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APPLICATION OF X-RAY POWDER DIFFRACTION TO NANO-MATERIALS – DETERMINATION OF THE ATOMIC STRUCTURE OF NANOCRYSTALS WITH RELAXED AND STRAINED SURFACES

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The applicability of standard methods for the evaluation of powder diffraction data of nano-size crystallites is analyzed. Based on theoretical considerations, it is shown that deviations of the structure of small particles from the Bragg approximation on an infinite crystal lattice leads to significant differences in the diffraction patterns, which may lead to an erroneous interpretation of the experimental results. An alternative evaluation of the diffraction data of nano-particles, based on the so-called "apparent lattice parameter", *alp*, is proposed. Based on this method, it is shown that real nano-crystals constitute a complex, heterogeneous multi-phase structure.

Keywords: Nano-crystals; SiC; Surface structure; Diffraction

1. INTRODUCTION

The properties of nano-crystalline materials critically depend on the atomic structure of the constituent grains. Nano-particles show unique physical properties compared with conventional poly-crystals (Edelstein and Cammarata, 1996; Howe, 1997; Fujita, 1998; Suryanarayana, 1999; Wang, 2000). Different from micro-size material, nano-particles pose a technological challenge in the production of large volume dense nano-materials. For instance, due to an enhanced surface and/or bulk diffusion during the sintering process, fast coarsening of the grains occurs. This leads to the irreversible loss of the unique properties conditioned by the small size of the individual grains and the surface of individual crystallites, which apparently plays a dominant role.

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The surface atoms of crystals are subjected to highly asymmetrical stress field as compared with those in the bulk. Hence, their spacings are expected to be different from those in the interior of the crystallites. Usually, the surface atoms constitute only a small fraction of the crystal and their effect on the overall properties of the material can be ignored. The situation is different in small, nano-size particles where, due to their size, a considerable fraction of the atoms forms the surface of the grain. Therefore, the surface layer (shell) should be treated as a separate structural phase relative to the bulk of the grain (the core). We assume that the grain surface is a three-dimensional object with its own characteristic atomic arrangement. So far, in the basic characterization of nanocrystals reported in the literature, the presence of a different surface layer is usually ignored. There are a number of reports on the dependence of different physical properties on the size of nano-particles (Buffat and Borel, 1976; Wolf and Merkle, 1992; Averback, 1993; Silvestri and Schroeder, 1995; Tolbert and Alivisatos, 1995a; Qadri *et al.*, 1996; Inoue and Hishimoto, 2001). Changes of physical properties of the materials are basically related to corresponding changes in their atomic structure, although the specific structure of nanocrystallites has not been determined yet. Changes of the atomic arrangement in a crystal are reflected by corresponding changes of its lattice parameters. It was reported earlier that the lattice parameters determined from powder diffraction data for a variety of materials depend on their grain size (metals such as Au (Harada and Ohshima, 1981; Solliard and Flueli, 1985), Al (Woltersdorf *et al.*, 1981), Cu (Montano *et al.*, 1986), semiconductors such as CdSe (Tolbert and Alivisatos, 1995b), ionic crystals such as NaCl, KCl, NaBr and Lif (Boswell, 1951)). These results were interpreted as "the effect of the grain size on the lattice parameters" and often attributed to the presence of a strong "internal pressure" in nano-particles caused by surface stresses (analogous to surface tension in liquids) (Shuttleworth, 1950; Gilman, 1960; Mays *et al.*, 1968; Vermaak *et al.*, 1968; Borel and Chatelain, 1985; Cammarata, 1992, 1997; Stoneham, 1977). This "straightforward" interpretation of the experimental findings ignores the fact that the structure of a nano-crystal is not uniform and should be considered either as being composed of two distinctive, grain core and shell phases, or as a structure where a large number of the atoms at the grain surface are displaced relative to their regular lattice positions (which is equivalent to the presence of strain in the vicinity of the surface). In large (micro-sized) crystallites, the number of atoms located in the vicinity of the grain surface is orders of magnitude smaller than the number of atoms in the grain core, and their effect on the bulk properties of the materials can be ignored. Also, the contribution of the surface atoms to the diffraction effects measured for such polycrystals in a conventional powder diffraction experiment is negligible. With a decrease in the dimension of the crystallites down to a few nanometers, the number of atoms located at the surface becomes comparable to those in the grain core. Since the surface atoms have different surroundings and their interatomic distances may differ from those in the bulk material, one set of lattice parameters for a nano-crystal may be inadequate for a unique description of its structure. Conventional diffraction techniques and standard methods of diffraction data analysis (e.g. Bish and Post, 1989; Young, 1993) are used to characterize the average crystallographic structure of materials through determination of the lattice parameters of the unit cell. These methods are insufficient to quantify small differences between the actual atomic positions in nano-grains and those in a regular crystallographic phase.

In this paper we show that, although a conventional diffraction experiment is appropriate for the characterization of the crystallographic structure of nano-size crystalline powders, routine methods of powder diffraction analysis may lead to erroneous interpretation of results. We show that the description of the crystallographic structure of such materials based on the unit cell is erroneous. Accordingly, the application of the lattice parameter concept, when used for the characterization of the structure of nano-crystals, has to be modified. We suggest a replacement of the classical lattice parameters, describing the dimensions of the unit cell, by a set of different values of lattice parameters associated with and determined from each individual Bragg reflection, each at its specific diffraction vector **Q**. In this study we present preliminary results of the application of the concept of the "*apparent lattice parameters*" (*alp*) for the elaboration of powder diffraction data of nano-crystals. The concept is illustrated for nano-crystals with a perfect crystallographic structure, as well as for those with the atomic structure of the surface different from that in the grain core. Preliminary experimental evidence of the presence of tensile surface strain in nano-crystalline SiC particles will be given.

In this work, we discuss the positions of the intensity maxima (i.e. geometrical aspects of the atomic structure of nano-crystals) through a comparison of the positions of intensity maxima between theoretically calculated and experimentally measured powder diffraction patterns. We do not discuss the intensities of the Bragg reflections; we assume that all sites are fully occupied (as in a perfect crystal lattice).

2. IMPLICATIONS OF THE CRYSTAL SIZE IN DIFFRACTION STRUCTURAL STUDIES

Routine methods of structural analysis of polycrystals are based on the simple assumption that a unit cell appropriately represents the repetition unit of the material. To characterize accurately the atomic structure, it is sufficient to determine a set of lattice parameters a, b, c, α, β, and γ, describing the dimensions and shape of the unit cell, and the locations of the atoms in the cell x_i, y_i, and z_i. The complete structural analysis (structure refinement) of poly-crystals is routinely achieved using powder diffraction and elaboration of the experimental data with crystallographic software based on the Rietveld method (Young, 1993). The accuracy of such analysis, i.e. of determination of the specific values of lattice parameters and atomic coordinates, is dependent primarily on the quality of the experimental data. The results can be precise if the fundamental underlying assumptions of a perfect lattice are met, i.e. (i), the unit cell of the lattice is identical throughout the entire volume of the sample, and (ii), the lattice is an array of points in space in which the environment of each point is identical. These conditions are never strictly met in real crystals, but, for larger crystallites, the deviations from the ideal model are negligible. When the dimensions of the object are comparable to those of the single unit cell deviations cannot be ignored. In a nano-particle, a large proportion of the atoms is located at the surface and with different coordinations from atoms in the core (Fig. 1). Thus, one unique cell cannot represent the entire atomic structure of a nano-particle. The methods of structural analysis developed for standard crystalline materials may be inadequate for nano-size crystallites.

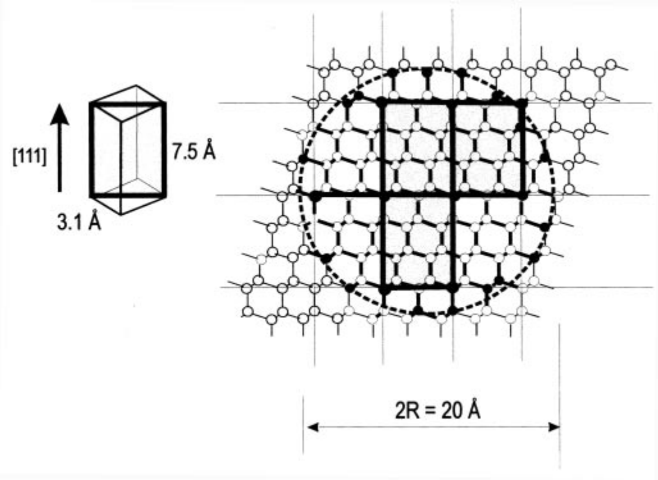

FIGURE 1 Schematic comparison of the dimensions of the unit cell and a nanocrystalline grain.

3. THEORETICAL CALCULATIONS OF POWDER DIFFRACTION PATTERNS OF NANO-CRYSTALS

The relatively small number of atoms forming a nano-crystal allows a complete, atom-by-atom, model of small crystals to be built. Using such models and the Debye equations, the corresponding diffraction patterns can be calculated. Their comparison with experimental data allows for the evaluation of the atomic structure of nanomaterials.

According to Debye, the intensity of radiation scattered by any array of atoms is given by:

$$l(\mathbf{k}) = \sum_{i=1}^{N} \sum_{i=1}^{N} F_i F_j \sin(\mathbf{k} \cdot \mathbf{r}_{ij})/\mathbf{k} \cdot \mathbf{r}_{ij}$$

where F_i and F_j are atomic scattering factors of the ith and jth atoms, respectively, $\boldsymbol{k} = 4\pi \sin\Theta/\lambda$ is the scattering vector, and $\mathbf{r}_{ij}$ is the distance between the atoms. The intensity $l(\mathbf{k})$ can be integrated over all spatial orientations of a given crystallite yielding the equivalence of the powder diffraction pattern of a large number of randomly oriented grains. Applying the Debye equation, we have calculated diffraction patterns for different models of nanocrystalline grains with diameters up to 20 nm. A reasonably short CPU time, on the order of hours (Bondars *et al.*, 1993; Pielaszek *et al.*, 2001), was sufficient to run one calculation.

4. APPLICATION OF CONVENTIONAL METHODS OF POWDER DIFFRACTION ANALYSIS TO NANO-CRYSTALS

A common approach for analysing data is based on the Bragg approximation. According to Bragg, if a unit cell represents a repetition unit, the crystals structure can be described as a set of infinite, equally spaced parallel planes. There is an unlimited number of families of planes which can be drawn for a given lattice by joining different nodes of the crystal lattice formed by periodically stacked unit cells. The planes are denoted by the Miller indices *hkl*. Each family gives its characteristic interference maximum, the *hkl* Bragg reflection. The directions where the intensity maxima occur are determined by the specific inter-planar spacing d_{hkl} and the wavelength of the incident beam. Determination of several Bragg reflections (one in the case of a cubic lattice) is sufficient to determine the symmetry, shape and dimensions of the unit cell.

To verify applicability of the Bragg approach to nano-crystals, we calculated (using the Debye functions) the diffraction patterns of crystallographically perfect nano-crystals, and calculated back the lattice constant(s) of the model using the Rietveld refinement program. The calculations were performed for SiC nano-crystals with grain sizes of 3, 4, 6, and 8 nm. A typical diffraction pattern obtained for the materials is shown in Fig. 2a.

The elaboration of diffraction data has to include two groups of parameters: instrumental and sample-dependent. Our virtual/"perfect experiment" does not require any instrument-related corrections. However, in real laboratory practice, the experiments are not perfect and any instrument/geometry imperfection is a source of errors. We will show the importance of one of the main sources of errors, the so-called "zero shift". The real beginning of the diffraction pattern is usually shifted

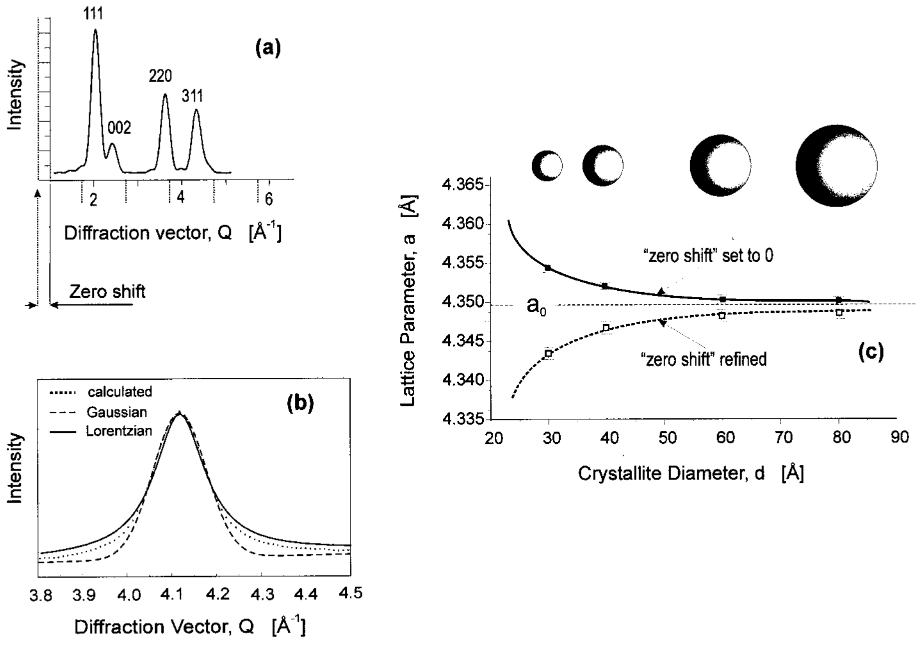

FIGURE 2 Application of the Rietveld method to evaluate diffraction patterns of nano-crystals of SiC. Lattice parameter of the model, $a_0 = 4.349$ Å. (a) typical diffraction patterns calculated theoretically; (b) representative shapes of the diffraction peaks; (c) the value of the lattice parameters back-calculated from the theoretical diffraction patterns computed for different size particles: full symbol and solid line – the refinement made without correction for the "zero shift", open symbols and dotted line – the refinement made with correction for the "zero shift".

("zero shift) relative to the apparent "zero" position of the experimental set-up (Fig. 2a) with obvious consequences for the accuracy of the experimental results.

The second type of experimental errors is due to the properties of the sample itself. The Bragg diffraction relations apply to infinite size crystals and in a model experiment, all diffraction peaks have Gaussian shapes. For small crystallites, the shape of the peak is no longer Gaussian but a combination of Gaussian and Lorentzian functions (Fig. 2b). Our calculated diffraction patterns were analyzed applying the Rietveld methodology, assuming that the reflections have shapes that are a combination of these two basic functions. We used two procedures of the elaboration of our diffraction data:

1. Perfect Experiment

In this method, we did not apply the procedure that corrects for the experimental/instrumental imperfections. We refined the as-calculated diffraction data, relaxing only the lattice parameter and the line shape. The line shapes were fitted using the pseudo-Voigt function. The calculated values of the lattice parameter for different sizes of the particles are shown in Fig. 2c (full symbols, solid line). Obviously, the procedure yields different lattice parameters from those of the starting model. In addition, it generated an artificial dependence of the lattice parameter on the size of the particle.

2. Imperfect Experiment

In this case, we treated our calculated diffraction data as if they were obtained experimentally and, so required a correction for the instrument imperfections. Therefore, we refined the lattice parameters using the 'zero shift" correction in the Rietveld program. The results of this calculation are shown by open symbols/dashed line in Fig. 2c. As we can see, the "zero shift" correction procedure generated another artefact. In spite of the fact that no real instrumental errors are introduced to our model diffraction pattern, the program led to a change in the values of the calculated lattice parameters relative to the model values. The effect is apparently even stronger then, and opposite in sign from that in the first procedure, so the combined results generated the "dependence of the lattice parameter on the size of the particle" in the opposite direction.

As shown above, a mathematically correct, commonly accepted, and widely used Rietveld refinement program yields erroneous results. The lattice parameter back-calculated using this procedure generated an incorrect dependence of the lattice parameter on grain size. The magnitude of this artificial effect decreases with an increase in the grain size and can be ignored for crystallites 10 nm in size or larger (Fig. 2c). The reason for these effects is the incorrect assumption used in derivation of the Rietveld method (infinite atomic planes) in relation to the real nature of crystals (finite size of real particles). This effect is negligible for micro-size or larger crystals. The above limitation of applicability of the Rietveld method has apparently been ignored in papers on nano-samples and has led to incorrect interpretation of diffraction results of nano-materials. Our analysis shows that the application of routine methods for the elaboration of diffraction data requires a critical assessment of the results. In particular, internal standards should be used to prevent the apparent errors introduced by the zero shift correction routine. This is particularly important for very small crystallites.

5. "APPARENT LATTICE PARAMETER" METHOD OF POWDER DIFFRACTION ANALYSIS

A dependence of the results of the diffraction data analyzed using the Rietveld program on the crystallite size is apparently the effect of the shifts of the positions of individual Bragg reflections from those corresponding to the perfect lattice. As we showed in Section 4, the approximation of the crystal lattice by a set of infinite atomic planes is not justified for nano-size crystals, thus the term "lattice parameter" loses its general meaning. As a consequence, the Bragg reflections cannot be related to unique values of the lattice parameters. Our analysis of the phenomena discussed in Section 4 lead us to conclude, that the effect of the limited number of atoms in nanocrystals on the diffraction pattern is different for different reflections. As a result, the individual peaks are incoherent to each other, and the diffraction pattern evaluation programs that assume coherency lead to erroneous results. For this reason we developed a new approach, based on the analysis of the diffraction data, but made individually for each peak. For a given Bragg reflection *hkl* (at the diffraction vector **Q**), we calculate the corresponding value of the lattice parameter that we call the *alp*. We can calculate the *alp* values for all Bragg reflections in a selected range of **Q**-values, which is particularly important in the case of more complex structures and overlapping reflections. The results of different evaluation options of our theoretical (model) diffraction pattern computed for a cubic SiC crystal of 8 nm in diameter are shown in Fig. 3. The calculated diffraction pattern and that refined using the Rietveld program (solid and dashed lines, respectively) are shown in Fig. 3a. Differences between these two patterns get smaller with increasing **Q** (Fig. 3b). That illustrates the inadequacy of standard methods of evaluation of diffraction patterns of nanomaterials, particularly for low diffraction vector values. The calculated values of the *alp* for different **Q**-ranges are shown in Fig. 3c. The lattice parameter, as refined for the whole calculated pattern (equivalent to the *alp* calculated for the entire diffraction spectrum) is 4.35032 Å and is much larger than the lattice parameter of our model, 4.349 Å ($\Delta a/a_0 = 0.03\%$). The *alp* value obtained for small **Q**-values (range 1) is larger by 0.08% from that of the model. The difference between the as-refined and the correct values decreases with the increase of the scattering vector **Q**.

From the results given above, it follows that, for a nano-crystal with a perfect, uniform structure, its lattice parameter can be derived from powder diffraction patterns using two methods:

1. a refinement of the lattice parameters using only the part of the pattern with very large **Q**-values (above 10 Å^{-1} for grains of several nm in size), or
2. a determination of the *alp* values for different reflections and matching them with the results of theoretical predictions for appropriate models. (This method requires knowledge of the size of the grains).

A series of our experiments made for nano-crystalline SiC, diamond, and GaN particles showed that the measured shifts of the Bragg reflections from their proper positions (i.e. expected for a unique and crystallographically uniform structure)

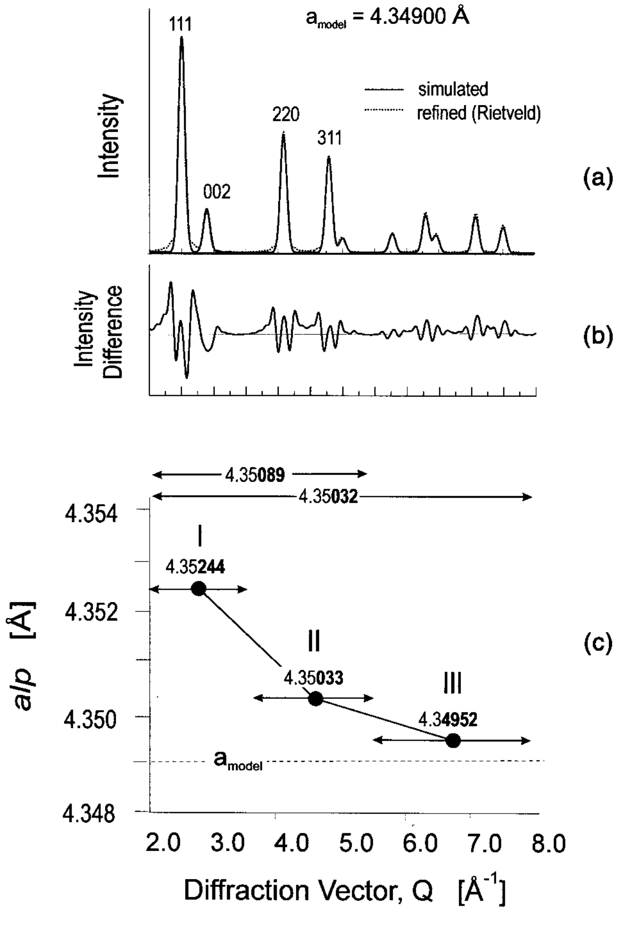

FIGURE 3 *Alp* values determined from theoretical diffraction pattern of a SiC nano-crystal computed for a particle 8 nm in diameter. (a) solid line – as-calculated diffraction pattern; dotted line – the pattern refined with the Rietveld program; (b) difference in intensity between the as-calculated and refined diffraction patterns; (c) *alp* values calculated for different ranges of the diffraction vector **Q**.

are much larger than those calculated for nanocrystals with a perfect (unstrained) lattice. These results imply that the crystallographic structure of nanocrystals is not uniform. Accordingly, more complex models of the particles need to be used to evaluate the structure of real nano-grains. In a further study, we applied the concept of the *alp* for models with a strain in the surface shell of the grains.

6. EFFECT OF STRAIN IN THE SURFACE SHELL ON THE *ALP*

According to the Laplace-type law (Mays *et al.* 1968; Vermaak *et al.*, 1968; Solliard, 1981; Borel and Chatelain, 1985; Cammarata, 1992; Stoneham, 1977) in nano-samples, the core lattice can either be expanded or compressed hydrostatically relative to large crystals due to the presence of surface free energy. We assumed above that the structure of the grain core is uniform and can be described unambiguously by the space group and lattice parameters. The surface structure is not clearly defined and we can apply only approximate models of the nano-particle surface. For example:

(a) The structure of the surface shell of a nano-grain is based on that of the grain core but is modified and resembles that of an extended surface of the macro crystal: it has well defined thickness, symmetry, and interatomic distances.
(b) A radial strain field exists in the vicinity of the surface: the interatomic distances decrease or increase from the surface towards the particle center.
(c) The atomic structure of the surface is randomly disordered (forming a glass-like phase).

In (a) and (b) the presence of long-range ordering of the surface atoms is assumed, while (c) assumes that only short-range order exists in the surface layer. In any case, the surface is a "low dimensional" system and has a defined thickness, but it also contains strain and, therefore, cannot be well described by a single unit cell parameter. No experimental methods which would allow for a direct and complete analysis of nanocrystals are available currently (Loeffler and Weissmueller, 1995; Weissmueller and Cahn, 1997). Analysis of the conditions required for the ordering of atoms in three-dimensional crystal lattices, and application of the general theory of the surface strain can be helpful for predictions of the surface structure of nanocrystalline grains. No general theory or model of the surface of nanocrystals is available yet.

In this study, we used the model of a nanocrystal where the grain core has a uniform crystallographic structure and is unambiguously characterized by the lattice parameter a_0. We assumed that the atomic structure of the surface is strongly correlated with the parent structure of the grain. It is basically the structure of the core, but centro-symmetrically deformed, compressed (Fig. 4) or expanded due to the presence of surface strain. Hence, the term "lattice parameters" cannot be applied to the whole nanocrystal or to the surface shell. No common, specific interatomic distance can be assigned to the surface shell. Nevertheless, for simplification, we introduce the parameter a_s which corresponds to the interatomic distances at the outmost atomic

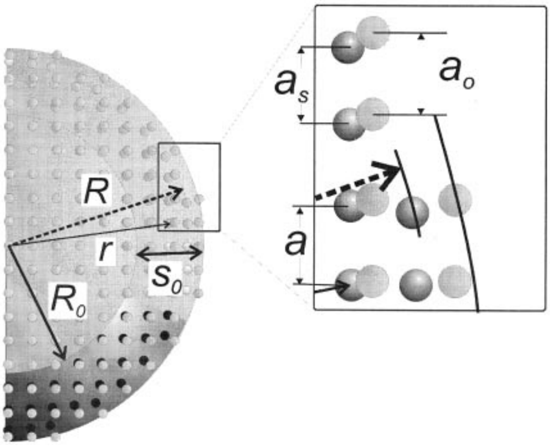

FIGURE 4 Model of a nanocrystal with strained (compressed) surface layer. R_0, radius of the core; R, radius of the grain; s_0, thickness of the un-strained surface layer; r, distance from the center; a_0, interatomic distance in the relaxed lattice; a_s, interatomic distance at the surface.

layer of the particle (Fig. 4). Assuming that the arrangement of the atoms in the surface shell is similar to that in the grain core, the value of a_s can be expressed as a fraction of the lattice parameter a_0. The actual values of interatomic distances within the surface shell can be expressed as a function of the distance from the particle center, and vary between a_0 in the grain core (at distances $r < R_0$) and $a_s = a_0 \pm \Delta a$ (for $r = R$). The sign of Δa depends on whether the surface is compressed (−) or expanded (+) relative to the grain core. The ratio $\Delta a/a_0$ is the surface strain.

Our model of a nanoparticle without and with tensile strain in the surface shell is shown in Figs. 5a and b, respectively. The presence of strain in the grain surface layer leads to deformation of the atomic planes (Fig. 5b). As shown in the figure, the atomic planes lose their planarity and mutual parallelism. As a consequence the interplanar spacings in such nano-crystals are not constant, although they can still, be used for the description of the grain core structure. The diffraction patterns calculated for 8 nm diameter SiC nano-crystals with tensile strain, no strain and compressive uniform strain ($\Delta a/a_0 = \text{constant}$) in the surface shell are shown in Figs. 6a, b, and c, respectively. The strain changes the profile of the Bragg reflections and shifts their positions.

For such asymmetric reflections, we determined the positions based on both the maximum and the weighted center of the individual reflections. The character of the dependence of the calculated *alp* values on **Q** is similar for both methods, although specific values of **Q** are somewhat different. For small strain in the surface shell, the asymmetry of the Bragg reflections is very small. For the purpose of the current discussion, the shapes of the peaks were fitted using a pseudo-Voigt function.

Nano-crystals with different thicknesses of the surface shell, magnitudes of the surface strain and different gradients of the stain in the shell are studied in our model. The dependence of the *alp* on **Q** for SiC nanocrystals with a strain of +5% and surface shell thickness 0.7 nm is shown in Fig. 7 for different grain size. For reference, the graphs contain also the *alp*-**Q** results for a fully relaxed (unstrained) lattice. Deviations from the core value a_0 of *alp*s for strained grains are much larger than for those with a relaxed lattice (Fig. 7). The deviation increases with decreasing

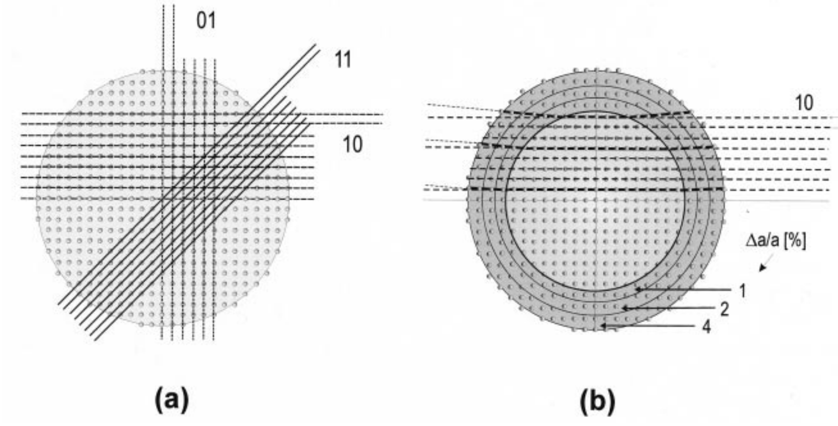

FIGURE 5 Two-dimensional cubic nano-structures. (a) perfect lattice; (b) grain with strained (expanded) surface shell.

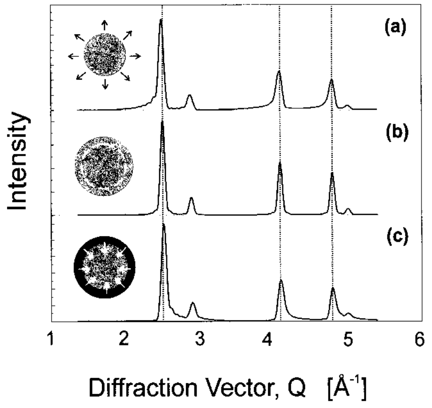

FIGURE 6 Diffraction patterns of 8 nm SiC grain with surface shell of 0.7 nm in thickness, calculated for different magnitudes of strain in the surface layer. (a) $\Delta a/a = +10\%$; (b) $\Delta a/a = 0\%$; (c) $\Delta a/a = -10\%$.

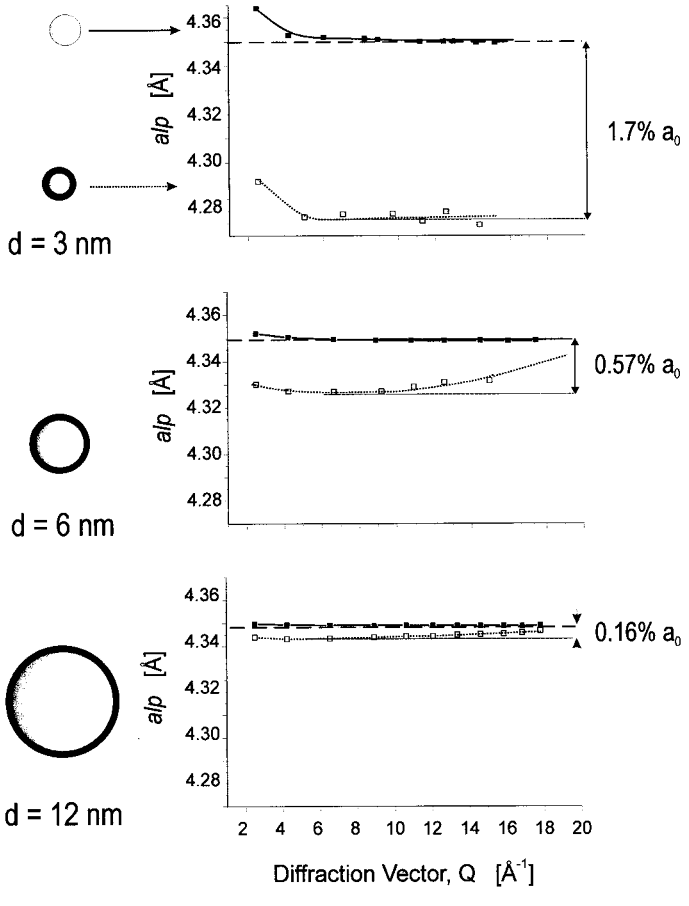

FIGURE 7 *A*l*p* values calculated for nano-crystalline cubic SiC of different particle size. $a_0 = 4.349$ Å; magnitude of the strain, $\Delta a/a = -5\%$; thickness of the surface shell, $s_0 = 0.7$ nm.

grain size. For 0.7 nm thick shell, the strained fraction of the grains contains 85% of all atoms in the particle for the smallest grain size (3 nm in diameter) and 31% for the largest grain size (12 nm). The results shown in Fig. 7 illustrate the consequences of using standard powder diffraction techniques combined with commonly applied radiation sources. The widely used Cu Kα X-ray radiation source allows diffraction data in the **Q**-range up to 5–6 Å^{-1} to be collected. For strained particles shown in Fig. 7, a routine analysis of the data using the Rietveld program would yield lattice parameters differing from a_0 of the relaxed lattice by up to about 1.7%.

It should be stressed that a single *alp* value determined from a diffraction pattern has no specific meaning. Only a set of *alp* values in a wider **Q** range can provide meaningful information about the structure of nano-crystals. The *alps* at sufficiently high **Q**-values correspond to the lattice parameters of the core lattice of the particle. Hence, the experimentally determined dependence of *alp* on **Q**, combined with numerical simulations, provides information about the structure of the surface shell of the nano-crystal.

7. *ALP*-Q PLOTS OF EXPERIMENTAL DIFFRACTION DATA OF SiC NANO-POWDERS

We applied our method to evaluate experimental diffraction data of SiC nano-crystals. Powder diffraction measurements up to **Q** $\sim$ 20 Å^{-1} were performed using synchrotron radiation (BW5 Station at HASYLAB, ID 11 and SNBL powder diffractometers at ESRF). From these data, we derived the *alp*-**Q** relations and compared them with our model simulations. Figure 8 shows example of the *alp* values derived from the experimental diffraction patterns for samples with different size of the nano-crystals (3, 8, and 30 nm). Figure 9 shows a typical result of our numerical simulations for a particle 8 nm in diameter with a surface thickness of 0.7 nm for three different (uniform) strain situations. The results show that the experimentally observed *alp*-**Q** relations are similar to those calculated for nano-crystals with a strained surface shell. Similar agreement between the experimental results and theoretical predictions was obtained for other nano-materials.

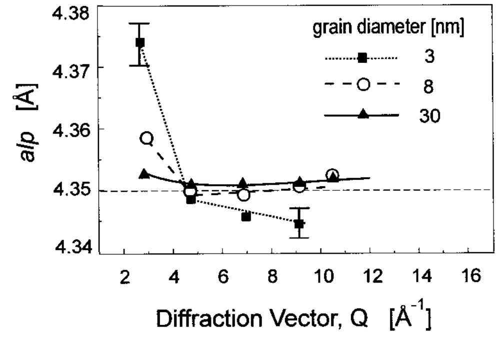

FIGURE 8 *Alp* values determined from experimental diffraction patterns of nano-crystalline SiC. Dashed line corresponds to undistorted lattice with $a_0 = 4.349$ Å.

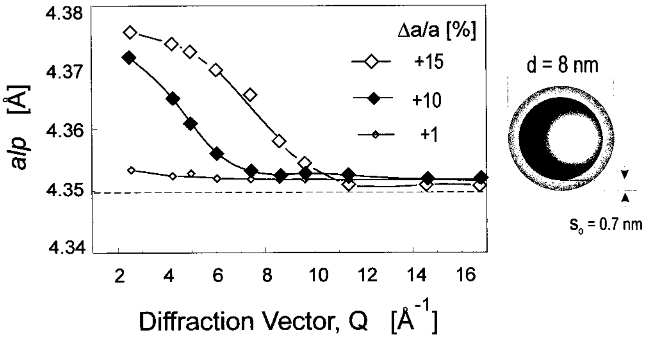

FIGURE 9 *Alp* values determined for models of SiC nano-crystals with tensile strain in the surface shell.

8. SUMMARY AND CONCLUSIONS

Lattice parameter and structure analysis of micrometer size poly-crystals is well established. However, conventional tools developed for the interpretation of powder diffraction data are not directly applicable to nano-crystals. There are several reasons for this:

(i) Nano-crystals have a complex structure that resembles a two- or multi-phase rather than a uniform, single phase material. Therefore, definitions and parameters used for the characterization of the atomic structure of crystallographically uniform phases are insufficient for the description of the complex structure of nano-crystals.
(ii) Conventional powder diffraction techniques and appropriate methods of data analysis have been developed for materials showing perfect three-dimensional, periodic order in an infinite crystal lattice. A nano-crystal is very limited in size and the effect of boundaries cannot be ignored. For such small crystallites, the number of atoms at the surface can even exceed the number of atoms in the grain core. Structural and other properties of the surface atoms can dominate the effects determined by the bulk atoms.

In this work, we have shown some limitations of a conventional structural analysis approach and proposed a new method for evaluating diffraction data of nano-size material. We have demonstrated a qualitative agreement between experimental results and those obtained by numerical modeling using the *alp* concept. The analysis of the diffraction experiments presented here concerned only geometrical parameters describing the ordering of atoms in nano-crystals. We did not discuss specific atomic structures such as the occupancy of the lattice positions by specific atoms or the effect of the atomic vibrations of the lattice. This would require a quantitative analysis of the intensity profiles of the scattering beams which is not the scope of the present work.

Nano-crystal are often referred to in the literature as two-phase materials. This is a useful concept although it defies the basic definitions of a crystallographic phase. The problem is that the two phases form essentially a composite crystal with interfering diffraction properties. The core-shell model of a nano-crystal applied in this work is, in fact, a kind of two-phase system. A more complete evaluation of powder diffraction data of specific nano-crystalline materials requires the consideration of a wider spectrum of structures (a gradient model), as well as the shape and size distribution of nano-particles in real materials. Apparently this situation requires a new approach to the structural analysis of such systems. The limitations of currently used definitions become obvious in the rapidly developing field of nanomateirals.

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