

## A novel method for the determination of grain size distribution and microstrain in nanocrystalline materials from single X-ray diffraction peak

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**Abstract** A new method for determining simultaneous grain-size distribution and microstrain from single X-ray diffraction peak is presented. The method combines both the single peak real-space method of Langford and single peak Fourier-space method of Nandi *et al* to determine two apparent size parameters. If the morphology of the grains is known from a separate experiment (*viz.* TEM) the apparent size value may be used to determine the grain size distribution. In the present work a log-normal distribution of spherical grains was assumed and the median and variance of the distribution was determined for ball-milled vanadium-pentoxide samples. It is proposed that the present method gives reliable information regarding grain size distribution and microstrain compared to any other single peak methods. The method may be widely applicable to most nanocrystalline materials with only limitation in case of materials exhibiting grain size disparity (*viz.* bi-modal or multi-modal size distribution) and does not require intensive TEM analysis.

**Keywords** Nanocrystalline materials, grain size, microstrain, XRD, TEM

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### Introduction

Crystallite size and the microstrain therein are essentially two parameters, which characterise the microstructure of materials. Most widely used and rigorous method for the evaluation of these parameters is the Warren-Averbach [1] method based on the Fourier transform of the profiles for a family of planes.

Often many materials (*i.e.* oriented thin films, polymers, heavily deformed metals and alloys, nanocrystalline materials etc.) exhibit only a single order of a particular reflection and an appropriate single-line analysis is warranted. Generally two approaches are widely used : (1) Fourier space method and (2) real space method based on the integral breadth of the profiles. Specific assumptions regarding the profile shapes are necessary for both the methods.

In the Fourier method either a Laue or Cauchy size-broadened and a Gaussian strain-broadened profile is assumed. Both these assumptions may be incompatible for specific cases. For example a crystallite size distribution is present Laue function is not

physically acceptable. If a Cauchy size-broadened profile is assumed it is indicative of a broad size distribution. Moderate size distribution cannot be accommodated by either of the two assumptions. Although both the functions have identical initial slopes, the estimate of effective crystallite size is identical in both cases. The estimate of strain may differ considerably from their true values. Furthermore since the crystallite size distribution is not known *a-priori*, the above choice of the size-broadened profile is purely empirical.

In the case of nanocrystalline materials, the main focus is on the determination of size of the nanocrystalline grains. Generally Transmission Electron Microscopy (TEM) or X-ray method are employed for the determination of size. The following points should however be taken into account, (i) TEM require extensive sample preparation technique, (ii) X-ray diffraction pattern shows only the most intense lines without measurable higher order, impairing the application of multiple order Fourier or the Integral Breadth methods, (iii) size determined from TEM and X-ray methods in general disagree; X-ray methods yield certain averages (area or volume) of effective column lengths, whereas, TEM yields average grain diameter, (iv) in general an asymmetric grain size distribution (*viz.* log-normal) exists. In view of the

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above shortcomings it is essential to develop a single line X-ray method; incorporating a grain size distribution such that the results from TEM and X-ray methods favourably compare with each other. The essence of this communication is to develop such a X-ray method complimentary to TEM studies.

## 2. Theoretical formulation

### (a) Fourier space method :

Most of the early size-strain separation methods from single order based on the Fourier coefficients assume the size-Fourier coefficients as

$$A_s = 1 - L/D_{\text{eff}} \quad (1)$$

which is correct only in the small  $L$  region in the presence of a column-length distribution, disorder Fourier coefficients  $A_d$  for small  $L$  values is expressed as

$$A_d = 1 - 2\pi^2 L^2 \langle \varepsilon^2 \rangle / d^2. \quad (2)$$

This two choice is applicable to the small  $L$  regions. If 'hook' effect is present in the small  $L$  region the separation method based on (1) and (2) gives unreliable results. Due to explicit dependence of  $\langle \varepsilon^2 \rangle$  on  $L$  the functional form of  $\langle \varepsilon^2 \rangle = k/L$  ( $k$  depends on the crystallographic direction) [2] often used in the single-line methods do not hold in the small  $L$  region.  $A_d$  in that case becomes

$$A_d = 1 - 2\pi^2 L k / d^2. \quad (3)$$

Combination of (1) and (3) in principle can neither be applied to the small  $L$  region due to inadequacy of the relation of  $\langle \varepsilon^2 \rangle$  with  $L$ , nor in the higher  $L$  region due to the inherent curvature in the  $A_s - L$  curve. A suitable compromise was used by Nandi *et al* [3] by assuming

$$A_s = \exp(-L/D_{\text{eff}}) \quad (4)$$

which when combined with (3) can give more realistic results. But this choice of  $A_s$  is particularly true for broad size distribution and overestimates the disorder Fourier coefficients if the size-distribution is narrow.

The size-strain separation method based on (1) and (2) (generally a product of the two terms is used) assumes a constant average value of  $\langle \varepsilon^2 \rangle$  and is hence discarded when compared with the rigorous two-order method. The method based on (1) and (3) [4] may yield good result for narrow size distribution subject to the absence of the initial hook in the Fourier coefficient curve and the method based (3) and (4) [3] gives good result for broad size-distribution. In addition the method of [3] assumes that the initial slope of the experimental  $A_s - L$  curve gives the value of effective crystallite size and the value is correct for crystals sensibly free of displacement disorder.

### (b) Modified Fourier space method :

In view of the above shortcomings a modified method is proposed combining both the initial slope method of [3] and a realistic model of particle shape proposed initially by Adler and Houska [5] and is expected to work well for materials having moderately wide distribution of column-lengths. The line shape analysis based on Warren-Averbach method provides information regarding the average column-length only. The construction of column-length distribution from the size-Fourier coefficients is often unreliable due to initial hook effect leading to physically impossible negative value of distribution function. In line-broadening analysis the assumed coherently diffracting domains are considered as stacks of unit cells the spatial extent of which is delimited by grain/subgrain boundaries. If it is assumed that the average grain/subgrain shape is spherical, the distribution of lengths intercepted by spheres can be utilised to construct a column length distribution. This assumption has a physical basis and such a column-length distribution is independent of the physical shape of the size-broadened profile. Assuming spheres of a single diameter  $D$  (a more realistic assumption would be spheres having a log-normal distribution of diameters, see below), the distribution of columns is given [5] in terms of diameter of the sphere as,

$$P(i) = \frac{2i}{D^2} \quad \text{for } 0 \leq i \leq D \\ = 0 \quad \text{for } i > D \quad (5)$$

or, in terms of area weighted average column length  $D_{\text{eff}}$ ,

$$P(i) = \frac{8i}{9D_{\text{eff}}^2} \quad \text{for } i \leq \frac{3}{2} D_{\text{eff}} \\ = 0 \quad \text{for } i > \frac{3}{2} D_{\text{eff}}. \quad (6)$$

The size-Fourier coefficients in terms of coherence length  $L$  can be calculated as

$$A_s(L) = 1 - \frac{L}{D_{\text{eff}}} + \frac{4}{27} \left( \frac{L}{D_{\text{eff}}} \right)^3 \quad \text{for } L \leq \frac{3}{2} D_{\text{eff}} \\ = 0 \quad \text{for } L > \frac{3}{2} D_{\text{eff}}. \quad (7)$$

The relation between  $D_{\text{eff}}$  and  $D$  is given by

$$D_{\text{eff}} = \frac{2}{3} D. \quad (8)$$

If, however, a log-normal distribution of the spherical grains is assumed the grain size distribution is given by

$$G(D) = \frac{1}{\sigma\sqrt{2\pi}} \frac{1}{D} \exp \left[ -\frac{\left[ \ln \frac{D}{D_0} \right]^2}{2\sigma^2} \right] \quad (9)$$

where  $D_0$  is the median and  $\sigma$  is the variance of the distribution.

For such a distribution the column-length distribution is given by

$$P(L) = \frac{L}{D_0^2} \exp(-2\sigma^2) \operatorname{erfc} \frac{\ln \frac{L}{D_0}}{\sqrt{2}\sigma} \quad (10)$$

and the corresponding size-Fourier coefficient is given by

$$A_L^S = \frac{D_0^3 \exp(4.5\sigma^2)}{3} \operatorname{erfc} \left[ \frac{\log(|L|D_0)}{\sqrt{2}\sigma} - \frac{3}{2} \sqrt{2}\sigma \right] \\ D_0^2 \exp(2\sigma^2) |L| \operatorname{erfc} \left| \frac{\log(|L|D_0)}{\sqrt{2}\sigma} \right| \sqrt{2}\sigma \\ + \frac{|L|^3}{6} \operatorname{erfc} \frac{\log(|L|D_0)}{\sqrt{2}\sigma} \quad (11)$$

It is clear from the above expression that  $A_S(L)$  is a two parameter function of  $D_0$  and  $\sigma$ . The eqns. (7) and (11) are the essence of the modified Fourier space method which is more physically based compared to the traditionally used Laue or Cauchy size broadened profile. The average column length  $D_{\text{eff}}$  is related to the variance and median of the log-normal size distribution as

$$D_{\text{eff}} = \frac{2}{3} D_0 \exp(2.5\sigma^2). \quad (12)$$

In all single line Fourier space methods based on eqns. (4), (7) and (11) it is assumed that

$$\frac{1}{D_{\text{eff}}} \frac{dA(L)}{dL} \quad (13)$$

where  $A(L)$  is the total Fourier coefficient.

It is clear that eq. (11) is two parameter function and it seems that sole use of single line Fourier analysis is not sufficient to simulate  $A_S(L)$  according to eq. (11).

(c) *Determination of grain/subgrain size distribution from single line analysis :*

It is evident from the discussion in the earlier section and also from the nature of the size distribution function (eq. 9) that if the parameters  $D_0$  and  $\sigma$  can be obtained from a single X-ray diffraction peak, then it is possible in principle to determine the grain size distribution  $G(D)$ . Earlier Ungar *et al* [6], Krill and Birringer [7] has developed techniques for the determination of  $G(D)$  from the analysis of least two orders of X-ray diffraction peaks. Their method can also be adopted in this case if both

Fourier space method and real space method based on the integral breadth are used simultaneously.

The integral breadth is defined as peak area divided by the maximum intensity. The integral breadth method can further be obtained from the following expression

$$\beta = \frac{1}{2 \sum A(L)} \quad (\text{in reciprocal units}). \quad (14)$$

If the X-ray line profile is approximated by a Voigt function, the Cauchy and the Gaussian components of  $\beta$  can be obtained following deKeijser *et al* [8]. If both size and strain broadening is present the volume weighted crystallite size  $D_V$  and microstrain is obtained from the Cauchy ( $\beta_C$ ) and the Gaussian ( $\beta_G$ ) components respectively according to the following equations [9]

$$D_V = \frac{1}{\beta_C} \quad \text{and} \quad e = \frac{\beta_G}{2d^*} \quad (\text{in reciprocal units}). \quad (15)$$

For a log-normal distribution of spheres  $D_V$  is further given by

$$D_V = \frac{3}{4} \exp(3.5\sigma^2). \quad (16)$$

Thus the parameters of the log-normal distribution,  $D_0$  and  $\sigma$ , can be obtained from the simultaneous application of eqns. (12) and (16).

The single line analysis based on such a column-length distribution is performed in the following steps :

- (1) The initial slope of the experimental Fourier coefficients is used to obtain the value of average crystallite (coherent domain) size  $D_{\text{eff}}$ . The volume weighted column length is obtained from eq. (15).
- (2) The size Fourier coefficients are calculated according to eq. (11).
- (3) Finally the grain size distribution is calculated using eq. (12), (16) and (9) simultaneously.

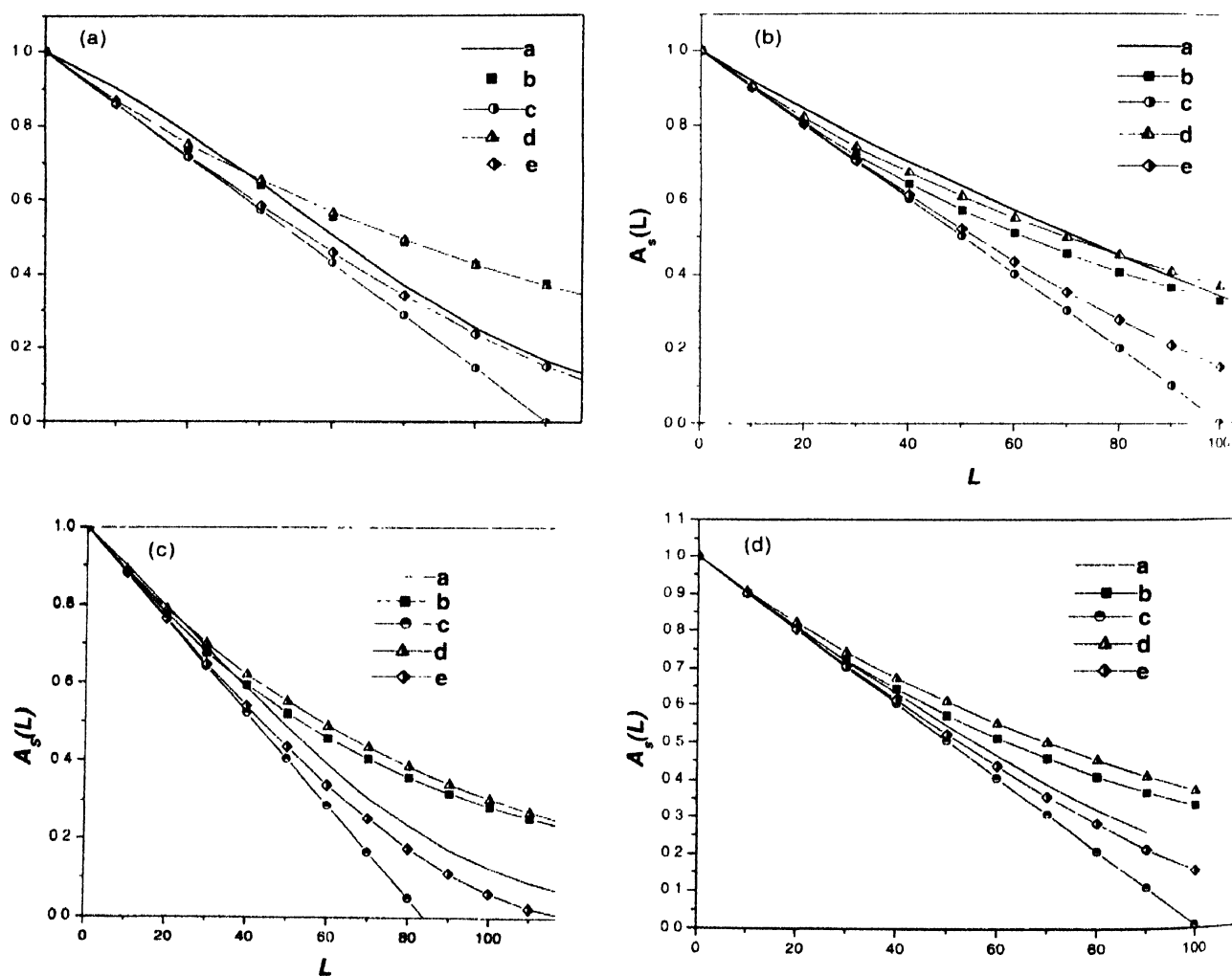
### 3. Application of the method

The method discussed in the earlier sections is compared with both the rigorous multiple line analysis (Warren-Averbach) and the single-line analysis of Nandi *et al* [3] and Mignot-Rondot [4]. As a first application of the present method samples with different relative widths of the column-length distribution function  $P_L(L)$  (calculated from the size-Fourier coefficients obtained from Warren-Averbach analysis) is chosen [10,11]. The samples named A and B are ball milled vanadium pentoxide powders milled for 150 and 200 hrs respectively. Ball milling is an isotropic deformation process and generally leads to a narrow distribution of sizes. Multiple line analysis of the samples

indicate that both size and strain broadening is present in appreciable amount [10]. Figure 1 shows the size-Fourier coefficients according to the models described earlier (eqns. (1), (4), (7) and (11) respectively). Figure 1 also shows the size-Fourier coefficients calculated according to more rigorous multiple order analysis of Warren and Averbach [10,11]. Though there is a large displacement disorder which may cause an underestimation of the values of the crystallite size obtained from the initial slope of total Fourier coefficients  $A_s(L)$ , it is shown that there is a good correlation between the size-Fourier coefficients of sample A (Figure 1a) calculated according to the single spherical crystallite model than an assumed Cauchy or Laue or log-normal (spheres) size distribution. Figure 1b, however, shows a better agreement for Cauchy size broadened profile. This is probably due to inhomogeneity of the grain shapes (a truly nanocrystalline state has not been achieved, see Chatterjee *et al* [11]). Thus it is clear from the above results that spherical crystallite model is a better approximation than Cauchy size distribution for moderately wide column-length distribution. This argument is further supported by the results

of analysis of sample B (Figures 1c, d). In this case the spherical crystallite model works well. The true size-Fourier coefficients always lie between the single sphere model and log-normal size distribution. Discrepancy at higher  $L$  values for the log-normal distribution generally arises due to the assumption in eq. (15) and neglecting. The Mignot-Rondot method also fails to give a unique solution. The grain size distribution is shown in Figure 2 for the sample B.

Thus it is clear from the above discussion that the choice of the size-Fourier coefficients depend on the relative widths of the column-length distribution function. But unfortunately in any single line analysis it is not possible to obtain information regarding the column-length distribution. So all choices are purely empirical. However, a suitable choice can be achieved by constructing the size-Fourier coefficients from different models, and comparing them with the experimental Fourier coefficients. A log-normal distribution gives a better flexibility since it can effectively model any column length distribution (from narrow to moderately wide). Further the estimate of strain Fourier



**Figure 1.** Variation of size-Fourier coefficient with coherence length for 150 hr milled  $V_2O_5$  along  $\langle 001 \rangle$  [Figure 1(a<sub>1</sub>)], 150 hr milled  $V_2O_5$  along  $\langle 200 \rangle$  [Figure 1(b<sub>1</sub>)], 200 hr milled  $V_2O_5$  along  $\langle 001 \rangle$  [Figure 1(c<sub>1</sub>)] and 200 hr milled  $V_2O_5$  along  $\langle 200 \rangle$  [Figure 1(d<sub>1</sub>)], obtained from (a) multiple order Warren and Averbach analysis, (b) considering log-normal distribution, (c) Laue function, (d) Cauchy function and (e) spherical model.

coefficient obtained from the deconvolution of total Fourier coefficient and simulated size Fourier coefficients, is more reliable when the present methodology is used.

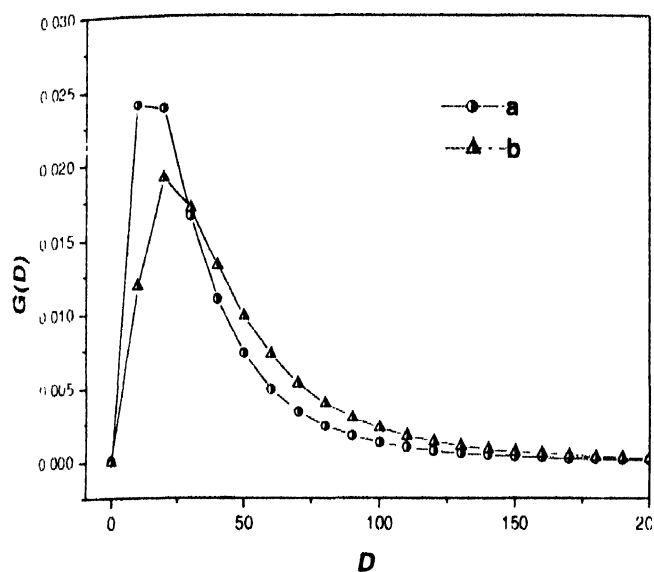


Figure 2. Grain size distribution for 200 h milled  $V_2O_5$  samples in the direction (a)  $\langle 001 \rangle$  and (b)  $\langle 200 \rangle$ .

#### 4. Conclusions

The present spherical crystallite model works well for narrow to moderate size distributions. In this sense the method is superior to the initial slope method which generally overestimates the disorder coefficients. Although the present method suffers from the fact that it underestimates the value of crystallite size in accordance with the initial slope method, the simulated size-

Fourier coefficients is less artificial as it has some physical basis. A log normal distribution of spheres would be more appropriate. The method, however, fails for predominant strain broadening. Thus in general the method is superior than the Mignot-Rondot method and gives better estimation of microstrain compared to the initial slope method for narrow to moderate size distribution. The method of combined use of single line Fourier space and single line real space can yield the size distribution, which can be favourably compared with TEM studies. The estimation of microstrain using a more physical model will be dealt in a separate communication.

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