Single-Peak Methods for Fourier Analysis of Peak Shapes

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Abstract

Several procedures for Fourier analysis of single diffraction peaks for microstrains and mosaic sizes are compared. A simple new method works well, especially when the size distribution is broad, and/or when the strains vary in an unusual manner.

Introduction

From Fourier analysis of the peak shapes of two or more orders of a reflection, the coherence length or mosaic size (M) and the mean-square reduced displacement disorder (Z^2) can be obtained (Warren, 1959). The latter quantity is frequently expressed as a microstrain defined as

$$\langle e^2 \rangle = \langle Z^2 \rangle / n^2.$$  (1)

Here n is the harmonic number of the Fourier coefficient and is related to the averaging distance normal to the diffracting planes, L = na, where a is the inverse of the period of the Fourier analysis. There is continuing interest in carrying out a similar evaluation of M and \langle Z^2 \rangle from a single diffraction peak, particularly in those cases when it is difficult to observe more than the first-order reflection (e.g. highly disperse heterogeneous catalysts, polymers). (The reader is warned, however, that the two-peak analysis should be employed whenever this is possible, to avoid unnecessary error.)

Peak breadths can also be used to evaluate size and disorder contributions to the line shape. It should be realized, however, that such methods give a volume-weighted size M_v, whereas Fourier analysis yields the surface or area-weighted size M (Guinier, 1963). These two measures of coherence length generally differ; in certain cases (e.g. dispersed catalyst particles), M can be compared directly to chemisorption results which also measure an area-weighted size. Furthermore, any peak breadth method evaluates a 'microstrain' averaged over all coherence lengths perpendicular to the diffracting planes, while Fourier analysis reveals the explicit dependence of \langle Z^2 \rangle or \langle e^2 \rangle on n. Finally, we note that experimental peak breadth must be corrected for instrumental effects. The most reliable way of performing the required correction is that of Stokes (1948), which gives the Fourier coefficients directly.
or
\[ C = g^2 \text{ (paracrystal)}. \] (7c)

The single-peak analysis of Mignot & Rondot (1975, 1977) combines (2), (3) and (7a) to obtain
\[ A_n \approx 1 - n\beta + n^2\gamma, \] (8a)
where
\[ \beta = a/M + 2\pi^2 m^2 C, \] (8b)
\[ \gamma = 2\pi^2 m^2 a C/M. \] (8c)

The observed coefficients are fitted to (8a), yielding estimates of \( M \) (mosaic size) and \( C \) (disorder). It should be clear that this procedure is model dependent, being subject to the correctness of (7a) to describe the disorder coefficients. A more critical problem is with (3) for the size coefficients; this expression is generally valid (in the presence of a distribution of mosaic sizes) only in the limit as \( n \to 0 \). Thus the Mignot–Rondot method must be applied to the low-harmonic coefficients. Unfortunately, it is precisely these coefficients which are most subject to baseline and truncation errors, leading to the well-known 'hook effect'. Rothman & Cohen (1969) have suggested a method for correction of the low-order coefficients which are assumed to follow the relation
\[ A_n \approx \exp[-\beta n]. \] (9)

Within the range of such a renormalization, any attempt to use (8a) for a single-peak analysis will give erroneous (imaginary) results, as can be seen by comparing (8a) to (9).

Zocchi (1980) has presented an equivalent single-peak analysis, which, in principle, works even in the presence of this hook effect. Here it is assumed that the disorder coefficients in (7) can be rewritten as
\[ A_n^0 = \exp[-2\pi^2 m^2 Cn]. \] (10)

This expression is correct for those particular cases where \( Z_n \) follows a Gaussian distribution function at any fixed \( n \). In general, the coincidence between (7a) and (10) is good for values of the argument less than \( 0.2 \). Zocchi suggests that one should analyze the first derivative of the Fourier coefficients, which yields
\[ \frac{dA_n}{dn} = -\beta + [2\gamma + (2\pi^2 m^2 C)^2]n. \] (11)

Truncation or hook-effect errors are demonstrated to cause the experimental derivative to oscillate in a damped fashion about the behavior predicted by (11). A straight line is drawn through the oscillating \( dA/dn \) values; the slope and intercept (at \( n = 0 \)) of this line permit evaluation of \( M \) and \( C \).

**Initial-slope method**

An extremely simple method of analyzing the Fourier coefficients of a single peak is applicable under the usually encountered conditions. We have pointed out that the linear expression for the size coefficients is generally valid only for small \( n \). In this same region the disorder coefficients are near unity, especially for the lowest-order peaks which are most commonly used for line-shape analysis. Thus we make the approximation
\[ \lim_{n \to 0} A_n \approx 1 - na/M. \] (12)

The initial slope of a plot of \( A_n \) versus \( n \) [using coefficients beyond any hook region or, preferably, coefficients renormalized according to (9)] is used to evaluate the average coherence length \( M \). This procedure is rigorously correct only for crystals sensibly free of displacement disorder (\( C \approx 0 \)), but is satisfactory when \( 2\pi^2 m^2 C \ll a/M \). One does not know a priori whether or not (12) is justified for a particular material. This can be determined only by comparison to results from multiple-peak analysis, as will be done in the following section. But it can be seen that (12) makes no assumption about the distribution of mosaic sizes or the particular functionality of the disorder coefficients.

Having determined \( M \), an estimate of the strains can be obtained by first assuming that the size coefficients are given by the exponential expression
\[ A_n^0 = \exp[-na/M]. \] (13)

Equation (13) is used, together with the experimental coefficient at \( na = M/2 \), to obtain the disorder coefficient \( A_{M/2}^0 \), and hence the disorder constant \( C \) in (7a):
\[ C = \left[ 1 - \frac{A_{M/2}^0}{\exp[-1/2]} \right] a/\pi^2 m^2 M. \] (14)

Before demonstrating the utility of this method, some general comments can be made. One expects the initial-slope method to underestimate \( M \) by some amount, as any decrease in \( A_n \) due to the disorder coefficients is ignored. A particular type of effective size distribution is postulated by using (13) for the size coefficients: this will, in principle, help the analysis when a distribution is present, though it will cause an overestimation of the disorder in the limit of no distribution of sizes. The choice of \( L = M/2 \) for evaluating the disorder term is arbitrary, but it ensures that one is working with coefficients of a reasonable magnitude (\( A_n \approx 0.5 \)). The final point is that this method is very simple and quick; an analysis can be accomplished manually in a matter of minutes, or it can be done with a small computer program.

**Results and discussion**

A comparison was made of two-peak and one-peak analyses on a series of platinum catalyst particles supported on silica gel. In these cases the size distribution was evaluated from the two-peak method and the mean size was measured independently by chemi-
Table 1. Comparison of methods for mosaic size (M) and root-mean square strains $\langle \varepsilon^2 \rangle_{1/2}$ for Pt/SiO$_2$ catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Two-peak (111-222)</th>
<th>Mignot–Rondot</th>
<th>Zocchi</th>
<th>Initial slope</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M$ (Å)</td>
<td>$\langle \varepsilon^2 \rangle_{1/2} \times 10^3$</td>
<td>$M$ (Å)</td>
<td>$\langle \varepsilon^2 \rangle_{1/2} \times 10^3$</td>
</tr>
<tr>
<td>$a$</td>
<td>93</td>
<td>3.1</td>
<td>133–252</td>
<td>3.2–3.6</td>
</tr>
<tr>
<td>$b$</td>
<td>51</td>
<td>2.9</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$c$</td>
<td>39</td>
<td>0</td>
<td>35–51</td>
<td>4.3–11.9</td>
</tr>
<tr>
<td>$d$</td>
<td>24</td>
<td>0</td>
<td>23–33</td>
<td>3.3–16.5</td>
</tr>
</tbody>
</table>

Table 2. Comparison of methods for mosaic sizes (M) and root-mean square strains $\langle \varepsilon^2 \rangle_{1/2}$ for cold-worked metals

<table>
<thead>
<tr>
<th>Method</th>
<th>Filed iron powder: 110 (a)</th>
<th>Filed brass powder: 110 (a)</th>
<th>Peened steel: 110 (b)</th>
<th>435 kbar shock loaded copper: 111 (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two peak</td>
<td>$M$ (Å)</td>
<td>$\langle \varepsilon^2 \rangle_{1/2} \times 10^3$</td>
<td>$M$ (Å)</td>
<td>$\langle \varepsilon^2 \rangle_{1/2} \times 10^3$</td>
</tr>
<tr>
<td>Mignot–Rondot</td>
<td>279</td>
<td>1.92</td>
<td>280</td>
<td>1.55</td>
</tr>
<tr>
<td>Zocchi</td>
<td>142</td>
<td>3.38</td>
<td>179</td>
<td>2.98</td>
</tr>
<tr>
<td>Initial slope</td>
<td>169</td>
<td>2.64</td>
<td>184</td>
<td>3.01</td>
</tr>
<tr>
<td>Miguez–Zocchi</td>
<td>500</td>
<td>1.98</td>
<td>539</td>
<td>2.04</td>
</tr>
</tbody>
</table>

References: (a) Rothman (1969); (b) Evans (1977); (c) DeAngelis (1965).

sorption (Sashital, Cohen, Burwell & Butt, 1977). For these specimens, the mosaic or particle size ranges from near zero to twice the mean value, $2M$. Table 1 summarizes the results of the two-peak analyses and the single-peak methods described above. The Mignot–Rondot method fails in these cases to give a unique solution; the values for mosaic size and disorder, here expressed as microstrains evaluated at $n\lambda = 50$ Å, depend on the interval over which the analysis is performed. A detailed investigation of the source of this problem has not been made, but we note that the average coherence length is smaller and the relative width of the size distribution larger for the platinum particles than for cold-worked metals, which gave good results with that method (Table 2). Thus it appears that the Mignot–Rondot analysis does not give reliable parameters when mosaic size is the dominant term in the Fourier coefficients.

The Zocchi analysis of unrenormalized coefficients (see Table 1) gives results which severely underestimate mosaic size, while the calculated microstrain is either too low (catalyst $a$) or too high (catalysts $c$, $d$).

The right-hand columns in Table 1 present the sizes and microstrains obtained by the initial-slope method. For comparison of microstrains, we adopted a procedure slightly different from that embodied in (14). The disorder coefficient estimated at $L = M/2$ is used to calculate $\langle \varepsilon^2 \rangle_{M/2}$ according to

$$A_{M/2}^0 = 1 - \pi^2 m^2 \langle \varepsilon^2 \rangle_{M/2} M^2 / 2d_0^2.$$

(15)

Then (5) is used to calculate $\langle \varepsilon^2 \rangle_{M/2}^{1/2}$, the r.m.s. microstrain averaged over $L = 50$ Å. This latter step assumes that the strains obey a hyperbolic law which has been well established in metals (Rothman & Cohen, 1969, 1971). The significant point is that the initial-slope method gives results which are clearly more accurate than those from the more elaborate single-peak analyses. One notices that the particle size $M$ is underestimated, but not more than 16%, an error which is not unexpected and which is much smaller than those with the other methods. The estimates of microstrain are quite good, presumably because the exponential form of the size coefficient (equation 13) approximates the effect of the size distributions, permitting more correct evaluation of $A_{M/2}^0$.

Since the relative success of the initial-slope method has been demonstrated with samples having broad distributions of coherence lengths, it is reasonable to ask about applicability when size distributions are more moderate. A similar comparison of Fourier analyses of several cold-worked metals is shown in Table 2. Here the agreement between the two-peak analysis and the single-peak method of Mignot & Rondot is good. Recall that the latter method requires a narrow distribution of mosaic sizes for (3) to be correct over an appreciable range of $n$. This distribution in cold-worked metals, i.e. the distribution of distances between dislocations or cell walls, is in fact narrow (Mikkola & Cohen, 1966; Brillhart, DeAngelis, Preban, Cohen & Gordon, 1967). The initial-slope method also gives satisfactory results in these cases, as can be seen in Table 2. Again we note a moderate underestimation of size, and the microstrains are generally larger than the correct (two-peak) values, a consequence of the absence of a size distribution discussed above. Nevertheless, the agreement is acceptable, even in this worst-case test of the initial-slope method. The mean error of the initial-slope entries in Table 2 (compared to the two-peak results) is 14% in $M$ and 13% in $\langle \varepsilon^2 \rangle_{M/2}^{1/2}$; the Mignot–Rondot method
has errors of 11% in $M$ and 12% in $\langle \varepsilon^2 \rangle_{50}^{1/2}$.

One additional test of the Mignot–Rondot procedure was done with the 111 peak of a paladium catalyst supported on silica. The Mignot–Rondot method was used to evaluate both $M$ and $C$; these quantities were in turn used to calculate an 'ideal' set of Fourier cosine coefficients with (3), (7a) and (2). From inspection it was clear that these reconstructed cosine coefficients were different from the experimental $A_n$ used to obtain the size and disorder parameters. To assess the effect of this discrepancy, the reconstructed cosine coefficients were combined with the small size coefficients $B_n$ of the experimental peak to resynthesize the profile. This synthesized profile was analysed completely by Mignot & Rondot's procedure, with results that the mosaic size from the second analysis were 41% larger than the original (100 vs 71 Å), and the r.m.s. strain was 27% larger (0.0070 vs 0.0055). This again illustrates the difficulties encountered in applying this method when particle size is small and/or the size distribution is appreciable. For comparison, the initial-slope method gives $M = 78$ Å and $\langle \varepsilon^2 \rangle_{50}^{1/2} = 0.0028$.

Still another potential source of failure of previous single-peak methods is the assumption that disorder is described by (7a). In polymers, for instance, it is sometimes observed that the factor $C$ in (7) increases with $n$ (Crist & Cohen, 1979). If this is the case, clearly the Mignot–Rondot and Zocchi methods are inapplicable. We show in Table 3 the results of Fourier analysis of the 110/220 reflections on slowly cooled linear polyethylene. Two-peak and one-peak results are presented; the Mignot–Rondot analysis gave imaginary results, and is therefore omitted. The disorder is expressed as $(Z^2)$ evaluated at $na = 100$ Å, since there is no constant $C$ for evaluating microstrains or paracrystallinity. Here again the simple initial-slope method gives excellent agreement with the two-peak results; this method is again superior to the Zocchi technique.

### Conclusions

Fourier analysis of single peaks can give erroneous results when underlying assumptions of uniform particle size and specific disorder behavior are not realized. The simple initial-slope method proposed here is less model dependent. Generally, one expects the initial-slope method to give reliable but somewhat small measures of $M$. This is because strain effects are ignored entirely at small $n$. When a broad distribution of sizes is present or when the strains behave in an unusual manner, the initial-slope results are more accurate than those from the Mignot–Rondot or Zocchi analyses. The success of the present technique lies in the use of the exponential approximation for the size coefficient $A_n^2$; this artificially creates the effect of a distribution of particle sizes, leading to more correct estimates of microstrain. For polymers or other materials in which the displacement disorder increases more rapidly than predicted by (7), the present analysis, by effectively letting the size coefficients decrease more slowly, causes the disorder coefficients to decrease more rapidly, again approximating the correct behavior of the strain. For those cases when the size distribution is narrow and the disorder coefficients follow (7), we have demonstrated that the initial-slope method still gives good values of coherence length, though the strains can be overestimated by ~20%.

The applicability of any single-peak analysis cannot be determined without knowledge of the correctness of any assumptions involved. The initial-slope method should give good estimates of mosaic sizes, since $\langle Z^2 \rangle$ approaches zero as $n$ approaches zero. All single-peak analyses, including the one presented here, will fail in the (unlikely) case of very large mosaic sizes and relatively large displacement disorder.

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### References


### Table 3. Comparison of methods for mosaic size $M$ and displacement disorder $\langle Z^2 \rangle$ for linear polyethylene

<table>
<thead>
<tr>
<th>Method</th>
<th>$M$ (Å)</th>
<th>$\langle Z^2 \rangle_{100} \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two peak (110, 220)</td>
<td>330</td>
<td>9.0</td>
</tr>
<tr>
<td>Zocchi (110)</td>
<td>225–270</td>
<td>7.1–6.0</td>
</tr>
<tr>
<td>Initial slope $M$ (110)</td>
<td>298</td>
<td>9.2</td>
</tr>
</tbody>
</table>