The Influence of the Grain Shape on X-Ray Line Broadening

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The analysis of X-ray reflections allows for the determination of the grain dimension in the direction of the bisector of the incident and scattered radiation. It is shown that correct results will be obtained only as long as the grain dimensions perpendicular to this direction are sufficiently large. The possible errors are estimated. The conditions for the determination of the shape anisotropy are discussed.

1. Introduction

X-ray diffraction patterns contain information about the spatial periodicity and the type of the scattering atoms, as well as about any deviation from the ideal periodicity. The methods applied to deduce and to specify this information increase in expense and subtlety as the number of details in question is increased. Hence, for the intensity of the scattered radiation an expression excluding or neglecting some influences a priori, is very often deduced with respect to a special diffraction problem. Simplicity, however, is mostly paid for by a lack of knowledge about the range of validity, and sometimes a simple model is easily overstressed. It is, therefore, more useful to perform the simplification under control, i.e. to use an intensity expression of high generality and to neglect some specific influences in this formula a posteriori. Moreover, such a strategy is well fitted to the estimation of the errors caused by specific approximations. In a previous paper [1] a general expression for the intensity of X-radiation scattered by an assembly of randomly oriented crystals has been established. This expression describes the diffraction profile over the whole range of diffraction angles and includes the contribution of particle size, varations of type and dimensions of the lattice, anisotropy in crystal orientation and shape, absorption of the radiation within the sample as well as instrumental effects. Its most general form is

$$I(K_0) \propto \frac{B}{\cos\vartheta \sin\vartheta} \int_0^1 \mathrm{d}c \, \frac{A\,H}{V} \int_0^\infty \mathrm{d}k \, L \iiint_{-\infty}^{\infty} \mathrm{d}x_j \, \frac{1}{K^2} \cdot R\,W\,G\,f^2\,P \prod_{j=1}^{3} I_{M_j}. \tag{1}$$

- I pulse rate per atom measured under fixed diffraction angle ϑ,
- B constant containing the slit dimensions of the diffractometer,
- c atomic concentration of the coherently scattering particle,
- A $A(c, \vartheta)$ absorption factor,
- H $H(c)$ concentration spectrum,
- $\boldsymbol{a}_j(c)$ fundamental translations of the crystal with concentration c,
- V $V(c) = \boldsymbol{a}_1(c) \cdot [\boldsymbol{a}_2(c) \times \boldsymbol{a}_3(c)]$ volume of the unit cell,
- L $L(k)$ wavelength spectrum of the radiation,
- k $2\pi/\lambda$ wave number,
- $\boldsymbol{a}_j$ base vectors of a reference unit cell,
- x_j $h_j a_j(c)/a_j$
- $\boldsymbol{b}_j$ reciprocal base vectors of the reference unit cell
- h_j coordinate in the reciprocal base $\{\boldsymbol{b}_j\}$,
- $K = 2\pi \Big/ \left| \sum_{j=1}^{3} h_j \boldsymbol{b}_j \right|$,
- $K_0 = 2k \sin\vartheta$,
- R $R([K - K_0]/k \cos\vartheta)$ instrumental function,
- W $W(c, h_j)$ texture function,
- f $f(c, K)$ atomic scattering factor,

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P $P(K)$ polarisation factor,

$I_{M_j}=\sum_{l_j=1}^{M_j}(\frac{1}{2}-l_j/M_j)\exp 2\pi i h_j l_j a_j(c)/a_j$ particle size function.

The usual correspondence between particular influences and single terms in the intensity formula has not been lost. However, their connection by a convolution, approximately valid for a small range of angles, had to be replaced by a more general integral equation of the Fredholm type. Although (1) is not very handy from the practical aspect, its advantage is quite obvious: Suitable formulations, which deal with special experimental conditions (e.g. negligible instrumental line broadening, large crystallites etc.), can be deduced from (1) by simply replacing the term to be neglected by the Dirac δ-function. Here we wish to demonstrate the influence of the shape of the coherently scattering particles on the diffraction profile. As is known, small particles give rise to a broadening of the Bragg-reflections. The commonly performed analysis of the line breadth [2, 3] is based on an approximation where the scatterer is assumed to be an assembly of independently diffracting columns of elementary cells aligned in direction of the bisector of the incident and scattered beam. This approximation is valid only as long as the real scattering unit, i.e. the grain, does not consist of only a few such columns. In many cases this requirement is fulfilled. However, if samples of extremely needle or disc shaped grains are examined one has to expect incorrect results from line breadth analysis. An estimation of the possible errors will be given in the following.

2. Simplifications

We consider a polyrcrystalline sample with grains consisting of uniform elementary cells. The instrumental function $R(x)$ should cause a negligible line broadening, compared with the diffraction line breadth given by the size effect. Like-wise the spectral distribution of the radiation is neglected: These assumptions are accounted for in (1) by

$$R(x)\propto\delta(x),\quad L(k)\propto\delta(k-k_0),$$
$$H(c)=\delta(c-c_0),$$

yielding

$$I(k_0)=\frac{BA(c_0)}{\cos\vartheta\sin\vartheta\,V(c_0)}\iiint_{-\infty}^{\infty}\mathrm{d}x_j\,\frac{1}{K^2}\cdot\delta(K-K_0/k\cos\vartheta)\,WGPf^2\prod_{j=1}^{3}I_{M_j}. \tag{2}$$

We confine the further treatment to a reflection $(0, 0, l)$ in a cubic lattice. The grains are considered as orthogonal prisms, each of dimensions $(M_1\boldsymbol{a}_1, M_2\boldsymbol{a}_2, M_3\boldsymbol{a}_3)$.

The range of integration may be limited to the small regions around the lattice points in the reciprocal space where the functions I_{M_j} differ significantly from zero. In a polycrystalline sample the reflection of type $(0, 0, l)$ is given by the contribution of the 6 lattice points corresponding to all permutations p_n of the triples $(0, 0, \pm l)$.

Hence the integral may be written as a sum of integrals over six regions:

$$\sum_{n=1}^{6}\iiint_{\Delta V_n}\mathrm{d}x_j\,\frac{1}{K^2}\,\delta\left(\frac{2\pi|\boldsymbol{x}|/a(c_0)-2k\sin\vartheta}{k\cos\vartheta}\right)\cdot WGPf^2\prod_{j=1}^{3}I_{M_j}(x_j), \tag{3}$$

where $\boldsymbol{x}$ is the vector (x_1, x_2, x_3).

If the regions ΔV_n are not too large, i.e. the coherently scattering particles are not too small, then the sphere $|\boldsymbol{x}|=\text{const}$ may be replaced by the tangential plane $x_i=\text{const}$ [2] in the respective lattice point. The index $i(=1, 2, 3)$ depends upon the lattice point under consideration. Each of the six integrals is split into

$$W(p(0,0,\pm l))GPf^2\int\mathrm{d}x_i\,\delta(\xi_i)\,I_{M_j}(x_i)/K^2\cdot\iint_{i\neq j\neq k}\mathrm{d}x_j\,\mathrm{d}x_k\,I_{M_j}(x_j)\,I_{M_k}(x_k)$$
$$\xi i=\frac{2\pi x_i/a(c_0)-2k_0\sin\vartheta}{k_0\cos\vartheta}. \tag{4}$$

We wish to emphasise that the texture function W describes the probability of the orientation of only one special type of lattice vector, e.g. $[\pm l, 0, 0]$. The equivalent lattice vectors $[0, \pm l, 0]$, $[0, 0, \pm l]$ are not considered, since their lattice planes are not in Bragg position simultaneously. Since W does not vary strongly within ΔV_n, we replaced it by its value $W(p_n(0, 0, \pm l)$ at the lattice point. The value of the latter integral yields 1, and since

$W(p_n(0, 0, +l) = W(p_n(0, 0, -l)$ we finally obtain for the measured intensity

$$I(\vartheta) = \frac{\tilde{B}\, A(c_0)\, G\, P\, f^2}{\sin^3 \vartheta} \cdot [W(l,0,0,)\, I_{M_1}(\xi) + W(0,l,0)\, I_{M_2}(\xi) + W(0,0,l)\, I_{M_3}(\xi)],$$
$$\xi = a(c_0)\, k_0 \sin \vartheta/\pi . \qquad (5)$$

($\tilde{B}$ is a constant including only terms independent of ϑ). — This is a linear combination of three unknown functions I_{M_1}, I_{M_2}, I_{M_3}. The pulse rate measurement at six distinct angles would at least in principle enable one to determine the unknown M_1, M_2, M_3 and the three W coefficients.

However, practice suffers from obstacles arising from measurement and calculation. Hence, it is not possible to obtain all three grain dimensions from one measured profile strictly. Only if $M_1 = M_2 = M_3 = M$, i.e. for cube shaped grains, can M be found. Since the abundance $W(p_n(0, 0, \pm l)$ of orientation weights the contribution of the size functions, we may find M_i in another special case, too, from the profile obtained in three orientations perpendicular to each other: Namely, if the sample is extremely textured (Fig. 1) so that $W(p_n(0, 0, \pm l)) = 0$ for two of the three permutations. Fortunately, significant deviations from the cube shape very often coincide with pronounced textures, (needle- or plate shaped grains are generally present in heavily cold worked metals together with a deformation texture). In such a case we obtain for instance I_{M_1} if the sample is oriented with $\boldsymbol{a}_1$ parallel to $(\boldsymbol{k}_0 - \boldsymbol{k})$.

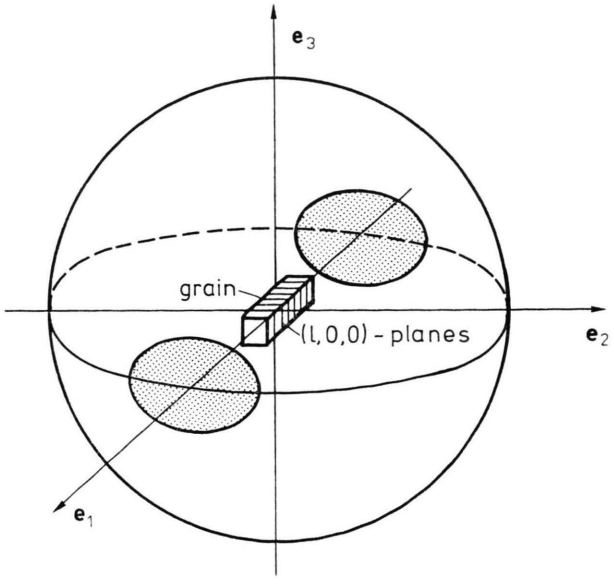

Fig. 1. Texture function W for a pronounced fibre texture. The abundance of the lattice planes $(l, 0, 0)$ disappears outside the dotted area. ($(0, l, 0)$-, $(0, 0, l)$-planes are not considered since they are out of Bragg position when $(l, 0, 0)$-planes are reflecting).

The integer M can be evaluated by a Fourier expansion of $W\, I_{M_1}$. The index of the harmonic where the series is truncated equals M_1. The direction $\boldsymbol{e}_1$ within the particle bisects the angle between the incoming and scattered beams. i.e. only the particle dimensions perpendicular to the lattice plane in glancing position is evaluated by the Fourier expansion.

M_2 and M_3 do not influence $I(\vartheta)$ in this well known approximation, which was introduced by setting $|\boldsymbol{x}| \doteq x_1$. This holds as long as I_{M_2} and I_{M_3} vanish outside a small region around $(l, 0, 0)$, speaking in terms of the reciprocal lattice. That is, M_2 and M_3 must not be too small or the grain must not consist of columns showing a diameter of only a few atomic spacings. In this approach the measured intensity I is found to be approximately proportional to I_{M_1}, and the calculated value M_1 differs from the actual one.

3. Estimation of Errors

The error in M_1 may be estimated by comparing the breadth of the profiles I and I_{M_1}. The breadth of the profile $I_{M_1}(x)$, given by the distance between the first zeros on both sides of the main maximum, is $\Delta x_1 = 2/M_1$. Exactly this breadth, expressed in ϑ, would be detected if only one grain were to contribute to the intensity. Slight tilting of the grain with respect to the diffractometer would shift the maximum of the profile without significantly altering the line breadth (Figure 2). Since in a textured specimen many grains, slightly tilted one against the other, contribute to the diffraction profile, its breadth will be enlarged by the value of the maximum line shift. From geometrical considerations in reciprocal space we obtain an excess in line breadth of the $(l, 0, 0)$ Bragg reflection:

$$\delta = \frac{1}{2\, l\, M_s^2}, \qquad (6)$$

where M_s is the smallest number of elementary cells perpendicular to $\boldsymbol{e}_1$. This enlargement approxi-

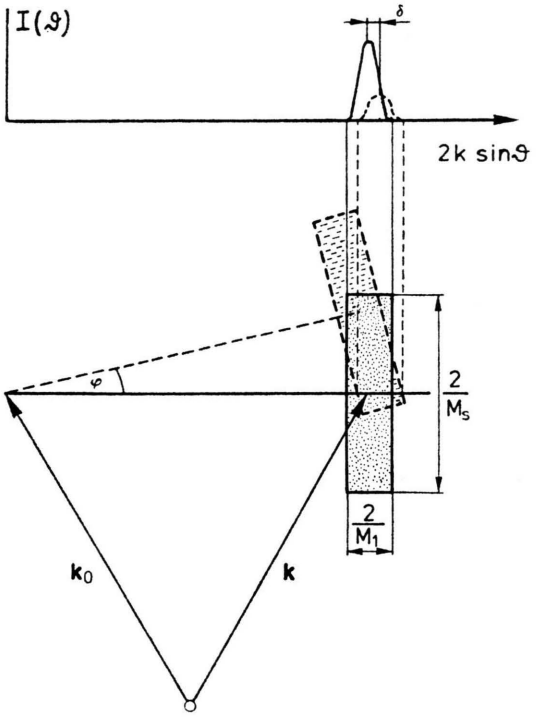

Fig. 2. Angular shift of the reflection profile caused by tilted grains. The displacement δ increases with tilt φ and reciprocal grain diameter $(1/M_s \cdot a)$. The reciprocal lattice point of a small crystall is broadened to an orthogonal prism of the dimensions $2/M_1$, as indicated by the dotted region. The dashed region corresponds to a crystal slightly twisted out of the Bragg-position.

mately equals $-2\Delta M_1/M_1^2$. Hence the relative error in M_1 induced by the approximation $|x| \doteq x_1$ is

$$\frac{\Delta M_1}{M_1} \doteq -\frac{M_1}{4 l M_s^2}. \tag{7}$$

We finally wish to demonstrate this influence by two examples:

For $M = 100$, $M_3 = 10$ (column—shaped grains) and $l = 1$ the relative error is about 25%.

However, such extremely anisotropic grains appear to be rare. In most applications the ratio of grain diameters is very much smaller than $M_1 : M_3 = 10$, hence the error induced is about some percent.

For small cube shaped grains (e.g. $M_1 = M_3 = 10$) the error is $\doteq 0.5\%$, and therefore may be neglected.

[1] P. Schattschneider und A. Wagendristel, Z. Naturforsch. **33a**, 693 (1978).

[2] B. E. Warren and B. L. Averbach, J. Appl. Phys. **21**, 595 (1950).

[3] W. H. Hall, Proc. Phys. Soc. London A 62, 741 (1949).