Diffraction Intensities from a Cluster of Curved Crystallites. II. The Effect of Curvature

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An attempt has been made to use the general expression derived by Mitra for the intensity of X-rays diffracted by a cluster of two-dimensional identical curved crystallites in studying the changes expected in the diffraction pattern when the curvature of the crystallite is changed. For this purpose, the previous expression has been modified into a form suitable for numerical computation. The modified expression for the intensity is expressed as a finite series of terms containing Bessel functions of zero order only. Further simplification is arrived at for the case of a cluster of crystallites consisting of single arcs only. On the basis of the expression derived, the intensity diffracted at different angles by a cluster of curved crystallites consisting of single arcs of different curvatures has been computed numerically. For studying the effect of different curvatures, calculations have been carried out for arcs subtending 0, 10, 20, 30, 60 and 90° respectively at the centre of curvature for two different values of the total number of atoms on an arc. Where the total number of atoms on each arc is 20, there is no appreciable variation with curvature of the displacements of the maxima from the Bragg angle. Intensity maxima and line profiles remain practically identical for all values of curvature for this value of the total number of atoms. However, when the total number of atoms on each arc is 4, the shifts in the positions of the maxima and the broadening of the line profile become more pronounced and the peak shifts increase, though by a small amount, as the curvature increases.

Introduction

In a previous publication (Mitra, 1965; hereafter called I) an expression has been derived for the intensity of X-rays diffracted by an axially parallel aggregate of curved crystallites. This expression reduces to the usual expression for ordinary straight crystallites leading to the Laue–Bragg laws if the curvature is made zero. On the other hand, when the crystallites are considered to be composed of atoms equiangularly arranged on the circumferences of concentric circles, the expression reduces to the one derived by Blackman (1951) for such cases. Thus the expression derived in I is of a very general nature and it should be possible to use this expression in studying the changes expected in the diffraction pattern when the curvature of the crystallite is changed. It would, indeed, be interesting to investigate the effect on the diffraction pattern of changing the curvature of the curved crystallite till it becomes zero, *i.e.* the crystallite becomes an ordinary one for which the Laue–Bragg laws are valid. With the results of such investigations available, it is expected that it might be possible, by studying the diffraction pattern, to distinguish between conglomerations of curved crystallites having different curvatures and also perhaps to make an estimate of the extent of curvature in the crystallites. The present work aims at carrying out this investigation.

Explanation of the symbols used

a = repeat distance between two neighbouring atoms on the first arc on the concave side of the bent crystallite.

b = the radial distance between two successive concentric arcs.

φ = the angle subtended at the common centre of the arcs by two neighbouring atoms on the same arc.

N = number of atoms on each arc.

M = number of concentric arcs in each crystallite.

$Q = 2\pi/N\varphi$

$h = 2a \sin \theta/\lambda$

$k = 2b \sin \theta/\lambda$

p = the order of the Bessel function.

θ = half the angle of deviation.

λ = wavelength of the X-rays used for recording the diffraction pattern.

$I(h,k)$ = intensity of the X-rays diffracted when the angle of deviation is 2θ. [See equation (8) of I.]

m,n = number indicating the position of an arc on which a particular atom is placed, counting from the concave side.

Simplification of the intensity expression

The intensity expression derived in I contains an infinite series of products of Bessel functions of the first kind in which the order of the Bessel functions increases monotonically to infinity. For crystallites of ordinary size and slight curvature, the arguments of the Bessel functions are generally very large. Hence numerical computations for such cases would require summing over a very large number of terms of this type. Evaluation of Bessel functions of such large arguments and orders and for so many terms would indeed be a stupendous task. A modification of the intensity expression, in a form suitable for numerical computation, is therefore highly desirable.

As has been shown in I, the intensity of X-rays diffracted by a random cluster of two-dimensional identical curved crystallites axially parallel to one another is given by

$$I(h,k) = N^2 \sum_{m=0}^{M-1} \sum_{n=0}^{M-1} J_0(QN\{h+mk\varphi\})$$
$$\times J_0(QN\{h+nk\varphi\})$$
$$+ 2 \sum_{p=1}^{\infty} [\sum_{m=0}^{M-1} \sum_{n=0}^{M-1} J_p(QN\{h+mk\varphi\})$$
$$\times J_p(QN\{h+nk\varphi\})] \frac{\sin^2 Np\varphi/2}{\sin^2 p\varphi/2} . \qquad (1)$$

It is also well known that

$$\frac{\sin^2 Np\varphi/2}{\sin^2 p\varphi/2} = N+2 \sum_{l=1}^{l=N-1} (N-l) \cos pl\varphi , \qquad (2)$$

where l is an integer.

Combining equations (1) and (2), we have,

$$I(h,k) = \sum_{m=0}^{M-1} \sum_{n=0}^{M-1} \{N^2 J_0(QN\{h+mk\varphi\})$$
$$\times J_0(QN\{h+nk\varphi\})$$
$$+ 2 \sum_{p=1}^{\infty} [J_p(QN\{h+mk\varphi\})J_p(QN\{h+nk\varphi\})]$$
$$\times [N+2 \sum_{l=1}^{l=N-1} (N-l) \cos lp\varphi]\} . \qquad (3)$$

It is further known (Bowman, 1958) that

$$J_0\{\sqrt{(x^2+y^2-2xy \cos \alpha)}\} =$$
$$J_0(x)J_0(y)+2 \sum_{p=1}^{\infty} J_p(x)J_p(y) \cos p\alpha . \qquad (4)$$

It follows from equation (4), setting $\alpha=0$, that

$$J_0(x-y)=J_0(x)J_0(y)+2 \sum_{p=1}^{\infty} J_p(x)J_p(y) . \qquad (5)$$

Combining equations (3), (4) and (5) we easily obtain

$$I(h,k) = \sum_m \sum_n NJ_0(QNk\varphi\{m-n\})$$
$$+ 2 \sum_m \sum_n \sum_{l=1}^{N-1} (N-l)J_0[QN(\sqrt{\{(h+mk\varphi)^2}$$
$$+ (h+nk\varphi)^2-2(h+mk\varphi)(h+nk\varphi)$$
$$\times \cos l\varphi\})] . \qquad (6)$$

Equation (6) can be computed with comparative ease since it is a series only in terms of J_0 for which tables even for comparatively large arguments are available and asymptotic terms may be conveniently used. The summation is over smaller number of terms, i.e. N terms only.

The case of a cluster of single arcs

Further simplification is arrived at for the case of a cluster of crystallites consisting of single arcs only. For this case both m and n are zero and equation (6) becomes

$$I(h)=N+2 \sum_{l=1}^{N-1} (N-l)J_0(2QNh \sin l\varphi/2) . \qquad (7)$$

For the case of zero curvature $\varphi\to0$, $l\varphi\to0$ and $\sin l\varphi/2\to l\varphi/2$; equation (7) for this case becomes

$$I(h)=N+2 \sum_{l=1}^{N-1} (N-l)J_0(2\pi hl) . \qquad (8)$$

Numerical computation for single arcs and discussion of the results

Calculations have been carried out for $N=20$ and $Q=\infty$, 36, 18, 12 corresponding to $N\varphi=0$, 10, 20, and 30° respectively and also for $N=4$ and $Q=\infty$, 36, 18, 12, 6 and 4 corresponding to $N\varphi=0, 10, 20, 30,$
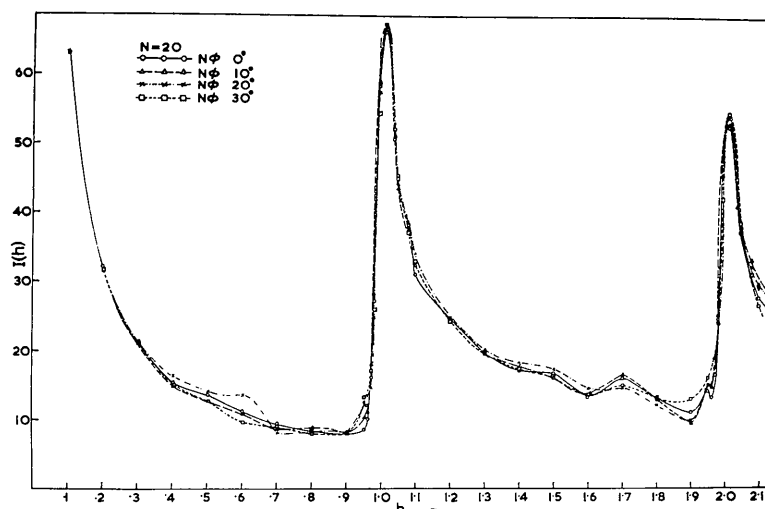

Fig. 1. Relative intensity at different angles of deviation of X-rays diffracted by an axially parallel aggregate of linear crystallites each consisting of 20 atoms arranged equiangularly on arcs subtending angles of 0, 10, 20 and 30° at the centre of curvature.

60 and 90° respectively. h has been taken from 0 to 2·2. Values of $J_0(x)$ for x up to 25 have been taken from the British Association *Mathematical Tables* VI, *Bessel Functions*, Part I (Cam, 1950) and for $x > 25$ have been calculated from the asymptotic expression

$$J_0(x) = \sqrt{(2/\pi x)} \cos (x - \pi/4) .$$

Results of the calculations are shown graphically in Figs. 1, 2, 3, 4 and 5.

Fig. 1 represents the $I(h)$–h curves for $N = 20$ and $Q = \infty$, 36, 18 and 12, while Fig. 2 represents similar curves for $N = 4$ and $Q = 36$, 12, 6 and 4. Calculations have shown that the values of $I(h)$ for $N = 4$ and $Q = \infty$ and 18 are almost same as those of for $N = 4$ and $Q = 36$.
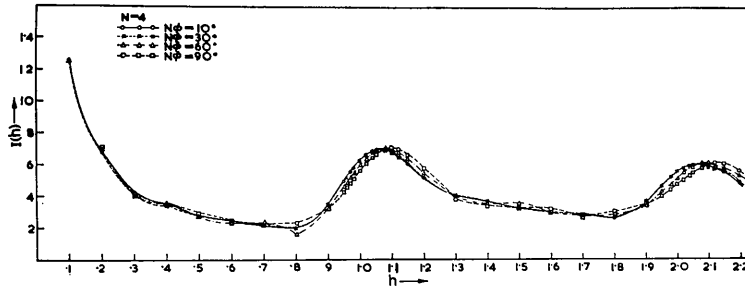

Fig. 2. Relative intensity at different angles of deviation of X-rays diffracted by an axially parallel aggregate of linear crystallites each consisting of 4 atoms arranged equiangularly on arcs subtending angles of 10, 30, 60 and 90° at the centre of curvature.
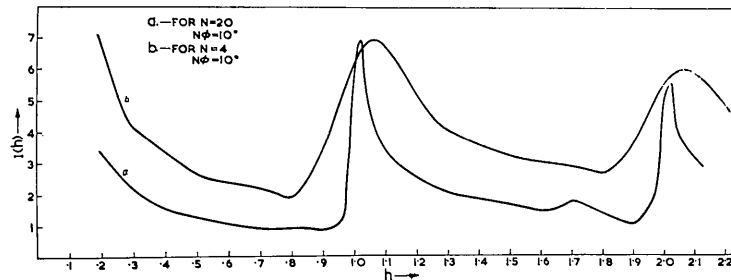

Fig. 3. Diffraction profile of X-rays diffracted by an axially parallel aggregate of linear crystallites each consisting of (a) 20 atoms (b) 4 atoms arranged equiangularly on arcs subtending angles of 10° at the centre of curvature.
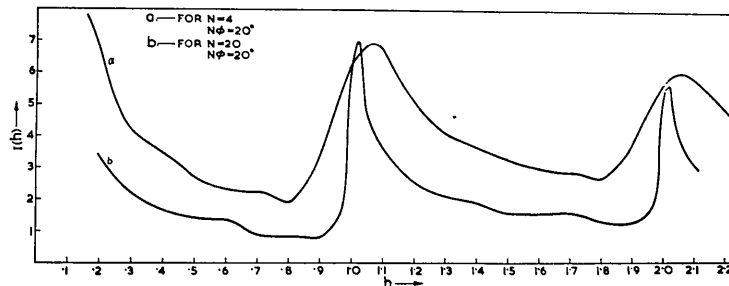

Fig. 4. Diffraction profile of X-rays diffracted by an axially parallel aggregate of linear crystallites each consisting of (a) 4 atoms (b) 20 atoms arranged equiangularly on arcs subtending an angle of 20° at the centre of curvature.
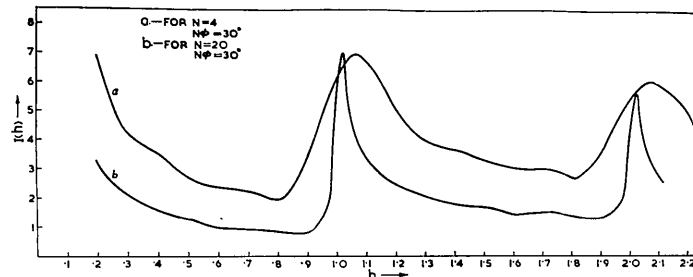

Fig. 5. Diffraction profile of X-rays diffracted by an axially parallel aggregate of linear crystallites each consisting of (a) 4 atoms (b) 20 atoms arranged equiangularly on arcs subtending an angle of 30° at the centre of curvature.

Hence they are not plotted separately. Figs. 3, 4 and 5 show the normalized $I(h)$–h curves for $N=20$ with $N=4$ for three different values of $N\varphi$, viz. 10, 20 and 30°.

$I(h)$–h curves in Fig. 1 show that for $N=20$ and $Q=\infty$, 36, 18 and 12 the maxima are slightly shifted in all cases and are no longer coincident with integral values of h. The maxima in the neighbourhood of $h=1$ are at $h=1\cdot02$ rather than at $h=1$ and those in the neighbourhood of $h=2$ are at $h=2\cdot02$ for all values of Q. The general features of all the curves are essentially same.

Fig. 2 shows that for $N=4$ and $Q=36$, 12, 6 and 4 the maximum in the neighbourhood of $h=1$ is at $h=1\cdot06$, $1\cdot075$, $1\cdot08$ and $1\cdot1$ respectively. The second maximum in the neighbourhood of $h=2$ is found to be at $h=2\cdot07$ for $Q=36$ and 12 whereas for $Q=6$ it is at $h=2\cdot10$ and for $Q=4$ at $h=2\cdot13$. The above two results show that the peak shifts become more appreciable as the value of Q decreases and also for the same value of Q as N decreases.

For $Q=1$ and $N=20$ it was observed in I that the intensity maximum in the neighbourhood of $h=1$ was at $h=1\cdot1$ rather than at $h=1$. For $N=10$ and $Q=2$ the maximum shifted to $h=1\cdot05$. It appears therefore, that the shift in maxima is a combined and complicated effect of the variation of N and φ.

Figs. 3, 4 and 5 show that the sharpness of the peaks for $N=20$ is more pronounced than that for $N=4$ for the same values of Q. Also it is observed from Fig. 1 that the intensity maxima and the broadening of the line profile remain almost the same for all values of Q. From Fig. 2 also similar observations can be made, but here the intensity maxima are less and the line profiles much broadened compared with Fig. 1. So from Figs. 1, 2, 3, 4 and 5 it can be concluded that the decrease in the value of N causes a decrease in the heights of maxima and broadens the line profile. This is an expected result as the decrease in the value of N is analogous to decrease in particle size. Further detailed numerical calculations for elucidating these points are being taken up.

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X-ray Measurements of Stacking Faults in Copper–Antimony Alloys

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The line profiles from cold-worked copper-base alloys containing pentavalent solute antimony in the primary solid solution range have been recorded by a Geiger counter X-ray diffractometer. The deformation fault probability α and the twin fault probability β have been obtained from peak shift and peak asymmetry measurements respectively. A roughly parabolic variation of α with increasing solute content has been observed. However, the increase of α with the increase of solute valency for fixed electron concentration per atom is not clearly established. The twin fault probability β also increases in a similar way as observed in other copper-base alloys.

During recent years extensive studies have been made of the presence and effects of stacking faults in copper- and silver-base alloys containing di-, tri- or tetravalent solutes and measurements with pentavalent solutes have been lacking. Recently, Sastry, Rama Rao & Anantharaman (1966) and Sen Gupta (1967) have determined the stacking fault concentrations in alloys of silver with the pentavalent solute antimony and observed the possible correlations between stacking fault probability α and the solute valence as well as electron concentration per atom, e/a. The present note reports results of our X-ray measurements of deformation and twin stacking fault probabilities α and β from peak shift and peak asymmetry in cold-worked copper–antimony alloys in the solid solution range.

Alloys were prepared from spectrographically standardized copper and antimony supplied by Messrs Johnson, Matthey & Co., Ltd, London, following the same method as adopted previously (Sen Gupta & Quader, 1966), the homogenization temperature being 650–750°C. The annealing treatments were terminated by quenching in water. Weight changes during preparation were negligible and hence no chemical analyses of the alloy specimens were performed. Preparations of the cold-worked and annealed samples and recordings of the line profiles of several X-ray reflexions were carried out in the usual way (Sen Gupta & Quader, 1966). Cold-working and the experimental observations were done at room temperature, 30 ± 1 °C. No phase transformation has been observed due to cold work.