

Neutron diffraction studies of the atomic vibrations of bulk and surface atoms of nanocrystalline SiC

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Abstract. Thermal atomic motions of nanocrystalline SiC were characterized by two temperature atomic factors B_{core} and B_{shell} . With the use of wide angle neutron diffraction data it was shown that at the diffraction vector of above 15 \AA^{-1} the Wilson plot gives directly the temperature factor of the grain interior (B_{core}). At lower Q values the slope of the plot provides information on the relative amplitudes of vibrations of the core and shell atoms.

Introduction

It is widely recognized that a nanocrystal has non-uniform structure where atoms located at the surface differ from those in the grain interior with respect to their surrounding and, thus, have different properties. A diffraction experiment can determine the static (average) equilibrium arrangement of the atoms and elastic properties of materials. This work is dedicated to examination of thermal atomic motions in nanocrystals based on the analysis of Bragg type scattering. Theoretical calculations show that vibrational density of states of the inner atoms of nanograins is similar to those in the bulk [1 - 3] and, since the atoms at the surface have fewer neighbors, they vibrate with amplitudes larger than those in the bulk. A diffraction experiment provides information on all atoms forming the material and their properties. The "only" problem is in finding methods of elaboration of the diffraction experiments (of nanocrystalline material) which would discern between different properties of the core and shell atoms. In this work we discuss whether in a diffraction experiment we can distinguish between and evaluate thermal vibrations of inner and surface atoms of nanocrystals of SiC. We focus on application of the Wilson method of determination of the atomic temperature factors with the use of wide angle neutron diffraction. Recently we used X-ray diffraction to examine thermal atomic motions in 8 nm nanocrystalline SiC for loose powders and dense sintered materials [4]. We showed that some qualitative information concerning overall

temperature factors and Debye temperatures can be withdrawn from those data. We found that the key problem in determination of the temperature factors is separation of Thermal Diffuse Scattering (TDS) from Bragg scattering. Here we show that neutron diffraction is much better suited for such studies. (*Note: alternate to examination of thermal atomic motions with application of Bragg scattering and Wilson method is PDF analysis [5]. It requires high quality data to obtain G(r) functions for which quantitative analysis of shapes of individual peaks can be done. Our data are not good enough to do such analysis.*)

Experimental

SiC powders with the average grain size of 8, 15, and 23 nm obtained from silane by laser-driven synthesis [6] were examined. Before the measurements, powders were annealed in vacuum for 3 hrs at 400°C. Based on the analysis of the core-shell structure of these powders with application of the concept of the apparent lattice parameter (*alp*) [7,8], we evaluated the thickness of the surface shell and found it to be between 0.5 and 1 nm. That corresponds to the content of the surface atoms between 50% in the smallests and 20% in the largest grains. Neutron diffraction measurements were done using the HIPD diffractometer at LANSCE in Los Alamos National Laboratory ($Q_{\max} = 28 \text{ \AA}^{-1}$).

Data analysis

Determination of the overall thermal parameter B_T using the Wilson plot

It is a common practice to describe isotropic thermal vibrations using an overall temperature parameter B_T [9, 10]. This parameter is a quantity proportional to the mean square of the atomic displacement $\langle u^2 \rangle$: $B_T = 8 \pi^2 \langle u^2 \rangle$. In a diffraction experiment, due to thermal vibrations which increase the effective volume of the atoms, a decrease in Bragg intensities with an increase in the diffraction vector Q is observed:

$$I = I_0 e^{-2M}, \quad (1)$$

where: $2M = 2B_T(\sin^2\Theta/\lambda^2)$, ($Q=4\pi\sin\Theta/\lambda$). Simultaneously with a decrease (attenuation) in Bragg intensities, there is an incoherent scattering (TDS) which increases with an increase in the diffraction vector:

$$\text{TDS} = N(1 - e^{-2M}). \quad (2)$$

The B_T values can be determined experimentally from a dependence of the relative intensity of Bragg reflections on the scattering vector Q using the formula (3) given by Wilson [9]:

$$\ln (I_{\text{exp}} / I_{\text{calc}}) = 2 \ln K - 2B_T(\sin^2\Theta/\lambda^2), \quad (3)$$

where K is the scaling factor associated with the structure factor $|F_o(hkl)|$; the logarithm of the relative Bragg intensities plotted against $(\sin^2\Theta/\lambda^2)$ yields a straight line with the slope of $2B_T$.

Application of the Wilson plot to nanocrystals; a need for determination of TDS

For microcrystalline materials individual Bragg reflections are relatively narrow and separated from each other. To obtain net Bragg intensities it is sufficient to determine the diffuse background scattering by joining the minima of intensity between the peaks. This background includes the instrument background, Compton scattering, fluorescence and other effects, and TDS (equation (2)). In a routine procedure of determination of B_T with use of the Wilson method TDS does not need to be accounted for. However, it has to be examined very carefully for nanocrystalline materials for which a large part of diffuse scattering belongs to Bragg intensities. This is caused by very strong broadening, thus overlap of the reflections due to the size effect, internal strains, disorder, etc. After all corrections for diffuse background are done, the remaining intensity is Bragg scattering and TDS. The distinction between Bragg and TDS scatterings has to be done very accurately and, in practice, *the analysis of attenuation of Bragg intensities for nanocrystalline materials has to be done simultaneously with the analysis of TDS.*

Comparison of application of X-ray and neutron scattering

In general, X-ray and neutron diffraction measurements provide the same information about the structure of materials, so they are equally appropriate for the analysis of the atomic thermal motions. However, determination of TDS from neutron scattering data is much more unique than a similar analysis of X-ray data. For our purpose, the biggest advantage of neutron diffraction is that the scattering amplitude is constant in the whole range of the diffraction vector and, therefore, the shape of TDS is much better defined than for X-rays.

Theoretical calculations of the effect of thermal vibrations on the diffraction patterns of nano-crystals

A presence of thermal vibrations leads to a scatter of atoms about their perfect lattice positions. The effect of these atomic motions on the diffraction pattern can be simulated by calculating scattering on crystal lattices where atoms are located not in their perfect lattice positions but occupy positions about equilibrium with probability proportional to the time they spend at a certain distance from the equilibrium position during thermal motions [4]. We did theoretical calculations of the diffraction patterns of the models of SiC nanocrystals assuming that the motions of individual atoms are not correlated and that they are harmonic and isotropic. Probability of finding an atom in a given position about its equilibrium position is described by the Gaussian function with a maximum at a given lattice site.

Strategy of analysis of thermal vibrations in nano-crystals

In a conventional study of thermal atomic motions done using the Wilson procedure one searches for a unique value of the overall temperature factor B_T . Such approximation obviously cannot be used for nanocrystals which have two kinds of atoms (the grain interior and the surface) with different properties. It was suggested that the temperature parameter B can be approximated by a linear combination of the temperature atomic factors of the core and surface atoms [10]:

$$B = pB_{\text{core}} + (1 - p)B_{\text{shell}}, \quad (4)$$

where p is the fraction of the atoms in the grain core.

Calculation of theoretical TDS scattering for nanocrystals

TDS is a kind of incoherent scattering with contributions from the atoms proportional to their vibration amplitude (equation (2)) and amount. Assuming only uncorrelated atomic motions, contributions to TDS from different atoms are additive. The Wilson plot is used to determine overall temperature factors, what is equivalent to the assumption that individual atoms are undistinguishable; thermal vibrations are referred to an average atom with an average amplitude. Accordingly, TDS which represents an incoherent scattering of the average atom can be calculated with equation (2). For a nanocrystal with a core-shell structure one has to discern between two kinds of such "average" atoms (of the core and shell), and equation (2) should be replaced with (5):

$$\text{TDS}_{\text{total}} = p\text{TDS}_{\text{core}} + (1 - p)\text{TDS}_{\text{shell}}. \quad (5)$$

For a given diffraction data this function has to be normalized before it is subtracted from the total scattering (yielding net Bragg intensity). On a normalized neutron pattern, $S(Q)$, TDS always reaches unity at very large Q values (c.f. figure 3).

Results

Effect of different vibrations in the core and shell atoms on the Wilson plot

We examined a series of models of SiC nanocrystals assuming different temperature factors for the core and shell atoms and different thickness of the surface shell. For these models we calculated theoretical diffraction patterns and Wilson plots. TDS was calculated using equation (5). Figure 1 shows the results of elaboration of two theoretical diffraction patterns with

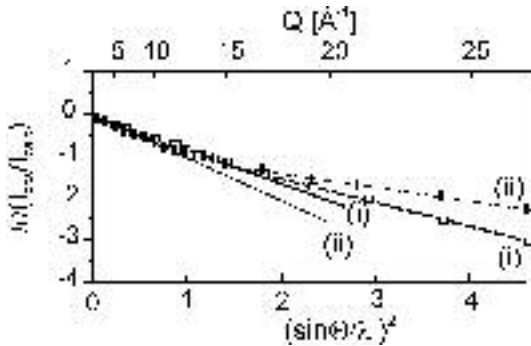


Figure 1 Theoretical Wilson plots obtained for diffraction patterns of 8 nm SiC nanocrystal with 1.0 nm thick surface shell calculated for two models of thermal vibrations with equal number of atoms in the grain core and shell:

(i) $B_{\text{core}}=0.24 \text{ \AA}^2$, $B_{\text{shell}} = 0.55 \text{ \AA}^2$; (ii) $B_{\text{core}}=0.14 \text{ \AA}^2$, $B_{\text{shell}} = 1.30 \text{ \AA}^2$.

different vibrations and equal number of the atoms in the grain core and the surface shell. For $Q > 15 \text{ \AA}^{-1}$ the plot is linear with a well defined slope corresponding to $B_{\text{core}}=0.24$ and 0.14 \AA^2 for models (i) and (ii), respectively. These are exactly the B_{core} values used in our models. That shows that for core atoms (small vibration amplitude) the Wilson plot yields reliable B values. For $Q < 15 \text{ \AA}^{-1}$ the plot shows a complex shape: the slope can be defined only for the smallest Q values and corresponds to B equal to 0.40 for model (i) and 0.72 \AA^2 for model (ii). Using equation (4) and taking B_{core} and B_{shell} of the models (i) and (ii) we get exactly the same B values. This shows that the Wilson plot can indeed be used to evaluate the atomic vibrations in the grain core and shell.

Experimental determination of the temperature factors B_{core} and B_{shell} for SiC powders

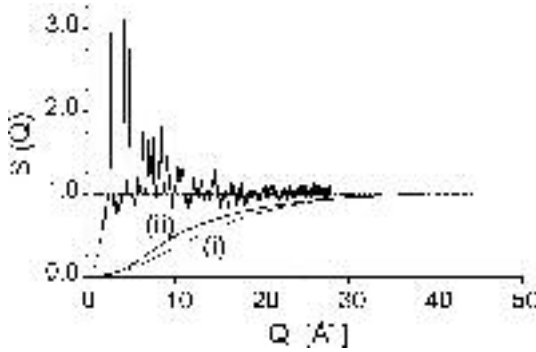


Figure 2 Experimental neutron diffraction pattern of 8 nm SiC nanocrystalline powder. TDS intensities were calculated for equal number of core and surface atoms and different vibrations: (i) $B_{\text{core}} = 0.165 \text{ \AA}^2$, $B_{\text{shell}} = 0.50 \text{ \AA}^2$; (ii) $B_{\text{core}} = 0.165 \text{ \AA}^2$, $B_{\text{shell}} = 0.85 \text{ \AA}^2$.

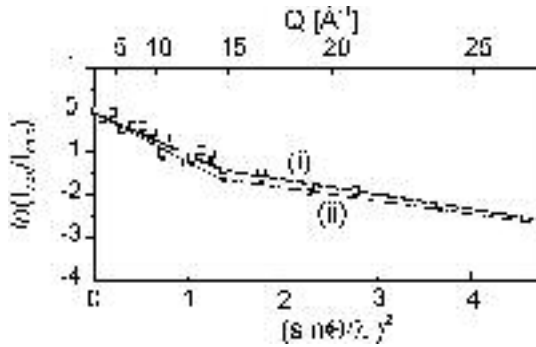


Figure 3 Experimental Wilson plots calculated for 8 nm SiC nanocrystalline powder after subtraction of TDS intensities corresponding to vibration models (i) and (ii) (c.f. figure 2).

value of B_{shell} is between these two values. They correspond to vibration amplitudes between 0.24 and 0.29 \AA , what is about two times larger than the average vibration amplitude of the inner grain atoms; $B_{\text{core}}=0.165 \text{ \AA}^2$ corresponds to the vibration amplitude of about 0.11 \AA . Figure 4 shows the Wilson plots obtained for 15 and 23 nm SiC powders, where TDS was taken assuming $B_{\text{core}}=0.165$ and $B_{\text{shell}}=0.85 \text{ \AA}^2$. The B_{core} values calculated for large Q for 15 and 23 nm samples are the same as for 8 nm sample. The B values calculated for small Q values are 0.41 and 0.34 \AA^2 , i.e. smaller than for 8 nm powder, what is consistent with a decrease in the content of the surface atoms with an increase in the grain size. The B_{shell} values calculated from equation (4) for those two samples are 0.9 and 0.95 \AA^2 , what agrees well with the value obtained for 8 nm sample (between 0.84 and 1.22 \AA^2).

To make a Wilson plot one needs to assume a certain shape of TDS_{total} scattering. That requires information on the relative number of core and surface atoms and amplitudes of their vibrations, i.e. information which we never know at the start of the work. At first approximation we assume that the atoms in the grain core vibrate as in the bulk material, what corresponds to the average value of $B_{\text{core}}=0.165 \text{ \AA}^2$. Next we assume that the atoms in the surface shell vibrate with the amplitude about two times larger than in the grain core; this yields B_{shell} between 0.5 and 0.9 \AA^2 . Figure 2 shows the experimental neutron diffraction pattern of our 8 nm SiC nanocrystalline powder and two different TDS intensities calculated from equation (5). The shape of the experimental Wilson plots in figure 3 is similar to the theoretical plots presented in figure 1. Taking TDS calculated for B_{shell} values of 0.5 and 0.85 \AA^2 we get the slopes for large Q corresponding to $B_{\text{core}}=0.16$ and 0.175 \AA^2 . This shows that the selection of TDS has little effect on B_{core} value determined by the Wilson method. For low Q we get slopes corresponding to B values of 0.5 and 0.7 \AA^2 . By using equation (4) and assuming $B_{\text{core}}=0.165 \text{ \AA}^2$ and equal number of core and surface shell atoms ($p = 0.5$) we get $B_{\text{shell}}= 0.84$ and 1.22 \AA^2 . We can tell that the real

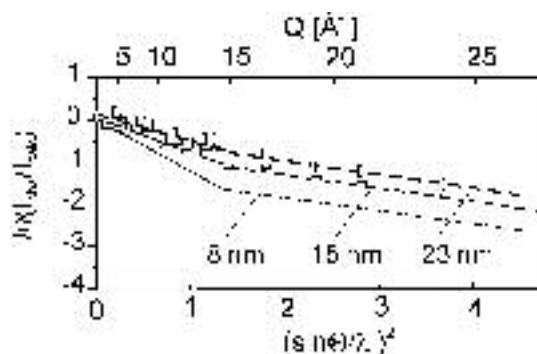


Figure 4 Experimental Wilson plots calculated for 15 and 23 nm SiC nanocrystalline powder after subtracting TDS intensities; 33% and 22%, respectively, of the atoms are in the surface shell. The plot of 8 nm powder is also shown.

Summary

Analysis of the atomic temperature factors of nanocrystals requires simultaneous evaluation of Thermal Diffuse Scattering. Wilson method can be applied for evaluation of thermal motions of the core and surface-related atoms in nanocrystals. Application of wide angle neutron scattering enables a direct evaluation of thermal vibrations in the core of nanocrystals. For SiC nanocrystals, the thermal factor B_{shell} for the surface atoms is 4 to 5 times larger than B_{core} ; this corresponds to 2 - 2.5 times larger amplitude of vibrations of the atoms at the surface relative to thermal vibration of the atoms in the interior of the grains. Although here we interpret the Wilson plots as if they reflected thermal vibrations only, one has to remember that B_T parameter determined by the method may include also a contribution from the static lattice distortions. The contribution of the static disorder can be evaluated using a similar procedure but investigating the temperature dependence of the temperature factors. That study is currently under way.

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