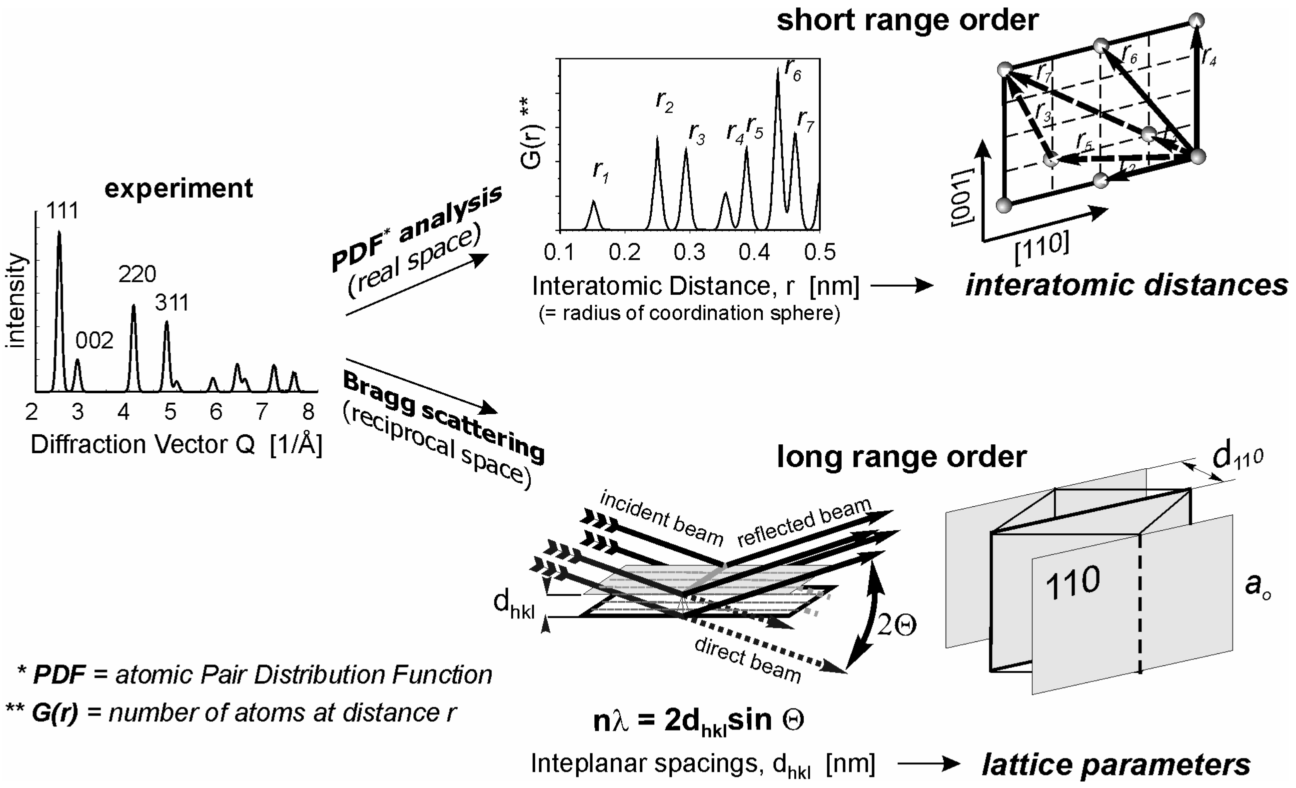

Fig. 1 Alternate methods of elaboration (and interpretation) of a powder diffraction experiment.

Note: A diffraction experiment provides information on the structure of the material, which is averaged over the whole sample volume illuminated by the beam. For that reason any quantitative *information derived from a diffraction experiment can give only an average value: the positions of the Bragg reflections are determined by the "average lattice parameter" (which averages atomic vibrations, strains, and other crystal imperfections); PDF analysis provides information on specific inter-atomic distances averaged over all corresponding atomic pairs in the sample.*

Analysis of long-range atomic order in nanocrystals: application of the Bragg equation

Nanocrystals, although very small, are, by definition, single crystals. As such, they belong to the class of materials with a long-range atomic order and thus, in principle, appropriate methods of elaboration of the diffraction data can be based on the Bragg-type scattering. For a perfect, infinite crystal the positions of all individual Bragg reflections are determined uniquely by the Bragg equation, thus the lattice parameters can be calculated from any set of individual reflections (for cubic structures it can be calculated even from a single reflection using the quadratic equation: $1/d_{hkl} = (h^2+k^2+l^2)/a_o^2$). However, in nano-size grains, the long-range order is limited by the size of the crystallite which may be smaller than the coherence length of the scattered beam. In this case the Bragg equation may not be applicable, since the positions of the Bragg reflections are not determined by the unit cell parameters alone but become strongly influenced by the grain size and shape. This effect is demonstrated in Fig. 2 which shows the lattice parameters (in terms of the ratio alp/a_o) of the cubic unit cell of diamond, calculated from a single (111) reflection of the theoretical diffraction patterns which have been computed for models of a diamond nanocrystal with a perfect crystal lattice but, different shape and size. Note that in Fig. 2 we use the term "*alp*" (*apparent lattice parameter, c.f. next section*) instead of the lattice parameter a_o since the latter, used to build the model, is not equal to the values calculated from the (111) reflection.

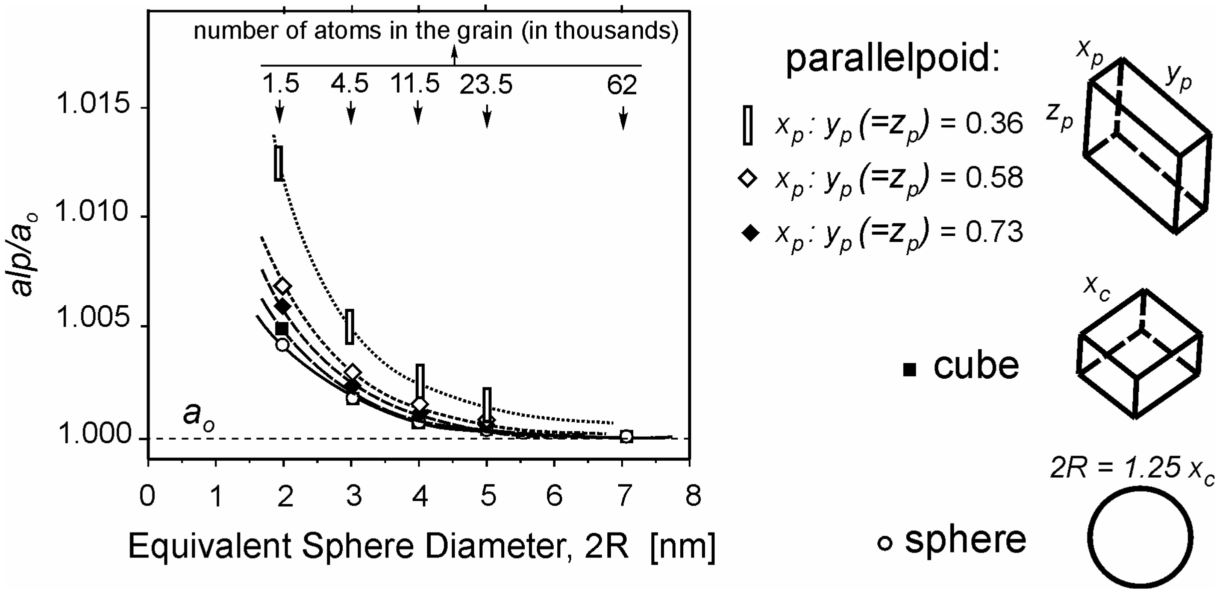

Fig. 2 Dependence of the alp/a_o ratio on the grain size calculated from (111) Bragg reflection of a diamond nanocrystal for different crystallite shapes.

Evaluation of powder patterns is done routinely using standard numerical procedures like the Rietveld method [32, 33]. We calculated the lattice parameters obtained with the DBWS-9807 Rietveld program from diffraction patterns calculated theoretically for spherical diamond nanocrystals of 3, 6, and 12 nm in diameter, c.f. refs. [30, 31]. Fig. 3a shows "as refined" lattice parameters for two different ranges of the diffraction vector Q: up to 6 and up to 16 $Å^{-1}$ (shown in Fig. 3b). Solid circles and solid lines in Fig. 3a show the values of the lattice parameters computed with the Rietveld program where refinement was done on the lattice parameter (*a*) only, all other sample and instrument parameters being fixed. Open circles and dashed lines additionally show the results obtained with refinement of the 2Θ zero point parameter (zero shift, z_s) [32, 33]. Note that the theoretical diffraction patterns that we used for Fig. 3 are equivalent to "perfect powder diffraction experiments" where all instrumental and structural parameters are uniquely defined. In a perfect experiment all sample and instrument parameters refined by the Rietveld program should always converge to their perfectly accurate values. The fact that the Rietveld program does not converge to the real instrument parameter $z_s = 0$ and does not reproduce the input lattice parameter value of $a_o = 3.5668$ Å of our starting model means, that the assumptions made for the refinement procedure are not met. The differences between the lattice parameters shown in Fig. 3a stem from the fact that the positions of the individual Bragg reflections are not constrained by the quadratic equation. In other words, the Bragg approximation does not apply to very small crystals. The difference between the real (model) value a_o and that calculated by the Rietveld program, (1), decreases with an increase in the grain size, and (2), is smaller if calculated for Bragg reflections of larger Q. The above dependencies disqualify the Rietveld program as a tool for direct determination of the lattice parameters of very small, nano-size crystals. The results of Fig. 3a show, that while the term "lattice parameter" has a unique meaning when applied to description of a perfect crystal lattice, it is not a constant in the Bragg equation when used for description of a diffraction pattern of very small crystals. In other words, lattice parameter is not a uniquely defined parameter for powder diffractograms of very small grain materials.

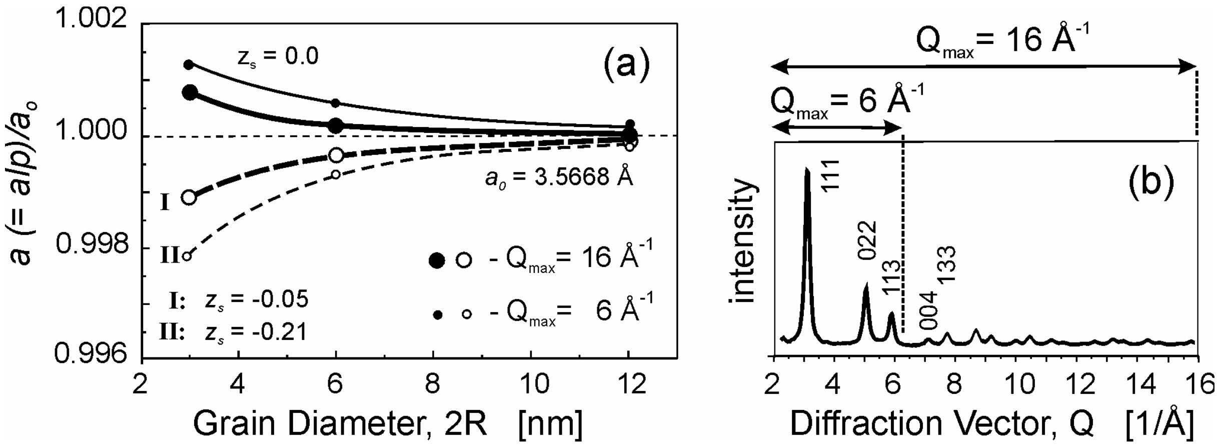

Fig. 3 (a) Effect of the grain size on the lattice parameters for two ranges of the Q vector, calculated with the Rietveld program for diamond nanocrystals; (b) corresponding Q-ranges.

The meaning of the lattice parameter in a perfect crystal lattice of very small crystals

Recently we proposed a methodology for analysis of powder diffraction data of nanocrystals based on calculations of the lattice parameter values from individual (or a group of) Bragg reflections [29 - 31]. We call such calculated quantities, which are linked to the Q-values of the corresponding reflections, the "apparent lattice parameters", *alp*'s (Fig. 3a). Diffraction patterns of simple structures have well separated individual reflections, thus their *alp* values can be calculated for each individual peak, c.f. Fig. 2. For more complex structures the individual peaks overlap and, therefore, the *alp* values need to be calculated using the Rietveld program for groups of peaks in selected Q-ranges. The dependence of the alp/a_o ratio on Q determined from theoretical diffraction patterns of diamond and SiC, for different grain sizes, is shown in Figs. 4a and 4b, respectively. (*Note: The dependence of* alp *values on Q-vector is a discreet relation. However, to emphasize the general trend, we connected respective individual* alp *values with arbitrary curves*). A dependence of *alp* values on the Q vector seems to be too complex to be described by a simple analytical function. An adequate analytical function would have to account for a dependence of *alp* on the grain shape and size (Figs. 2 and 3, respectively) and should account for the specific atomic structure of the material [38]. Such an analytical function, if existing at all, would be very complex. Evaluation of the crystal structure in this work is based on a comparison of the experimental and theoretical *alp*-Q relations.

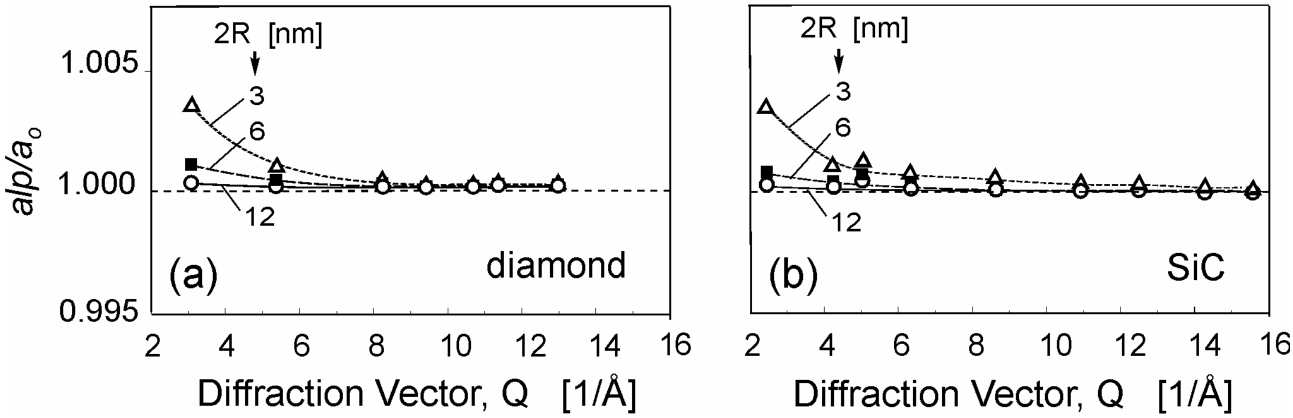

Fig. 4 Dependence of the alp/a_o ratio on the diffraction vector Q for spherical grains of different size. (a), diamond; (b), SiC.

Application of the apparent lattice parameter for description of the atomic structure of nanocrystals with non-uniform, core-shell structure

As discussed above, determination of the lattice parameters for very small crystals based on diffraction data is difficult. The problem becomes even more complex when internal strains and stresses are present in the crystal, in particular when they concentrate in the surface shell of the grains. In a diffraction experiment it is practically impossible to separate the signals from the grain core and those from the surface layer: the beam scattered by the core atoms interferes with that from the surface atoms. To evaluate the nanocrystal surface structure we applied the *alp* concept, presented above for a relaxed crystal lattice, to a two-phase, core-shell model of nanocrystals.

Following the general concept of surface tension, the surfaces of a single crystal are in a state of tension (its magnitude specific for each face) which subjects the interior of the crystal to stresses. As a result, the developed stresses may be expected to lead to an internal pressure that manifests itself by a compression or expansion of the crystal lattice [39]. This effect can, in principle, be measured experimentally from the change of the lattice parameters. However, in literature the changes observed were attributed to the whole crystal volume. This is a very rough, and in fact unacceptable, simplification since nanocrystals are composed of a core and a surface shell that have somewhat different structures. In our investigation we began with an assumption of a two-phase structure of nanocrystals (see the model in Fig. 5). We used a simple model of a spherically shaped nanocrystal with a grain core of radius R_o having a uniform crystallographic structure unambiguously characterized by the lattice parameter a_o. We assumed that the atomic structure of the surface layer (of width s_o) is correlated with the parent structure of the grain such that it is basically the structure of the core but centro-symmetrically deformed. To describe the model we introduce the parameter a_s which corresponds to the lattice parameter a at the outmost atomic layer of the particle. Without compression the width of the surface layer would be s_o. The actual values of the inter-atomic distances within the surface shell are expressed as a function of the distance r from the particle center and vary between a_o in the grain core (at distances $r \leq R_o$) and $a_s = a_o + \Delta a$ (for $r = R_o$). The ratio $\Delta a/a_o$ is quantifying the surface strain.

Fig. 5 presents theoretical alp/a_o-Q plots determined from diffraction patterns of simple models of nanocrystals of diamond and SiC with a uniform compression of the surface shell lattice. These *alp*-Q plots were calculated for 5 nm diameter crystallites with the surface shell 0.7 nm in thickness and all inter-atomic distances within the shell compressed uniformly with $\Delta a/a_o$= -5%. The *alp* values were calculated by refinement of the *alp* values for selected Q-ranges. Figure 5 shows that, for a model with compressed surface layer, the calculated *alp* values are lower than those of the relaxed lattice in the whole Q-range, the decrease being larger for greater strains. There is a distinct difference between Figs. 4 and 5. For a relaxed lattice the largest *alp* value is for the smallest Q and decreases gradually approaching the real value at very large Q (Fig. 4). For a strained lattice (Fig. 5) the alp/a_o-Q relation shows a complex dependence with some characteristic minima and maxima. This feature is obviously related to the presence of a two-phase system, and can be used for identification and evaluation of the surface structure as discussed below. *(Note that presence of homogenous strain in the sample volume, corresponding to the simple concept of internal pressure, would lead to a change of all* alp *values by the same amount without changing the shape of the dependence of* alp *on Q).*

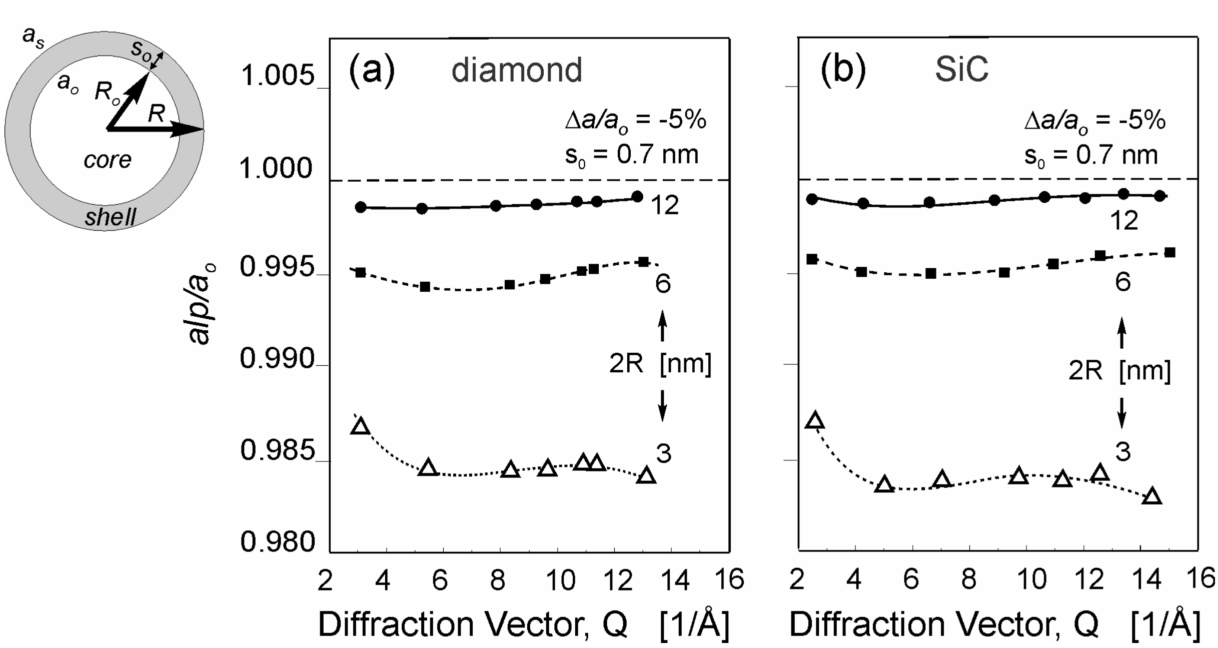

Fig. 5 Effect of stress in the surface shell on *alp* values calculated for different Q ranges for diamond and SiC nanocrystals.

Experiment: analysis of Bragg-type scattering

We examined four diamond and four SiC polycrystalline powders, each having a different (average) grain diameter. The powder diffraction experiments were performed using both synchrotron and neutron sources and collecting the data in a large Q-range. We used Stations ID11 at ESRF and BW5 at HASYLAB (wavelength 0.1 - 0.2 Å), and SNBL Station at ESRF (wavelength 0.5 - 0.7 Å) approaching Q_{max} = 10 - 15 $Å^{-1}$. For each X-ray diffraction experiment the specific *alp* values were determined with reference to Si microcrystalline powder used as a standard and measured in the same experimental set-up before and after the sample scan. Neutron diffraction measurements were done using the HIPD diffractometer at LANSCE in Los Alamos National Laboratory, in the diffraction vector range approaching Q_{max} = 26 $Å^{-1}$.

Fig. 6 shows experimental alp/a_o-Q plots determined with the Rietveld method from the neutron diffraction patterns obtained for diamond and SiC nanocrystals of different size (similar plots were obtained from synchrotron diffraction data). Specific *alp* values strongly depend on the diameter of the nanocrystallites, with similar tendencies observed for both diamond and SiC samples:

Diamond (Fig. 6a): The *alp* (*alp*/a_o) values determined for the microcrystalline sample are close to the value of the lattice parameter a_o of a perfect diamond crystal. The *alp*'s of nanocrystalline powders show characteristic minima and maxima, similar to those calculated theoretically for core-shell models (Fig. 5a). The deviation from a_o increases with a decrease in the grain size. The sample with 12 nm diameter grains does not match this scheme: this specific sample is very different from the other ones, since it consists of diamond crystallites with average diameter of 12 nm but strongly bonded together (sintered) and existing in 1 - 2 micron size agglomerates. As a result, the sample contains many grain boundaries between individual crystallites instead of free surfaces, while other powders consist of individual crystallites with large free surface (where surface stresses are located). That underlines the importance of surface environment for the actual structure of nanocrystals, c.f. [31].

SiC (Fig. 6b): The dependence of *alp* on Q is similar to that observed for diamond nanocrystals (Fig. 6a). However, the minima are shallower and their positions are slightly different to those observed in diamond. The character of the experimental *alp*/a_o-Q results is consistent with those calculated theoretically and shown in Fig. 5: there is a maximum of *alp* observed at the smallest Q followed by a minimum occurring within the range 5 $Å^{-1}$ < Q < 8 $Å^{-1}$, and the next maximum at about Q = 10 $Å^{-1}$ for diamond and at larger Q for SiC. A presence of minima and maxima on the *alp*/a_o-Q plots is clear evidence of strain present in the crystallites, c.f. Figs. 4 and 5. The span between the minimum and maximum *alp* values is obviously different for diamond than SiC, the difference apparently being due to different surface strains in the materials.

A comparison of the experimental (Fig. 6) and theoretical (Fig. 5) *alp*/a_o-Q relations proves very clearly that the surface of the grains is under stress, and the surface shell lattice is compressed relative to the grain core (for both SiC and diamond powders). The *alp* values obtained from the experiment, Fig. 6, are larger than those expected based on our model calculations (Fig. 5) for both diamond and SiC. To achieve the right match between the experimental and modeling results, the lattice parameter of the core in the model has to be larger than the value a_o of the relaxed lattice. That indicates that the compression of the surface shell lattice is accompanied by a simultaneous expansion of the lattice of the core.

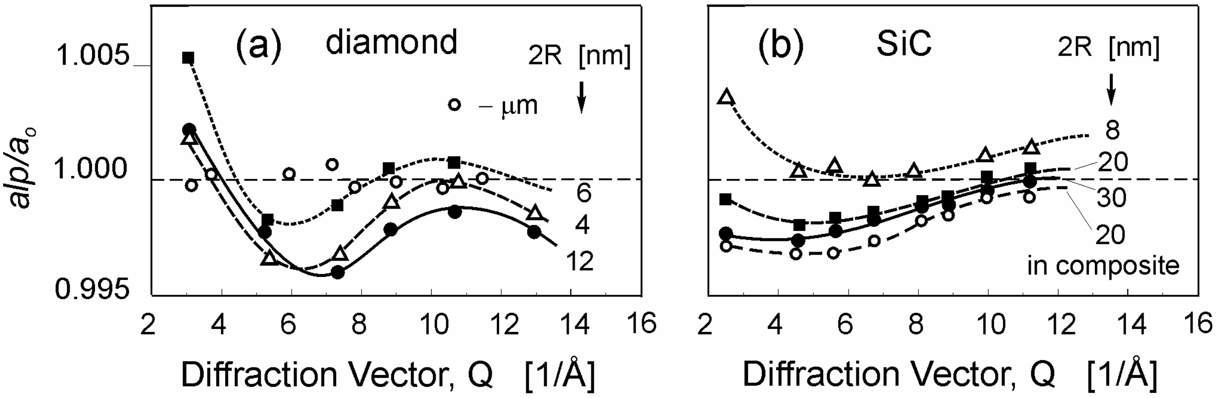

Fig. 6 Experimentally determined dependence of the *alp*/a_o ratio on the diffraction vector Q for different size grains. (a), diamond; (b), SiC.

Determination of short-range atomic order in nanocrystals: PDF analysis

Calculations. Analysis of the *alp*/a_o-Q plots presented above refers to the unit cell that represents three-dimensional ordering of atoms in the crystal. This kind of analysis does not provide direct information on the specific atomic positions in the lattice. In general, a number of different arrangements of atoms corresponding to a given lattice parameter exist. Therefore complete information on the crystal structure should contain (in addition to the unit cell and its lattice parameters describing the long-range order) the positions of the atoms in the cell (which describe the short-range atomic order, c.f. Fig. 1).

In this work we present an analysis of changes of the first seven shortest inter-atomic distances in diamond and SiC nanocrystals with change in the crystallite size. Figure 7a shows the arrangement of atoms in (110) plane of the diamond lattice. A perfect diamond-type cubic lattice is combined of two face-centered (F-type) sub-lattices shifted relative to each other by the lattice vector [¼, ¼, ¼]; in diamond the entire lattice is made of carbon, in SiC one sub-lattice is made of carbon, the other of Si atoms. Fig. 7a shows also the seven inter-atomic distances in the lattice. Fig. 7b shows the corresponding atomic Pair Distribution Function, G(r), of the diamond lattice. (Note: in the theoretical calculations we accounted for thermal motion of the atoms assuming the amplitude of isotropic, harmonic oscillations of 0.1 Å. A presence of thermal motion, implemented in the models as a positional static disorder of all atoms, leads to broadening of the lines on the G(r) plots and makes the theoretical plots more compatible with those obtained experimentally, c.f. Fig. 9).

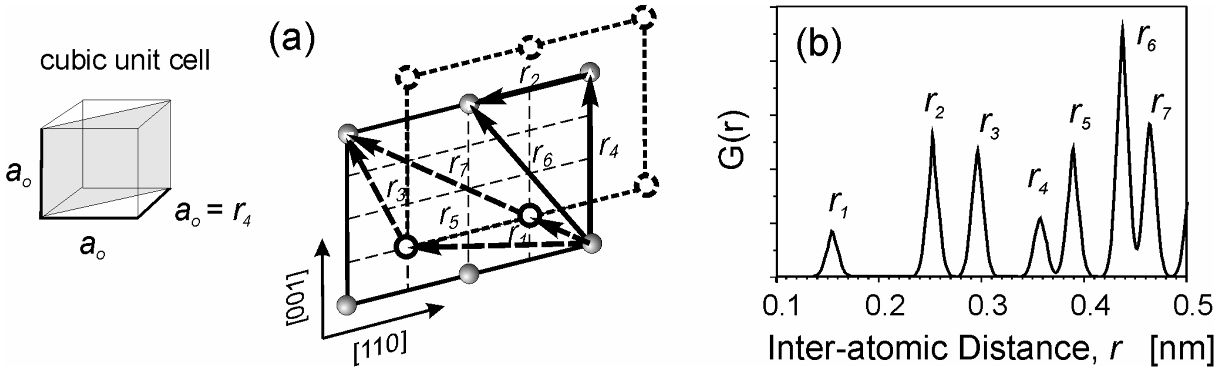

Fig. 7 The seven shortest inter-atomic distances, r_1 - r_7, in a diamond-type lattice. (a), (110) atomic plane of the cubic unit cell; (b), the corresponding atomic Pair Distribution Function, G(r). The second sub-lattice is drawn with dashed lines.

Relations between the lattice parameter and inter--atomic distances in the lattice

Fig. 7 shows that there is a close relationship between the lattice parameter of the crystal lattice and inter-atomic distances within individual sub-lattices. The even inter-atomic distances, r_2, r_4, and r_6 correspond to inter-atomic distances within the same sub-lattice (Si-Si and/or C-C bonds). In a diamond-type cubic lattice the inter-atomic distance r_4 should be equivalent to the lattice parameter *a* of the cubic cell. Of the first seven inter-atomic distances the odd distances, r_1, r_3, r_5, and r_7 correspond to the inter-atomic distances between atoms belonging to separate sub-lattices (Si-C bonds in SiC lattice). The relative shift between individual sub-lattices has no direct effect on the (overall) lattice parameter of the unit cell, therefore no direct relation between inter-atomic distances across different sub-lattices and the lattice parameter exists.

As discussed above, presence of strain in the surface shell leads to some characteristic changes in the shape of the alp/a_o-Q plots relative to a relaxed lattice (c.f. Figs. 4 and 5) which can be used for identification and further evaluation of the surface stresses. A presence of surface strains is also reflected by changes of inter-atomic distances and corresponding changes to the G(r) functions. Fig. 8 shows G(r) of a relaxed diamond lattice and those calculated for a model of 6 nm diameter diamond crystals with 0.7 nm thick surface shell and the shell inter-atomic distances compressed by 3 and 5% relative to the bulk. Obviously the presence of strain in the surface shell leads to shifts of individual peaks on the G(r) plot, a different and non-proportional shift for each atomic pair.

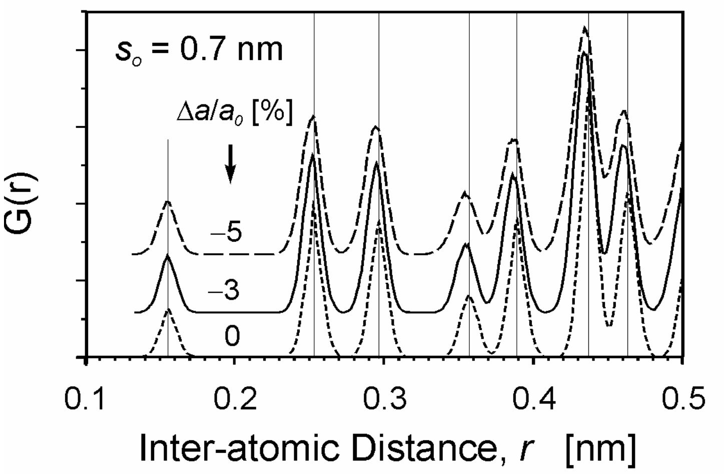

Fig. 8 Inter-atomic distance function, G(r), calculated for 6 nm diameter diamond nanocrystal relaxed and with a 0.7 nm thick surface shell compressed by 3 and 5%.

Experiment. We performed PDF analysis of powder diffractograms of diamond and SiC samples applying the same data that were used to obtain the alp/a_o-Q plots shown in Figs. 6. The neutron diffraction patterns were collected in the Q-range up to 30 Å^{-1} and above. The useful part of the patterns used for PDF analysis was up to Q = 26 Å^{-1}. The analysis was made using the PDFgetN program of Peterson et al. [40].

Fig. 9 presents the experimental G(r) functions determined for four diamond powders. In order to resolve the positions of individual peaks we fitted (refined) the peak shapes using the Gaussian function taking the positions of the peak maxima. For a reference, the theoretical G(r) function calculated for a perfect relaxed diamond lattice is also shown.

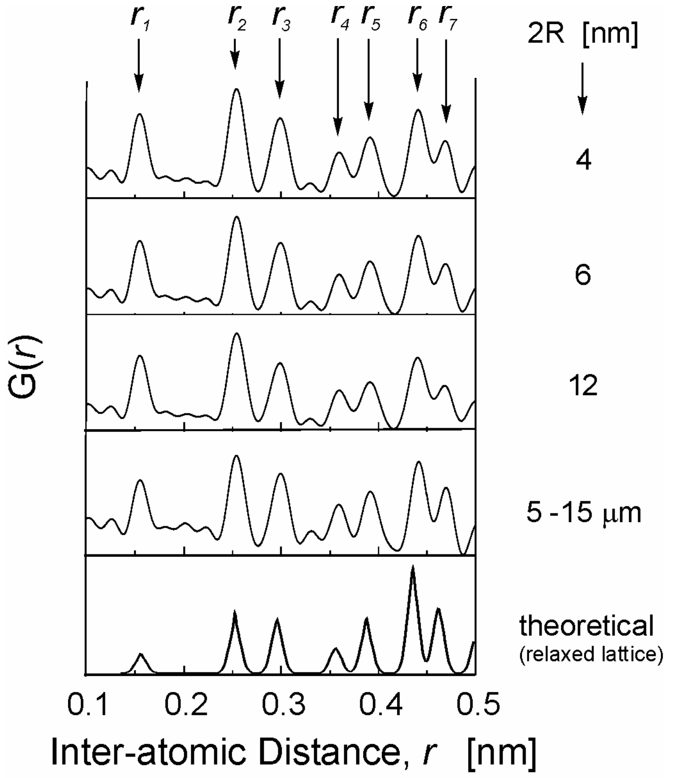

Fig. 9 G(r) functions determined experimentally for diamond powders of different grain size.

The inter-atomic distances determined from experimental G(r) functions for diamond and SiC nanocrystals are given in Fig. 10. (The interatomic distances obtained from our measurements of microcrystalline diamond differ from well established literature data, i.e. the experimental value of r_4 (3.5918 Å), which corresponds to the cubic lattice parameter a_o, is slightly different than the literature data of 3.5668 Å. The discrepancy is apparently the result of somewhat inaccurate calibration of the instrumental parameters used by the computer program for data reduction and calculation of G(r). The *r* values in ideal diamond lattice are given in Fig. 10 in parenthesis at the bottom of the axes.) The changes of the inter-atomic distances related to changes of the grain size in diamond are very different than those in SiC. The relative changes of inter-atomic distances within and between sub-lattices for diamond and SiC are as follows:

Within the same sub-lattice: in diamond: the distances r_2 and r_6 decrease, and r_4 increases with a decrease in the grain size;

in SiC: all distances increase.

Between adjacent sub-lattices:

in diamond: all distances decrease with a decrease in the grain size;

in SiC: r_1 and r_5, decrease, r_3 and r_7 increase.

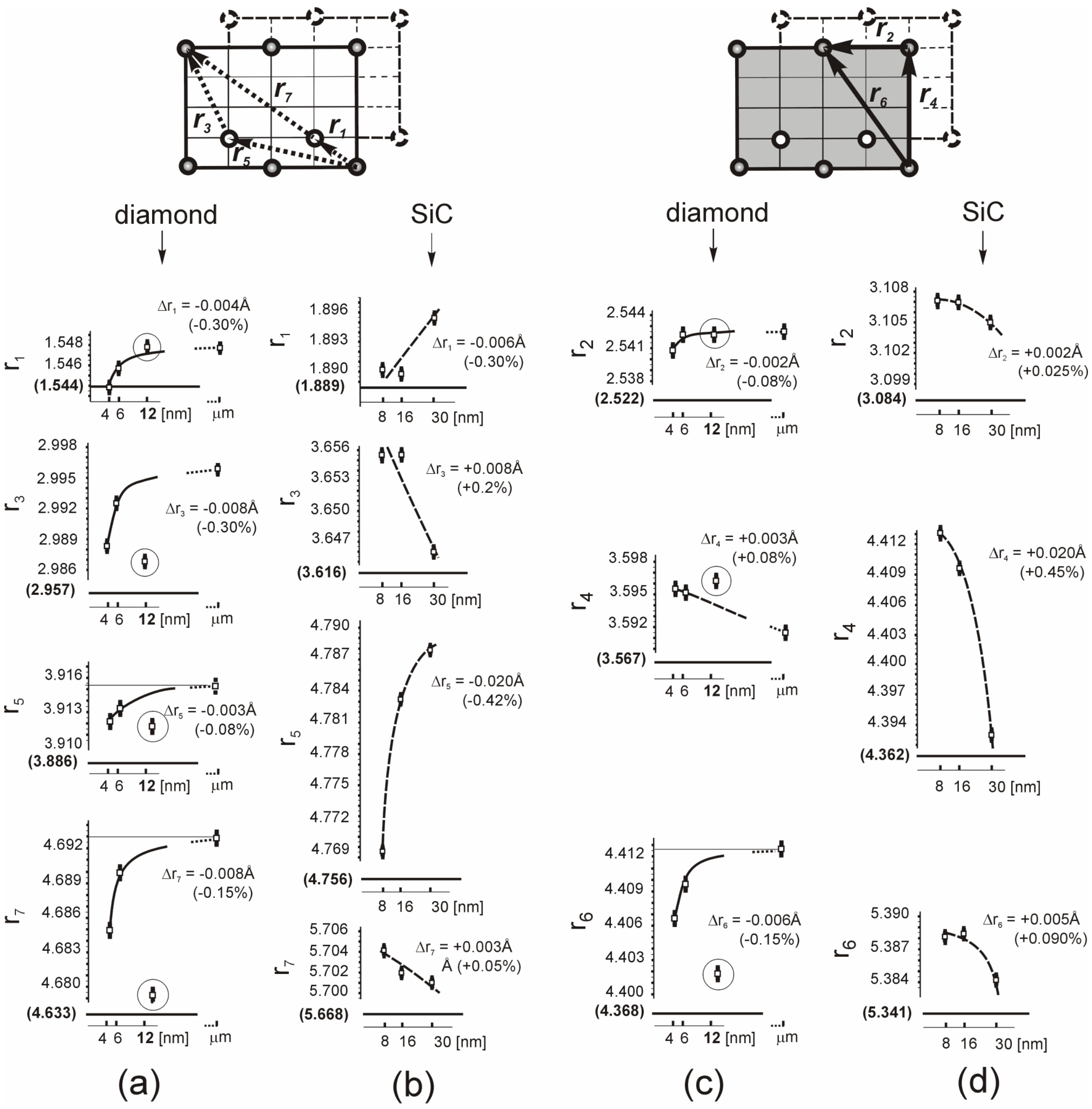

Fig. 10 Experimentally determined dependence of inter-atomic distances on the grain size. (a) and (b), inter-sublattice distances (r_1, r_3, r_5, and r_7) for diamond and SiC, respectively; (c) and (d), intra-sublattice distances (r_2, r_4, and r_6) for diamond and SiC, respectively.

The magnitude and direction of change of the inter-atomic distances are:

in diamond: six out of seven distances decrease, the largest change (0.3%) is observed for r_1 and r_3; one inter-atomic distance, r_4 increases (by 0.08%);

in SiC: two out of seven distances, r_1 and r_5, decrease by 0.3 and 0.4%, respectively; five distances increase, the largest increase occurring for r_4 (0.4%).

Discussion

In this work we used the model of a spherical crystallite with radial symmetry of the strain in the surface shell. This is a very rough approximation of strains that might be present in real crystals, thus interpretation of the diffraction data that refers to our model is approximate. A more complete evaluation of powder diffraction data of specific nanocrystalline materials would require investigation of models of atomic structure of nanocrystals accounting for specific physical properties. In an advanced physical model of real materials one should account for the shape and size distribution of individual nanocrystals and for anisotropic strain field in the planes terminating the real crystallites. But even a simple core-shell model examined in this work and used for interpretation of our powder diffraction experiments appears sufficient to show the presence of non-uniform structure in nanocrystals. The results of the analysis of the long-range order (analysis of Bragg-type scattering: alp/a_o-Q plots) and of the short-range order (PDF analysis: individual inter-atomic distances) give a clear evidence of a presence of strains in nanocrystalline diamond and SiC powders.

The analysis of Bragg-type scattering leads to the following conclusions:

(i) the shape of the alp/a_o-Q plots of diamond and SiC with apparent minima and maxima can be explained assuming a presence of strain at the surface of individual crystallites;

(ii) in diamond and SiC the surface shell is compressed relative to the grain core and the lattice parameter of the core is larger than that of a standard single crystal, both for diamond and SiC materials.

From the analysis of the atomic Pair Distribution Function the following can be concluded:

(i) the changes of individual *r*-distances are diversified, and different for diamond than for SiC powders. Some of the distances are shorter and some are longer than in the relaxed lattice, which indicates that the structure of the material is heterogeneous and that the changes of the bond lengths do not result from a hydrostatic-type compression or decompression (expansion).

(ii) the magnitude of the change of individual inter-atomic distances in diamond and SiC varies. It is reasonable to assume that the largest changes occur at the surface and that they determine the distribution of strains in the grains. The largest changes are in distances r_1 and r_3 in diamond, r_4 and r_5 in SiC. These distances probably change very significantly at the surface and they contribute most to the surface strains in these materials. This is an indication that real grains have anisotropic shape with well defined facets. Therefore the core-shell model of nanocrystals must be modified to include anisotropy of the surface and faceting.

Summary

This work shows limitations of a conventional approach to the structural analysis, and demonstrates the application of a new method of evaluation of powder diffraction data of nano-size polycrystalline materials: the *alp* methodology. The applicability and usefulness of the method has been tested using our experimental powder diffraction data for several different diamond and SiC powder samples. We have demonstrated a qualitative agreement between the experimental results and those obtained by numerical modeling using our *alp* methodology. This agreement also shows that the lattice parameters, as-derived from a routine powder diffraction experiment, do not have a meaningful significance for nanocrystals.

The results of the analysis of powder diffraction data of diamond and SiC nanocrystals presented above are mostly indicative and we do not attempt at present to provide a quantitative description of the atomic structure of these materials. The main limitation of standard powder diffraction analysis is that it provides information on the structure averaged over the entire sample volume. This limitation is particularly important in the analysis of nanocrystals with sizes up to 10 - 20 nm, which can be regarded as constituting a two-phase, core-shell system: no method that permits separating diffraction effects arising from the two phases is available. However, we believe that a simultaneous analysis of Bragg-type scattering using the methodology of *alp* and examination of the short-range order by PDF analysis can lead to determination of the structure of the core-shell system of nanocrystals. We have already shown that the system is anisotropic, with compressed and dilated regions existing within nanocrystalline grains. Such analysis requires a further development of the model of nanocrystals to account for, (i), the specific grain shape, and (ii), anisotropic elastic properties of the crystallites. Work on this subject is in progress.

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