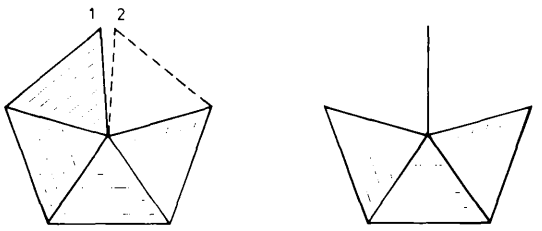

(*a*) (*b*)

Fig. 7. (*a*) The two possibilities for packing four face-sharing tetrahedra. (*b*) Nature's solution to the problem.

triangles. This could be the reason why the cluster is limited to 26 atoms; further capping gives more and more distorted tetrahedra.

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Diffraction-Broadening Studies of Textured Materials

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Abstract

Reciprocal-space calculations are carried out with the aim of finding out where on an electron or X-ray diffraction picture one has to measure diffraction line broadening, so as to obtain reliable information about the apparent domain size (DS) and the microstrain (MS) in a textured material. It has been shown that in both cases there are geometrical limitations. They are greater for X-ray diffraction broadening studies, and if the texture axis is arbitrarily inclined, a readjustment of the texture axis to positions parallel to the X-ray beam, or parallel to the camera axis, is required. Deviation of the texture axis from an ideal orientation increases the number of diffraction spots requiring correct correlation of their diffraction broadening with the DS and MS of the material.

Introduction

Measurements of coherent domain size (DS) and microstrain (MS) of randomly oriented and of textured polycristalline materials are expected to possess specific features, since there are differences between their corresponding reciprocal lattices. There are reliable methods for calculating DS and MS, as summarized, for example, by Lipson & Steeple (1970), but the question of where to measure diffraction line broadening in the case of textured materials remains unclear.

Kagan (1964) has pointed out some of the existing uncertainties, but his calculations are in real space and cannot be easily generalized.

A treatment in reciprocal space is carried out in the present paper, with the aim of finding out where on an electron or X-ray diffraction picture one can obtain reliable information about DS and MS of a textured material in the cases of ideal and real textures. The accent of the calculations is on electron diffraction, but the results are extended for X-ray diffraction broadening studies as well.

Essentials

The reciprocal lattice of a strained, fine grain texture is obtained by rotating around the texture axis the reciprocal lattice of a strained small single-crystal. As a first approximation, the reciprocal volume around each *hkl* lattice point is assumed to be a sphere with radius *r*.

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The thickness of the obtained toroid is therefore $2r$. The measured diffraction broadening is to be equal to $2r$ if the real values of DS and MS of the textured material are to be evaluated.

Electron diffraction

A toroid from the reciprocal lattice of a texture is defined in the $OXYZ$ coordinate system and is presented in Fig. 1. The texture axis $[uvw]$ (OZ') is in the OXZ plane and makes an angle φ with OXY. Rotational symmetry of OZ' around OZ is assumed for the case of transmission electron diffraction, and around OX for the case of reflection electron diffraction. The repeat distance along OZ' is l (OO'). An enlarged picture of the toroid is presented in Fig. 2. Here m $(O'P)$, is the radius of rotation of the toroid, and $2r$ is its thickness. If there is no MS in the film, $r = 1/t$, where t is equal to DS of the material.

In electron diffraction studies, the electron beam is directed along the z axis, and the Ewald sphere is defined as

$$S: x^2 + y^2 + z^2 - 2Rz = 0. \tag{1}$$

Here $R = 1/\lambda$, where λ is the electron wavelength. λ is of the order of 10^{-2} Å, and an accepted approximation is $S: Z = 0$. The parametric equations of the toroid are

$$S_1: \begin{cases} x = (r\cos\alpha + m)\cos\beta\sin\varphi + (r\sin\alpha + l)\cos\varphi, \\ y = (r\cos\alpha + m)\sin\beta, \\ z = -(r\cos\alpha + m)\cos\beta\cos\varphi \\ \quad + (r\sin\alpha + l)\sin\varphi, \end{cases} \tag{2}$$

where $0 \le \alpha \le 2\pi$ and $0 \le \beta \le 2\pi$, see Fig. 2. The general solution $S \cap S_1$ is not required since diffraction broadening measurements are usually carried out for diffraction lines where the approximation $S: Z = 0$ is justified. $S_1 \cap Z = 0$ gives

$$C_1: \begin{cases} x = (r\cos\alpha + m)\cos\beta/\sin\varphi, \\ y = (r\cos\alpha + m)\sin\beta, \end{cases} \tag{3}$$

which can be derived from equations (2) by substituting $z = 0$. C_1 is the curve $P_1P_3P_2P_4$ and the symmetrical

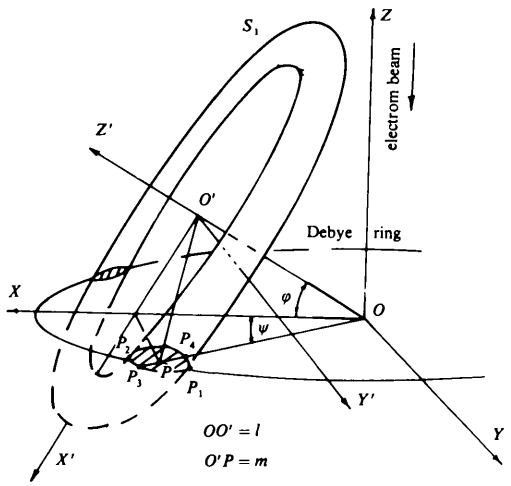

Fig. 1. A toroid from the reciprocal lattice of an ideal texture. The texture axis $[uvw]$ (OZ') is at an angle φ to OXY. The repeat distance along OZ' is l (OO'). The specimen under investigation is at O, and the electron beam is directed along the z axis (OZ).

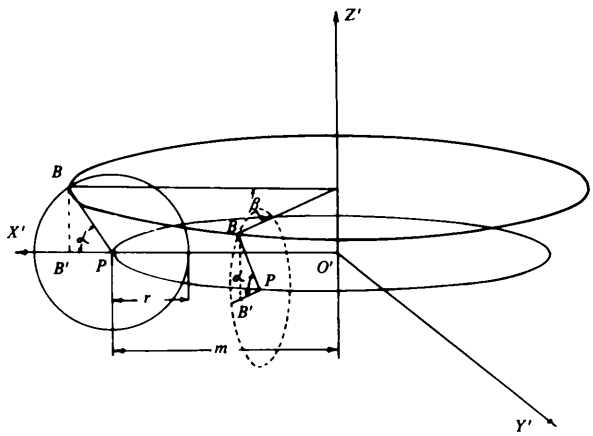

Fig. 2. An enlarged picture of the toroid of Fig. 1. It is obtained by rotating a sphere of radius r around $O'Z'$. The radius of rotation is m. r is related to DS and MS of the material. For any point B on the toroid, α is the angle between PB and $O'X'Y'$. It is measured in a plane perpendicular to $O'X'Y'$ at an angle β from $O'X'Z'$.

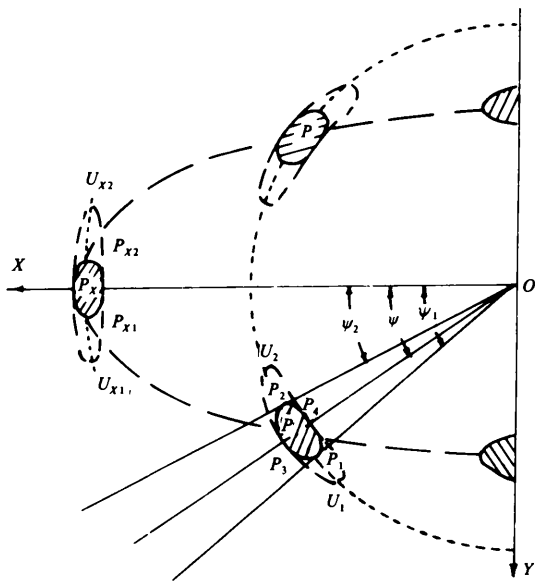

Fig. 3. Sketch of an electron diffraction picture obtained by intersecting the Ewald sphere $(Z = 0)$ with a system of toroids with radii of rotation m and with repeat distance, l, along OZ'. The texture axis is at an angle φ to OXY. The indexing of the texture can be carried out according to Vainshtein (1956). The theoretical length of the diffraction spot $P_1P_3P_2P_4$ measured along the respective Debye circle is P_1P_2. The length of the same spot for a real $\varphi \pm \Delta\varphi$ texture is U_1U_2. For spots on OX, the respective lengths are designated as $P_{x1}P_{x2}$ and $U_{x1}U_{x2}$.

curve in Figs. 1 and 3. The central circle of the toroid C_2,

$$C_2: \begin{cases} x = m\cos\beta\sin\varphi + l\cos\varphi, \\ y = m\sin\beta, \\ z = -m\cos\beta\cos\varphi + l\sin\varphi, \end{cases} \quad (4)$$

is obtained by setting r equal to zero in equations (2). The condition $C_2 \cap Z = 0$ yields two solutions for points P, Figs. 1, 3. If $l = 0$, these points are on the y axis. The limiting condition for C_2 to have a common point with $Z = 0$ is

$$m = l\tan\varphi. \quad (5)$$

In that case $C_2 \cap Z = 0$ has only one solution, and the corresponding point P is lying on the x axis.

A line is drawn between O and P, Figs. 1, 3. It intersects the curve C_1 at points P_3 and P_4. If P_3P_4, measured along OP (Fig. 3), is equal to $2r$ of the respective toroid, the line width of the particular diffraction spot is a measure of DS and MS of the material. In general P_3P_4 is a complicated function of α, β and φ:

$$P_3P_4 = 2r[(\cos\alpha\sin\beta)^2 + (\cos\alpha\cos\beta\sin\varphi + \sin\alpha\cos\varphi)^2]^{1/2} \quad (6)$$

Equation (6) is obtained from equations (3). Points P_3 and P_4 have one and the same values of β and φ but the values of α differ by π.

Along OY (transmission electron diffraction) P_3P_4 is always $2r$ since $\beta = \pi/2$ and $\alpha = 0$. Along OX (reflection electron diffraction), the value of β is zero. P_3P_4 will be equal to $2r$ if the central circle of a particular toroid has a common point with $Z = 0$ – point P_x in Fig. 3 – which is on the x axis. For an ideal texture with a particular inclination of the texture axis OZ' to OXY (φ in Fig. 1), this condition is fulfilled only for a toroid with radius m – equation (5). The possibility for real textures to be studied by reflection electron diffraction comes from the fact that textures are never ideal. One has to show that in the angular interval $\varphi \pm \Delta\varphi$ of a real texture, there is at least one toroid at an angle φ^* fulfilling equation (5). In the case where both DS and MS of the sample are to be measured (Peneva, Babulska & Rudarska, 1977), this condition must be checked for several diffraction spots lying on the OX axis. Calculations of DS and MS from diffraction broadening in all other directions can be used for relative measurements, but not for absolute measurements (Peneva, Rudarska & Babulska, 1977).

The deviation of the texture axis by $\pm\Delta\varphi$ from its mean value φ can be calculated by comparing the theoretical length of a diffraction spot of an ideal texture, measured along a Debye circle, the arc P_1P_2, with the experimentally observed arc U_1U_2, as in Fig. 3. Since measurements are carried out along OX, the notation $P_x, P_{x1}, P_{x2}, U_{x1}, U_{x2}$ will be used (Fig. 3). Points P_{x1} and P_{x2} have their z coordinates zero, and β may be derived from equation (2) as

$$\cos\beta = (r\sin\alpha + l)\sin\varphi/(r\cos\alpha + m)\cos\varphi. \quad (7)$$

The x and y coordinates can be calculated from equations (3) and (7), with the additional relations

$$x^2 + y^2 = d^2, \quad \text{where } d = l/\cos\varphi \quad (8)$$

and d is the radius of the respective Debye ring. Sin α of P_{x1} and P_{x2} are given by

$$\sin\alpha(P_{x1}, P_{x2}) = Al \pm m(l^2 + m^2 - A^2)^{1/2}/(l^2 + m^2), \quad (9)$$

where

$$A = (d^2 - r^2 - m^2 - l^2)/2r.$$

The x and y coordinates of the final points U_{x1}, U_{x2} of a real texture can be measured and the calculations can be performed in a reverse way. The calculated φ values corresponding to each point U_{x1} and U_{x2} define two ideal textures which enclose series of ideal textures in the angular interval $\varphi \pm \Delta\varphi$. The corresponding interval of Debye ring radii, where DS and MS must be measured, is calculated from $d = l/\cos\varphi$. For these calculations one can use an approximate value of r calculated from the half width of any diffraction textured spot along OX.

X-ray diffraction

The X-ray beam is directed along the x axis and the Ewald sphere S' is defined as

$$S': x^2 + y^2 + z^2 - 2Rx = 0; \qquad R = 1\ \text{Å}^{-1}. \quad (10)$$

The solution $S' \cap S_1$ is

$$r^2 + m^2 + l^2 + 2r(m\cos\alpha + l\sin\alpha) - 2(r\cos\alpha + m)\cos\beta\sin\varphi - 2(r\sin\alpha + l)\cos\varphi = 0. \quad (11)$$

Since measurements of diffraction broadening are carried out in the OXY plane, S' is modified to

$$C': x^2 + y^2 - 2x = 0. \quad (12)$$

$C' \cap S_1$, combined with equation (7) gives

$$(r\sin\alpha + l)^2\cos\varphi - 2(r\sin\alpha + l) + (r\cos\alpha + m)^2\cos\varphi = 0. \quad (13)$$

The coordinates of the points of intersection of C' with S_1, Q_1 and Q_2, see Fig. 4, can be calculated from equations (2), (7) and (13) if the texture is ideal and φ is known. For an arbitrarily inclined texture axis OZ', as shown in the figure, the coordinates of Q_1 and Q_2 depend on α, β and φ in a complicated way, and do not give directly the thickness of the toroid $2r$.

Interesting cases in practice concern textures with $\varphi = 0$ (Fig. 5), and $\varphi = \pi/2$ (Fig. 6).

If $\varphi = 0$, α and β for points Q_1 and Q_2 become $\pi/2$ and $3\pi/2$, respectively, and equation (13) reduces to the equation of a circle

$$(l \pm r)^2 + m^2 - 2(l \pm r) = 0. \qquad (14)$$

For an ideal texture Q_1Q_2 can be considered as a line and is equal to $2r$, if the repeat distance l and the radius of rotation m are unity. For other toroids, with different repeat distances l along OZ', and with different radii of rotation, m, a deviation of the texture axis by $\pm\Delta\varphi$ from $\varphi = 0$ is required so that their central circles C_2 (equation 4) cross the equatorial Ewald circle C' (equation 12). This requires indexing the diffraction spots due to the texture in a way resembling the methods of electron diffraction (see for example Vainshtein, 1956).

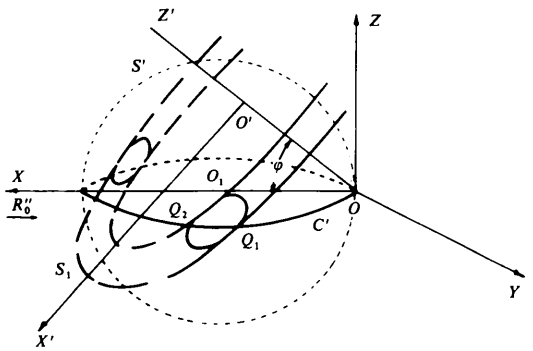

Fig. 4. Intersection of an arbitrarily inclined toroid S_1 with the Ewald sphere S' for the geometry of X-ray diffraction. Q_1 and Q_2 are the points of intersection of the equatorial Ewald circle C' with the toroid S_1.

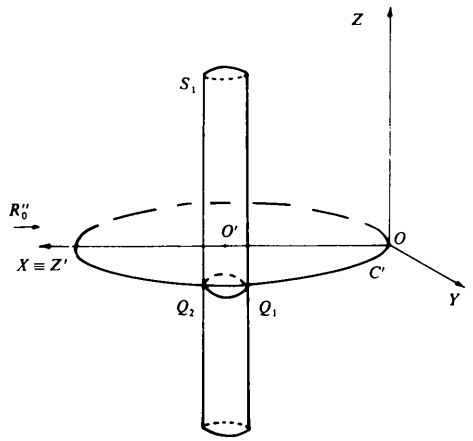

Fig. 5. Intersection of the equatorial circle of the Ewald sphere C' with a toroid from a $\varphi = 0$ texture. For an ideal texture the arc Q_1Q_2 is equal to $2r$ of the toroid, if l and m are equal to 1 Å^{-1}. A deviation of the texture axis of $\pm\Delta\varphi$ is required if Q_1Q_2 of other toroids are to be measured.

If the texture is of the $\varphi = \pi/2$ type, α for points Q_1 and Q_2 becomes zero and 2π, respectively (Fig. 6). Equation (11) then reduces to

$$(m \pm r)^2 + l^2 - 2(m \pm r)\cos\beta = 0, \qquad (15)$$

which shows that Q_1 and Q_2 are not lying on a circle. The x and y coordinates of both points can be found from equations (2) and (7). A simpler approach is to approximate the curve Q_1Q_2 to a straight line, and to calculate the correct thickness of the toroid from the equations

$$\cos\beta = m/2; \quad 2r = Q_1Q_2 \sin\beta = Q_1Q_2 \cos\theta, \qquad (16)$$

where θ is the respective Bragg angle.

With the angular correction of equation (16), the Lorentz factors of a $\varphi = \pi/2$ texture and of randomly oriented polycrystalline materials become equal, but with a different physical meaning for $\cos\theta$ in each case. $1/\sin^2 2\theta$ is the Lorentz factor both for electron diffraction and for X-ray studies of $\varphi = 0$ textures.

The performed calculations show that there are no special requirements for the type of standard used to account for instrumental line-broadening both for X-ray and electron diffraction. Any suitably prepared, randomly oriented polycrystalline standard can be used.

A line X-ray source, as considered by Kagan (1964), irradiates a height h on the specimen. The diffraction conditions can be described by series of Ewald spheres, obtained by shifting the initial one in the OXZ plane at distances $\pm h/2$. Each Ewald sphere at a height η from the OX axis is defined by

$$S(\eta): x^2 + y^2 + z^2 - 2Rx - 2\eta z + \eta^2 = 0. \qquad (17)$$

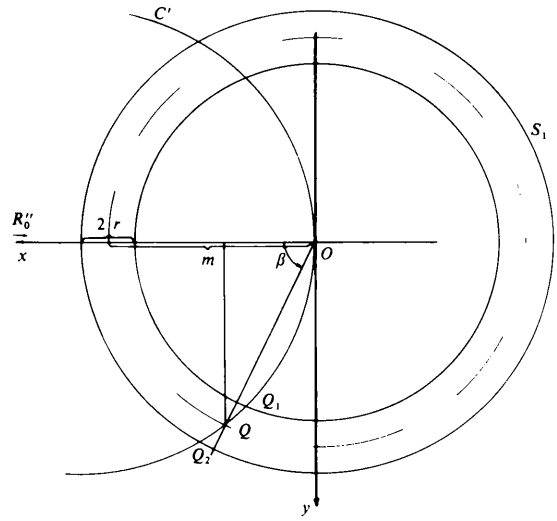

Fig. 6. Similar to Fig. 5, but for a $\varphi = \pi/2$ texture. Points Q_1 and Q_2 define an arc which can be correlated with the thickness of the corresponding toroid through the relation $2r \simeq Q_1Q_2 \sin\beta = Q_1Q_2 \cos\theta$, where θ is the respective Bragg angle.

Each contributes to reflections measured in the *OXY* plane with its cross section

$$C(\eta): x^2 + y^2 - 2Rx + \eta^2 = 0. \quad (18)$$

By considering each $C(\eta) \cap S_1$ for an arbitrary φ, for $\varphi = 0$ and for $\varphi = \pi/2$, equations analogous to (13), (14), and (15) will be obtained, each containing an additional constant η^2. These constants will be the same for the specimen under investigation and for the standard used to measure the instrumental line broadening, and, therefore, will not affect the value of the calculated physical broadening.

Conclusions

The possibilities of measuring coherent domain size (DS) and microstrain (MS) in textured materials from electron and X-ray diffraction line broadening have been discussed. In the case of transmission electron diffraction, DS and MS of textured films are to be measured along *OY* (Fig. 3). The measurements are not affected by deviations of the texture axis from an ideal orientation. Reflection electron diffraction measurements of DS and MS are to be performed along *OX*, for reflections fulfilling equation (5). Since textures are never ideal, there will be several angles φ^* in the angular interval $\varphi \pm \Delta\varphi$ of a real texture, fulfilling equation (5) for the particular toroids under consideration.

X-ray diffraction line broadening of a textured material, for an arbitrarily inclined texture axis, is not directly correlated to DS and MS of the material under investigation. An arbitrarily inclined texture can be reoriented to positions $\varphi = 0$ and $\varphi = \pi/2$. This requires indexing the diffraction picture obtained from the texture. In the case $\varphi = 0$, the measured line width is directly correlated with the thickness $2r$ of the *hkl* toroid. For $\varphi = \pi/2$ textures an angular correction is necessary.

It has been shown that the final height of the X-ray source does not affect the calculated physical broadening of textured materials (Kagan, 1964).

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Optimisation de la Correction d'Absorption

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Abstract

It is shown that the bias in absorption corrections can be reduced by a method based on a least-squares fit of an anisotropic linear absorption coefficient from Ψ-scan observations. This method is carried out by a Fortran program and has been used with success on many data collections, especially for electron density studies.

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