P-01

THE WARREN-AVERBACH METHOD OF PEAK SHAPE ANALYSIS TESTED BY ATOMISTIC AB-INITIO MODELING OF NANOCRYSTALS

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Most of the diffraction structure analysis methods developed for polycrystals meet their application limit for crystal size of few nanometers. The Bragg law itself ceases to apply strictly [1] what appears to be a direct consequence of short atom raws and thus of short, truncated Fourier series in the peak harmonic representation. With advent of nanotechnologies and rising interest in experimental analysis of nano-sized structures it is increasingly important to test application limits of the available structural methods.

Below we present a test for the Warren-Averbach (W-A) method of peak shape analysis [2] enabling separation of the size distribution and stress contribution to the diffraction peak broadening. The XRD pattern used for the test was calculated directly via the Debye formula for a log-normal size distribution of cubooctahedral palladium clusters. The log-normal distribution was centered at size ~4 nm and all the involved clusters were energy relaxed using Sutton-Chen [3] potentials and the program CLUSTER [4]. The use of the Debye formula is justified for polycrystals with no dynamic diffraction phenomena in the range of coherency down to amorphous material, where this formula is used as a conceptual basis in the Radial Distribution Function method. The Sutton-Chen potentials have proved to be well applicable for structure modeling of palladium clusters larger than ~2 nm [5] and this is approximately the lower limit of the log-normal distribution applied in this work.

Application of the W-A method to the XRD pattern calculated for this well defined physical model of nanoclusters meets considerable technical difficulty. The most pronounced one concerns background estimation and subtraction. Estimation of the stress distribution function was thus strongly background dependent – the overall profile being dominated by crystallite size broadening. In effect the simulated peak profile compares well to that calculated ab initio from the known, model atomic column length distribution (Fig. 1). The minute misfit of these distributions contributes to the model strain distribution and this shows disagreement with both – gaussian and lorentzian models of stress distribution. Nevertheless, the application of the standard W-A analysis for 002, 004 and 008 reflections enables extraction of the column length distribution resembling that theoretically *ab initi*o calculated (Fig. 2).

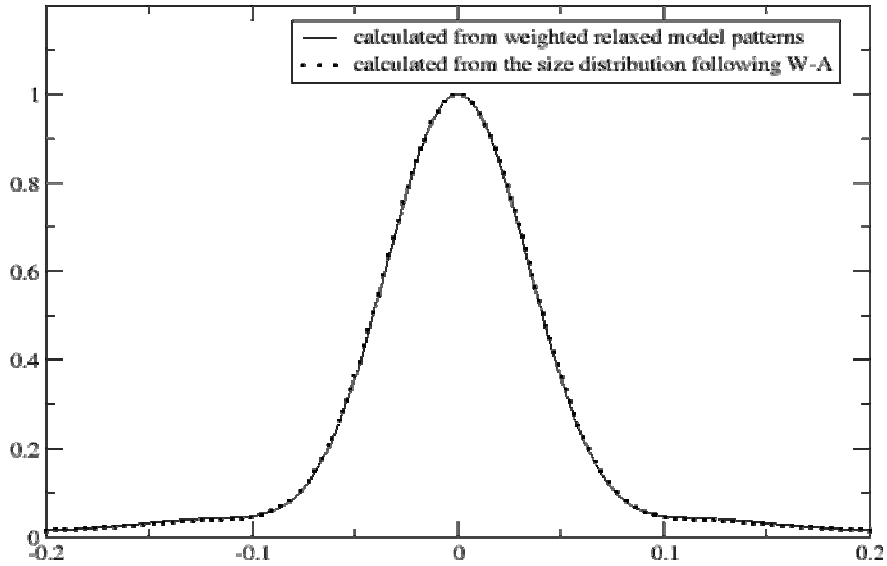

Figure 1. Comparison between 002 peak profile calculated from the Debye formula for the log-normal distribution of relaxed cubooctahedra, and 002 profile calculated from the log-normal weighted model column length distribution.

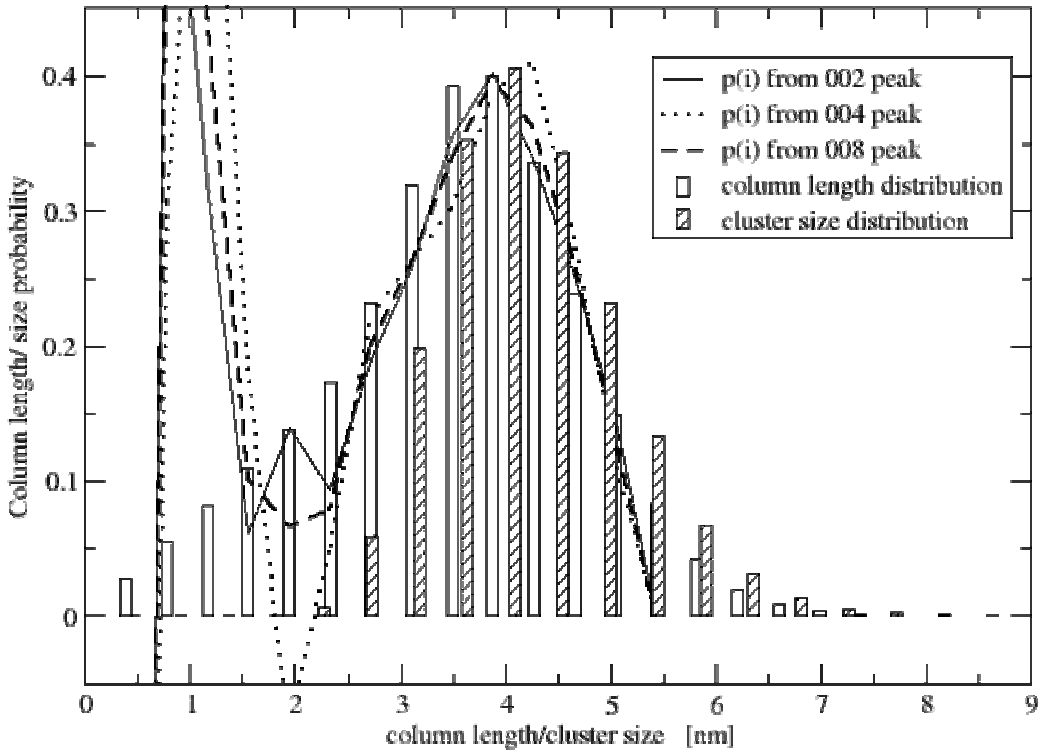

Figure 2. Ab initio cluster size and column length distribution compared to a column length probability obtained from the W-A method for three diffraction peaks.

Figure 2 displays also the log-normal cluster size distribution assumed for the model pattern (hatched bars) where the size of the cubooctahedron was defined as the diameter of a sphere having the same volume. The column-length distribution to be compared with the results of the W-A analysis, is thus directly derived from the assumed log-normal distribution (open bars). The obtained from the analysis column-length probabilities p(i) display considerable error for column length lower than ~2 nm – this effect we atribute also to uncertainity of the background estimation.

The W-A method interprets directly only cosine terms of the Fourier Transform and averages both slopes of the asymmetrical peak. This makes the method less sensitive to the peak asymmetry. On energy relaxation the peak position of a metal cluster shifts to the higher angles and the effect quickly fades with cluster size [1]. This cause of asymmetry is however hardly noticeable in our model pattern where the contribution from the larger crystallites has a significantly larger intensity.

The obtained results have shown that the Warren-Averbach method when applied to nanocrystals may give reliable results provided a considerable care is devoted to the background estimation routine. The natural, inherent to the nanocrystallinity stress gives less important contribution and is difficult to determine by the W-A approach. This stress-related effect is however clearly detectable via the simple Williamson-Hall plot analysis.

References

[1] Z. Kaszkur, *J. Appl. Crystallogr.* **33** (2000) 87

[2] B.E. Warren, *Prog. Metal Phys.* **8** (1959) 147

[3] A.P. Sutton, J. Chen, *Philos. Mag. Lett*. **61** (1990) 139

[4] B. Mierzwa, Z. Kaszkur, to be published in: *Applied Crystallography*, Proceedings of the XIX-th Conference, Kraków 2003, World Scientific 2004

[5] Z. Kaszkur, B. Mierzwa, *Philos. Mag. A* **77** (1998) 781