Rev.Adv.Mater.Sci. 10 (2005) 427-433

PROCESSING AND EVALUATION OF X-RAY LINE PROFILES MEASURED FROM NANOSTRUCTURED MATERIALS PRODUCED BY SEVERE PLASTIC DEFORMATION

Michael B. Kerber, Erhard Schafler and Michael J. Zehetbauer

Department of Materials Physics, University Vienna, Vienna, Austria

Received: May 15, 2005

Abstract. The classification of the microstructure of nanostructured materials and its relation to macroscopic properties is essential for the development and application of nanomaterials. X-ray line profile analysis is a nondestructive method yielding a series of interesting microstructural parameters: The Bragg reflection of an ideal crystal is a narrow delta-function like peak. Distortions of the regular crystal lattice as well as a finite size of the coherently scattering domains (CSDs) lead to a significant broadening of the peak. By using physical models describing the individual types of broadening it is possible to relate the broadening of the peak to the microstructure of the material. From these models various techniques have been developed to evaluate the same physical quantities via individual methods. Usually the measured data can not be used for evaluation immediately and preprocessing is necessary. A number of typical problems arising during data preparation and evaluation are presented and a procedure to optimize the processing of the experimental data is given.

1. INTRODUCTION

The classification of the microstructure of nanostructured materials and its relation to macroscopic properties is essential for the development and application of nanomaterials. X-ray line profile analysis (XPA) has proven to be a powerful tool to obtain a number of interesting microstructural parameters [1-4].

The main advantages of XPA are: it is a nondestructive method, it can be applied from powder to bulk material, from single crystals to nanomaterials and it can be used in in-situ investigations. It is the only method to quantitatively determine the high dislocation densities often found in nanomaterials and at the same time assess the coherently scattering domain (CSD) size distribution in good accordance with others methods (E.G. electron microscopy) but over larger sample volumes and with better statistics. Another advantage of XPA concerning crystallite size is that the method is very sensitive to small differences in the orientation of the crystallites (tilt angle > 2°).

XPA has been successfully used in the analysis of a number of nanocrystalline materials produced by, for example: sintering ceramics [5], thermal decomposition [6], ball milling [7], inert gas condensation [8], crystallization from the amorphous state [9], electro-deposition [10] as well as severe plastic deformation, i.e. equal channel angular pressing (ECAP) [11] and high pressure torsion (HPT) [12].

Corresponding author: Michael Kerber, e-mail: a9405544@unet.univie.ac.at

© 2005 Advanced Study Center Co. Ltd.

The experimental setup for XPA is a good monochromatic X-ray source, with a low divergence of the beam, thereby minimizing instrumental broadening. For the measurement of the profiles a position sensitive detector providing an angular resolution of at least 0.01° at convenient distances from the sample is necessary.

The actual microstructural parameters can be obtained by various procedures, using different quantities derived from the measured profile(s):

- by computing the lowest order Fourier coefficients, the Warren Averbach analysis [13] and variants [3];
- from the full width at half maximum (FWHM) or the integral breadth, the Williamson Hall plot [14] and its modified version [3];
- fitting of the Fourier transformed of the profile (i.e. fitting of the Fourier coefficients) [15];
- computing a physical profile in real space from the Fourier based models and directly fitting it to the measured profile;
- the momentum method [16,17], in which quantities computed directly from the profile are compared with the corresponding predictions of the asymptotic behaviour of the models of broadening.

2. METHODS OF PROFILE ANALYSIS

The evaluation of the recorded data can be done by analysing single peaks or by considering multiple peaks. In both cases the profiles measured usually consist of background scattering plus the Bragg peak. The latter is a combination of instrumental broadening and broadening of the peaks by properties of the sample, like finite size of the CSD, strain within the crystallites, stacking faults, *etc.* Thus one has to somehow handle the background and instrumental broadening to obtain a profile, which can be analysed by the methods described below.

Warren-Averbach analysis. The basis for X-ray line profile analysis is the Warren-Averbach analysis. Warren and Averbach calculated the diffracted intensity of a X-ray beam in Fourier space for the case of small crystallites and strain being present in the sample [2,13]. The result is that the intensity of the profile is given by the convolution of size and strain broadening. Thus in Fourier space it is possible to separate the contributions via the well known Warren-Averbach equation:

$$\ln A_L \approx \ln A_L^S + \ln A_L^D . \qquad (1)$$

Here A_L are the Fourier coefficients computed from the profile, A^S_L are the coefficients associated with size broadening, the ones for strain broadening are denoted by A^D_L. The variable L is the so called Fourier length and given by $L=n\lambda/[2(\sin\theta_1-\sin\theta_2)]$, where n are integers, starting with zero and $(\theta_2-\theta_1)$ is the range of the measured peak. The size broadening coefficients A^S_L depend on the length of the CSD in direction of the diffraction vector and it is independent of the diffraction order. The strain broadening coefficients computed by Warren and Averbach are given by

$$A_L^D = \exp(-2\pi^2 L^2 g^2 < \varepsilon^2_{g,L} >). \qquad (2)$$

Here g is the diffraction vector and $<\varepsilon^2_{g,L}>$ is the mean square strain. The strain broadening coefficients depend on the diffraction order and vanish for $g^2=0$.

One can therefore separate size- and strain broadening by plotting $\ln(A_L)$ versus g for the lowest order Fourier coefficients. The extrapolation to $g^2=0$ gives the A^S_L, the slopes give the argument of the exponential in Eq. (2). From the size coefficients the average CSD in the direction of the diffraction vector is given by the initial slope of the plots of A^S_L versus L. The second derivative of these curves directly gives a CSD distribution [2].

Modified Warren-Averbach analysis. For the case that the strain is caused by dislocations, Wilkens computed the mean square strain, assuming that the dislocations are 'restrictedly randomly' distributed [18-20]:

$$< \varepsilon^2_{g,L} > \approx \frac{\rho C b^2}{4\pi} \ln\left(\frac{R_e}{L}\right), \qquad (3)$$

where b is the length of the Burgers vector, ρ the dislocation density, R_e is the outer cut-off radius and C is the contrast factor of dislocations. The contrast factor depends on the relative orientation of line-, Burgers- and diffraction vector as well as the elastic constants of the material. Because of the actual dislocation distribution in a sample, it is necessary to average over the C factors of edge and screw dislocations, different slip systems and orientation of the slip system with respect to the diffraction vector, denoting the average contrast factor by $\overline{C}$. Ungar and Tichy [21] showed that for cubic or hexagonal crystals, if the Burgers vector distribution is completely random, the dependce of $\overline{C}$ on the *hkl* can be explicitly calculated. For cubic crystals

$$\overline{C}_{hkl} = \overline{C}_{h00}\left(1 - qH^2\right), \qquad (4)$$

where $\overline{C}_{h00}$ is the average contrast factor of the $h00$ reflection, q is a constant, depending on the elastic constants of the crystal and the dislocation type, and $H^2 = (h^2k^2+h^2l^2+k^2l^2)/(h^2+k^2+l^2)^2$. Both $\overline{C}_{h00}$ and q have been calculated numerically for a number of cases in [22]. In the case of a hexagonal crystal the average contrast factor of a given sub slip system is given by [23]:

$$\overline{C}_{hk,l} = \overline{C}_{hk,0}\left(1 + q_1 x + q_2 x^2\right). \quad (5)$$

Here $x=(2/3)(l/[ga])^2$ with g as the absolute value of the diffraction vector and a is the lattice parameter within the close packed layer. $\overline{C}_{hk,0}$, q_1, and q_2 have meanings analogous to the cubic case, numerical evaluations can also be found in [23].

Inserting formula (3) into (2), Eq. (1) becomes the modified Warren-Averbach equation [3]:

$$\ln A_L \approx \ln A_L^S + \frac{\pi}{2} L^2 g^2 b^2 \rho \overline{C} \ln\left(\frac{R_e}{L}\right). \quad (6)$$

It is clear from Eq. (6) that if the strain is caused by dislocations, $\ln A_L$ must be plotted versus $g^2\,\overline{C}$ instead of g^2. This is called the modified Warren-Averbach analysis. It should be mentioned that the effects of stacking faults and twins can be considered in this analysis [2]. The successful application of this scheme was done by Ungar *et al.* [24] by including a term $\beta' W(g)$ in the modified Warren-Averbach equation, adding one more parameter to the analysis.

Williamson-Hall plot. The most direct evaluation of XPA is the Williamson-Hall plot. In their 1953 paper [14] Williamson and Hall calculated the integral line breadth of a Bragg peak from the work of Warren and Averbach [13]. It turns out that by plotting the integral width (or the FWHM) of each peak against the absolute value of the diffraction vector, the size and strain broadening effects can be separated if an average particle size accurately describes the CSD distribution. As for the Warren-Averbach analysis, the assumption that the broadening is predominantly caused by dislocations leads to a "modified" version of the plot. The models presented in the Warren-Averbach analysis predict the following behaviour of the peak breadth:

$$\Delta K \approx \frac{0.9}{D} + \left(\frac{\pi}{2}\right)^{\frac{1}{2}} M b \rho^{\frac{1}{2}} K \overline{C}^{\frac{1}{2}}. \quad (7)$$

Here ΔK is the peak-breadth in terms of $K=2\sin\theta/\lambda$ (with θ the diffraction angle), D is the average CSD-size, ρ, b, $\overline{C}$ are the same quantities as in the previous section and M is the dislocation-arrangement parameter and depends on R_e.

As demonstrated by Ungar and co-workers in a number of papers starting with [3], the modified Williamson-Hall plot (i.e. peak breadth versus $K\overline{C}^{1/2}$) does show if the strain is caused by dislocations.

The disadvantage of an peak-breadth based method is that for a CSD distribution different from one average crystallite size, strain and size effects cannot be separated. This limits this method to the determination of the parameters for the average contrast factors. Furthermore it can be used to decide whether additional effects like stacking faults are present [24].

Fitting the Fourier coefficients. Nowadays the wide availability of fast computers with sophisticated software allows to fit complicated models to experimental data using least squares optimization algorithms for example. It is thus possible to use the physical models presented in the Warren-Averbach analysis and fit these to the low order Fourier coefficients computed from the experimental data.

The fitting parameters would then be e.g. m and σ from the size distribution, the q's from the average contrast factor, ρ and R_e describing the dislocation arrangement. In order to determine all these parameters multiple reflections must be taken for the evaluation. If a single reflection is used, most of the parameters must be known but e.g. ρ and R_e can be fitted.

Fitting of profiles with physical functions. The most advanced method of XPA is to compute a real space function from the Fourier space models describing the Bragg peak. This function can then be used to fit the measured data directly. This method adds two more parameters to the physical ones: the intensity and the peak position. Both can be either fitted or must be accurately provided by other means. The successful implementation of this scheme was independently done by Ribarik, Ungar and Gubicza [25] and by Scardi and Leoni [26].

Momentum method. The momentum method (also called variance method) [16,17] uses a different approach to separate size and strain effects to peak broadening and to determine the corresponding microstructural parameters. The idea is to perform a transformation of the intensity distribution. In the case of the momentum method one computes M_i, the so called restricted moments of order i:

$$M_{k(q)} = \frac{\int_{-p}^{p} s^i I(s) ds}{\int_{-\infty}^{\infty} I(s) ds}. \qquad (8)$$

Here $p = 2(\sin\theta - \sin\theta_0)/\lambda$, where λ is the wavelength of the X-rays, θ is the diffraction angle and θ_0 is the Bragg angle. *I(p)* is the intensity distribution of the profile. The idea of the method is that the models for size and strain broadening predict a certain behaviour of the M_i for large *p*, that is in the tails of the profiles. Groma [16] derived a generalised version of the variance method of Wilson [27] using only analytical properties of displacement field of straight dislocations without making assumptions on the dislocation distribution. Borbely and Groma [17] added size broadening to Groma's work and derived the following large *p* behaviour for the second order moment:

$$M_2(p) = \frac{p}{\pi^2 \varepsilon_F} - \frac{t}{4\pi^2 k^2 e_F^2} + \frac{C\rho \ln(p/p_0)}{2\pi^2}. \qquad (9)$$

The second restricted moment of interest is the fourth order one. Its asymptotic form is given by

$$M_4(p) = q^2 \left[\frac{p}{3\pi^2 \varepsilon_F} + \frac{C\rho}{4\pi^2} + \frac{3C^2 \langle \rho^2 \rangle}{4\pi^2 p^2} \ln\left(\frac{p}{p_1}\right) \right]. \qquad (10)$$

For practical purposes, M_4/p^2 is used instead of the M_4 and usually the third summand in the brackets of Eq. (10) can be neglected for large *p*.

The important parameters in Eqs. (9) and (10) are ε_F - the area-averaged CSD size, *t* - the taper parameter, associated with the geometry of the CSD and *s* - the Scherrer constant. Both *t* and *s* depend on the *hkl* of the reflection, *C* is the contrast factor of dislocations, ρ is the dislocations density, $\langle\rho^2\rangle$ is the average of the square of the dislocation density and p_0 and p_1 are fitting parameters not interpreted physically.

The advantage of this method is, due to the relatively simple dependence of the microstructural parameters, that the contributions to broadening can be seen immediately by plotting M_2 and M_4/p^2 versus *p*. A quantitative determination of the physical quantities can be done by linear regression of the large *p* behaviour of the restricted moments.

3. IMPLEMENTATIONS OF THE METHODS

Current state of XPA. The most important point about evaluating X-ray profiles is to ensure good experimental data. Neither an evaluation technique nor any trick can replace properly measured data. For the implementation of the methods the leading rule should be to stick with the data as long as possible thus altering the measured values only when absolutely necessary. As already mentioned, the measured data consists of background scattering, an instrumental profile, and the peak due to scattering by an imperfect crystal. For the evaluation the background needs to be removed and the instrumental broadening has to be eliminated. When trying to determine the background by fitting, physical models for the background function are not applicable because the possible causes for diffuse background scattering are numerous. So one has to use simple analytical functions (e.g.: polynomials or bezier-splines) with the disadvantage that these functions can give unphysical solutions, like becoming negative in an interval. The downside of the background fitting is that it adds more parameters to a physical fit, with the fitting parameters having a strong influence on the (weighted) sum of the squared residuals (WSSR) due to the high number of points being changed. It is thus possible that adjusting the background to an (non physical) value reduces the WSSR more than keeping the background and changing the peak parameters. The fits for the background can also result in number of different solutions, which look equally good but differ mainly at peak positions. The difference in overall background scattering for these solutions can reach 10%.

Following the leading rule described above, the found background should not be subtracted from the data but rather be added to the model prediction, if possible.

After the background removal, the instrumental effects can be taken care of by Stokes correction: Stokes [28] showed that the intensities of instrumental effects and effects due to the sample are in convolution. Thus by recording an instrumental function, i.e. a reference sample with negligible broadening due to the sample itself, the effects due to the measurement process can be removed. The correction can be done in principle in different manners: one can either divide the Fourier transformed of the data by the Fourier transformed of the instrumental function or one can multiply the Fourier space model with the Fourier transformed of the instru-

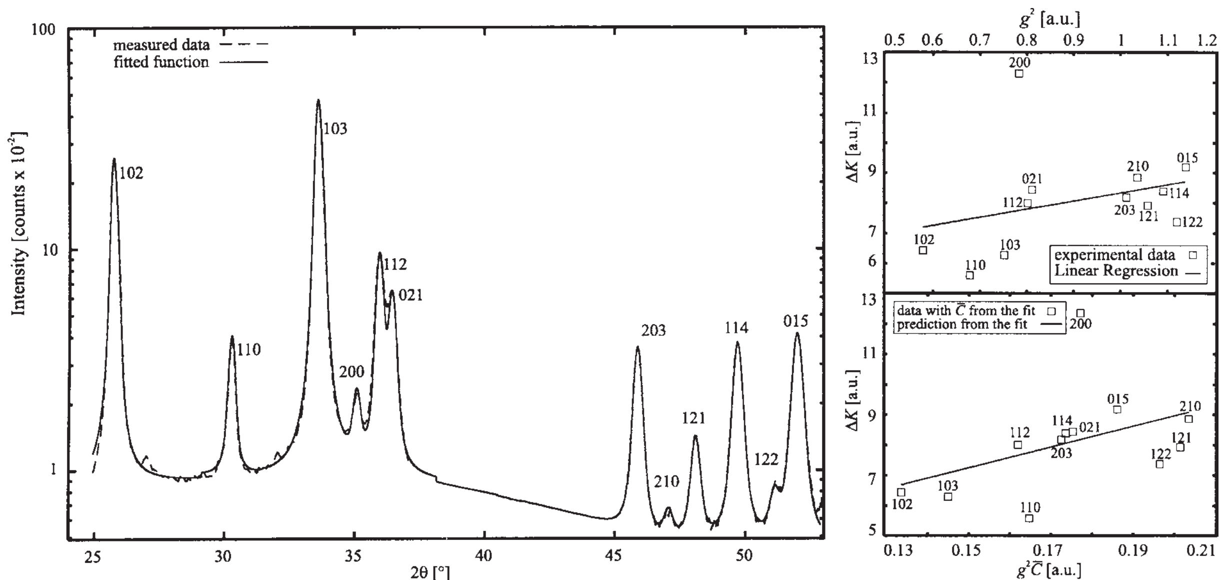

Fig. 1. Fit of a X-ray measurement of nanocrystalline Ti with MWP-fit [26] and the corresponding Williamson-Hall plot as well as its modified version. Due to the strong overlap of peaks, the crucial reflections are the 102, 110, 103, 203, 114, and 015.

mental function before comparing with the measured data. Another approach is to compute the convolution of the instrumental function with the model in real space numerically. From all these possibilities the division in Fourier space is the least favorable one because it usually involves division by numbers close to zero, usually problematic for computers. Again the preferred way should be to include the instrumental profile into the modelfunction.

If the peaks (partly) overlap, they have to be separated. This has to be done by fitting the two peaks and, following the leading rule, the first peak should be subtracted from the data to obtain the second and additionally the second should be subtracted from the data to obtain the first. After the above correction the quantities explained in the previous chapters can be computed and the methods can be applied. Whenever linear functions are involved (Williamson-Hall plot, momentum method or the extrapolations in the Warren-Averbach analysis) linear regressions can be used. Alternatively one can fit the linear breadth to the Williamson-Hall prediction for example. It should be mentioned that this can lead to troubles: whenever fitting is involved it is in principle always possible to find a solution, but this must not be physical meaningful. As an example, fitting experimental data to formula (7) together with Eq. (4) using as free parameters D and q does give solutions for every value of $\chi = Mb\,(\pi\rho C_{h00}/2)^{1/2}$, but if the latter is included in the fit only unphysical solutions are found. The reason for this is that the solution space has no nontrivial minima with respect to χ.

When fitting physical functions to the Fourier transformed there are only a few nonzero coefficients. Compared with the number of data points of a well resolved profile this is a drawback of this approach. Another disadvantage is that a wrong background or a low angular resolution of the profile have a considerable influence on the computed Fourier coefficients thus affecting the evaluation. Fitting the measured data with physical functions has some advantages. First it compares the physical models directly with the data without any manipulation. Furthermore it is possible to include background as well as the instrumental correction into the fitfunction quite easily. When fitting only the physical parameters, the number of fit parameters can be matched by the number of peaks ensuring that a proper physical solution is obtained. The disadvantages of fitting physical model functions compared with nonphysical analytical ones is that for the physical models the fitting parameters do not independently influence the shape of the profile whereas the fitting parameters of the nonphysical functions have a direct and independent influence on the peakshape of each peak. The most often used analytical functions like Pearson-VII or (pseudo-)Voigt for example have as parameters peak position, intensity, full width at half maximum (FWHM) and tail-shape. The peak

position and intensity as well as the FWHM can be determined quite well for every peak within a few iterations and only the shape must be adjusted by the minimisation thus enabling fast fitting. Experience also shows that when fitting the data with physical functions and the peak-intensities and position are included in the set of parameters to be fitted, the latter are adjusted to proper values quite fast, but the fit does not converge with respect to the physical parameters.

Another key difference between using physical and nonphysical analytical functions is that, as mentioned above, the adjustable physical parameters for multiple reflections are identical compared to the independent parameters of the analytical functions. Although this reduces the number of solutions, this is not only an advantage. The solution space of the physical parameters is usually very flat with few local minima therefore a proper choice of starting values is therefore very important. Especially for peaks that overlap strongly this may be a problem: finetuning the starting values for two overlapping peaks is very hard with the physical functions because all peaks change when adjusting the values only for the two overlapping reflections. Using analytical functions in this case is more suitable for peak-separation.

The momentum method is a direct way of evaluation and does not necessarily require fitting. It is quite sensitive with respect to background removal as well as to the quality of the measured data. One of its main advantages is that is uses the most general model for strain broadening and is straight forward to implement. Yet not all parameters have a physical interpretation making it difficult to determine if the results of the evaluation are the physical one with respect to these parameters.

Improving the state of the art. Currently only a few of the above methods are generally used for evaluation. Since all of them share common parameters not using as many methods as possible means discarding valuable information which can be used to increase the accuracy and applicability of XPA.

One way to make use of all ways of evaluation can be the following: For a generic evaluation scheme first the background and the major peak parameters (position, intensity) are determined by fitting. Due to the advantages and disadvantages presented this is preferably done by using nonphysical analytical functions. Especially when separating peaks only the overlapping peaks can be readjusted when using this approach. Fitting the background simultaneously with the peaks is especially useful when dealing with profiles recorded from in-situ measurements, where a large number of similar datasets need to be evaluated. The results from this must best be confirmed by a human.

From the resulting values it is quite easy to do a Williamson-Hall plot and its modified versions to see the possible causes of broadening. The parameters for the average contrast factors determined by such a scheme can then be used as start values for fitting the physical model. Due to the simplicity of the Williamson-Hall plots, it can always be done to verify fitting results.

As can be seen in Fig. 1, presenting a Williamson-Hall plot with values obtained from the fit does also help to determine if a physical minimum has been found. There the fit with physical functions is excellent, but as can be seen in the corresponding Williamson-Hall plot and its modified version, neither does the sample show isotropic strain-broadening nor does an average contrast factor describe the anisotropic broadening. In this particular case the sample has strong texture and neither model can be directly applied. From the quality of the fit alone this could not be seen.

Additionally the Warren-Averbach and/or the Momentum Method may be used to determine values for the physical parameters that can be used as starting values for fitting and/or to determine if fitting has given a physical solution.

The results of the 'pre-fit' with non-physical functions (i.e. the background, peak-positions, …) together with the parameters determined as described above should give a fast and physical solution when fitting (in Fourier space as well as in real space).

A much more interesting approach is to regard all methods as one set of 'equations' for a given set of physical parameters and to try to adjust the physical parameters by optimisation. Fitting Fourier coefficients simultaneously with the corresponding real-space function is one simple example to be implemented.

4. SUMMARY.

Analysing the microstructure of nanostructered materials with XPA has proven to be very successful as an independent as well as supplementary method. One of the advantages of XPA is that different ways have been developed to determine a number of parameters of interest. Each method has its advantages and disadvantages yet they are independent ways to determine sets of quantities which do (partly) overlap. It is always useful to make use

of all possibilities of evaluation thereby enhancing the accuracy of the results as well as the usability of the procedure. For the evaluation of X-ray profiles of nanocrystalline materials it is thus sensible to use the modified Warren-Averbach and Williamson-Hall methods as well as fitting of analytical functions to determine starting values for a fit with physical functions in real- or Fourier space. The Momentum-method may serve as a cross-check and to determine if the results found by fitting correspond to a physical meaningful minimum.

ACKNOWLEDGEMENTS

The Austrian Science Funds (FWF) is acknowledged for support under project P-17095-N02 (A).

REFERENCES

[1] M. A. Krivoglaz, *X-ray and neutron diffraction in nonideal crystals* (Springer, 1996.)
[2] B. E. Warren, *X-ray diffraction* (Dover, 1990).
[3] T. Ungar and A. Borbely // *Appl. Phys. Lett.* **69** (1996) 3173.
[4] A. Guinier, *X-ray diffraction* (Freeman, 1963).
[5] J. Gubicza, J. Szepvolgyi, I. Mohai, G. Ribarik and T. Ungar // *J. Mater. Sci.* **35** (2000) 3711.
[6] J.I. Langford, D. Louer and P. Scardi // *J. Appl. Cryst.* **33** (2000) 964.
[7] P. Scardi and M. Leoni // *Acta. Cryst. A* **58** (2002) 190.
[8] C.E. Krill and R. Birringer // *Phil. Mag. A* **77** (1998) 621.
[9] I. Bakonyi, F. Mehner, M. Rapp, A. Cziraki, H. Kronmuller and R. Kirchheim // *Z. Metallk.* **86** (1995) 619.
[10] T. Ungar, B. Revesz and A. Borbely // *J. Appl. Cryst.* **31** (1998) 554.
[11] E. Schafler, K. Nyilas, S. Bernstorff, L. Zeipper, M. Zehetbauer and T. Ungar // *Z. Krist*. (2005), accepted for publication.
[12] A. Dubravina, M. Zehetbauer, E. Schafler and I. Alexandrov // *Mater. Sci. Eng.* **387-389** (2004) 817.
[13] B. E. Warren and B. L. Averbach // *J. Appl. Phys.* **21** (1950) 595.
[14] G. K. Williamson and W. H. Hall // *Acta Metall.* **1** (1953) 22.
[15] T. Ungar, J. Gubicza, G. Ribarik and A. Borbely // *J. Appl. Cryst.* **34** 298.
[16] I. Groma // *Phys. Rev. B* **57** (1998) 7535.
[17] A. Borbely and I. Groma // *Appl. Phy. Lett.* **79** (2001) 1772.
[18] M. Wilkens // *Phys. Stat. Sol. A* **2** (1970) 359.
[19] M. Wilkens, In: *Fundamental Aspects of Dislocation Theory, vol. II,* ed. by J.A. Simmons, R. de It and R. Bullough (Nat. Bur. Stand. (US) Spec. Publ. No. 317, Washington D.C., 1970) p. 1195.
[20] M. Wilkens // *Phys. Stat. Sol. A* **104** (1987) K1.
[21] T. Ungar and G. Tichy // *phys. stat. sol. (a)* **171** (1999) 425.
[22] T. Ungar, I. Dragomir, B. Revesz and A. Borbely // *J. Appl. Cryst.* **32** (1999) 992.
[23] I. Dragomir and T. Ungar // *J. Appl. Cryst.* **35** (2002) 556.
[24] T. Ungar, S. Ott, P. G. Sanders, A. Borbely and J. R. Weertman // *Acta Mater.* **46** (1998) 3693.
[25] G. Ribarik, T. Ungar and J. Gubicza // *J. Appl. Cryst.* **34** (2001) 669.
[26] P. Scardi and M. Leoni // *Acta Cryst. A* **58** (2002) 190.
[27] A.J.C. Wilson // *Nuovo Cimento* **1** (1955) 277.
[28] A.R. Stokes // *Proc. Phys. Soc.* **61** (1948) 382.