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EVALUATION OF BENDING EFFECTS ON DIFFRACTION INTENSITIES

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Abstract—The effects of bending on diffraction profiles and intensities have been directly evaluated. It has been shown that:

(1) bending may cause large reductions in intensities or even the total loss of them,

(2) due to bending, the profile of the reflection may become asymmetrical and it may display two or more maxima,

(3) bending effects vary with the class of reflections and they become larger with the increasing order of diffraction, and

(4) the interference function for a bent lattice must be evaluated for each set of lattice parameters, whereas the interference function for an undeformed lattice can be made invariant with respect to lattice parameters.

INTRODUCTION

Thin crystallites of clay minerals are rather susceptible to being bent during the sample preparation processes for electron and X-ray diffraction analysis. Bending of crystallites seems to be caused by structural factors in some of these minerals. How bending may affect the intensities and the profiles of reflections is the subject of this report. A special case of bending (cylindrical one) was the subject of the investigations by Blackman (1951), Whittaker (1955 and the reference given there), Waser (1955), and Kunze (1956). A more general approach to bending effects was proposed by Cowley (1961). Unlike the simple method described in the following, the formulations in these previous studies are either mathematically complex or do not lend themselves readily to a systematic evaluation of bending effects on diffraction intensities.

The effects of bending on diffraction intensities and profiles can be directly evaluated by studying the properties of the interference function for bent lattices. The latter function expresses the interference effects between the waves scattered by each of the unit cells in a crystalline solid. For an undeformed and orthogonal lattice the interference function (S) may be expressed as:

$$S = \sum_{m=0}^{M-1} \sum_{n=0}^{N-1} \sum_{p=0}^{P-1} \exp[2\pi i \mathbf{s} \cdot \mathbf{R}_{mnp}] \qquad (1a)$$

$$\mathbf{R}_{mnp} = m\mathbf{a} + n\mathbf{b} + p\mathbf{c}, \qquad (1b)$$

where the magnitude of the reciprocal lattice vector $|\mathbf{s}|$ is equal to $2\sin\theta/\lambda$, and M, N, P are the number of unit cells along the X, Y and Z directions. The vectors **a**, **b**, and **c** are the lattice parameters. The position vector $\mathbf{R}_{mnp}$ defines the location of each lattice point with respect to a common origin. For intensity calculations one needs the quantity $|S|^2$ which can be expressed in the following form:

$$|S|^2 = \frac{\sin^2 \pi M u_1}{\sin^2 \pi u_1} \cdot \frac{\sin^2 \pi N u_2}{\sin^2 \pi u_2} \cdot \frac{\sin^2 \pi P u_3}{\sin^2 \pi u_3}, \qquad (2)$$

where the parameters u_1, u_2 and u_3 are fractional coordinates in terms of reciprocal lattice parameters. The interference function (equation 2) is independent of any real or reciprocal cell parameters and it therefore needs to be calculated but once. The function affects each reciprocal lattice point in the same way, namely depending on the thickness of the crystal in the direction of the reciprocal lattice vector. Furthermore the above function is symmetrical at the reciprocal lattice point, resulting in a symmetrical diffraction profile.

DERIVATION OF THE INTERFERENCE FUNCTION FOR BENT LATTICES

When a crystal lattice is bent, in general the lattice points will be randomly displaced. This will then give rise to a randomness between the phases of their scattering and in this sense the scattering from such a collection of unit cells becomes noncoherent. For sake of simplicity, an orthogonal crystal with one atom per unit cell will be considered. For the evaluation of the interference function one needs to define the position vector $\mathbf{R}_{mnp}$ in the equation (1b) for each of these displaced lattice points. This will be done in the following for two special cases of bending: spherical and cylindrical. Any other mode of bending may well be expressed as a combination of these special cases.

Spherically bent lattice

In Fig. 1(a) a spherically bent lattice plane is shown. The plane was coincident to the XY plane

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before the deformation. Each lattice point after the bending can be defined by the spherical coordinates r, ϕ, and θ. From these, r is the radius of the sphere and also the radius of the curvature for the bending. For a three-dimensional case, one can consider several such concentric spheres with radii $r_p = r + p \cdot c$, where p is the number of unit cells in the Z direction and c is the cell parameter in that direction. The spherical coordinates can be transformed to the original XYZ cartesian coordinates via the other cartesian coordinate system $x'y'z'$ (Fig. 1a):

$$X = x' = r_p \sin\phi \cos\theta$$
$$Y = y' = r_p \sin\phi \sin\theta$$
$$Z = z' - r_p = r_p(\cos\phi - 1{\cdot}0).$$

The angles ϕ and θ may be computed in radians as:

$$\phi = (\sqrt{m^2a^2 + n^2b^2})/r_p \quad (3)$$
$$\theta = \tan^{-1}(nb/ma). \quad (4)$$

The position vector of any lattice point may now be given by:

$$\mathbf{R} = \mathbf{j}_x X + \mathbf{j}_y Y + \mathbf{j}_z Z.$$

Where $\mathbf{j}_x$, $\mathbf{j}_y$, and $\mathbf{j}_z$ are unit vectors along the X, Y, and Z directions. The interference function can be rewritten:

$$S = \sum_{m=0}^{M-1}\sum_{n=0}^{N-1}\sum_{p=0}^{P-1} \exp\{2\pi i\mathbf{s}\cdot[\mathbf{j}_x r_p \sin\Phi\cos\theta + \mathbf{j}_y r_p \sin\Phi\sin\theta + \mathbf{j}_z r_p(\cos\Phi - 1{\cdot}0)]\}.$$

Remembering $\mathbf{s} = h'\mathbf{a}^* + k'\mathbf{b}^* + l'\mathbf{c}^*$, where h', k', and l' are not only integers but also continuous variables:

$$S = \sum_{m=0}^{M-1}\sum_{n=0}^{N-1}\sum_{p=0}^{P-1} \exp\left\{2\pi i r_p\left[\frac{h'}{a}\sin\Phi\cos\theta + \frac{k'}{b}\sin\Phi\sin\theta + \frac{l'}{c}(\cos\Phi - 1)\right]\right\}. \quad (5)$$

The ϕ and θ angles actually possess subscripts of (m, n, p) as defined by the equations (3) and (4). These subscripts have been dropped for simplicity of expression.

Cylindrically bent lattice

The model for cylindrically bent crystal is given in Fig. 1b. The stack of lattice planes parallel to XY becomes, after deformation, cylindrical surfaces with a radius r_p around a common cylinder axis. The radius of any one of the cylinders is given by $r_p = r + p \cdot c$, where p is the number of lattice planes and c is the spacing between them. The lattice points may now be first defined by cylindrical coordinates r, θ, z' (Fig. 1b). The XYZ cartesian coordinates may be obtained from these cylindrical coordinates via the other orthogonal coordinate system $x'y'z'$ shown in the same figure:

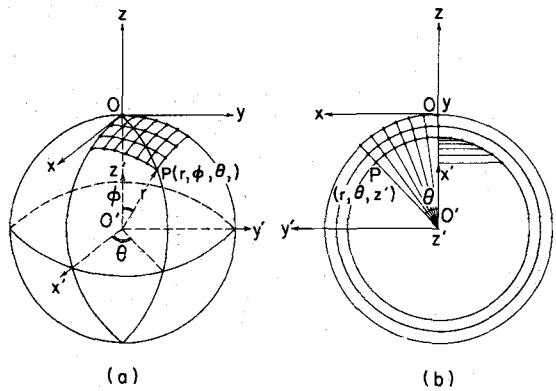


Fig. 1. Bending models with their curvelinear and rectangular coordinate systems. (a): Spherically bent lattice where r, Φ, and θ are the spherical coordinates of the lattice point P. (b): Cylindrically bent lattice where r, θ, and z' are the cylindrical coordinates of the lattice point P.

$$X = y' = r_p \sin\theta$$
$$Y = z' = nb$$
$$Z = x' - r_p = r_p(\cos\theta - 1{\cdot}0).$$

As in the case for spherical bending the interference function may be written for a cylindrical lattice:

$$S = \sum_{m=0}^{M-1}\sum_{n=0}^{N-1}\sum_{p=0}^{P-1} \times \exp\left\{2\pi i\left[r_p\frac{h'}{a}\sin\theta + r_p\frac{l'}{c}(\cos\theta - 1{\cdot}0) + k'n\right]\right\}$$

or

$$S = \sum_{m=0}^{M-1}\sum_{p=0}^{P-1} \exp\left\{2\pi i\left[r_p\frac{h'}{a}\sin\theta + r_p\frac{l'}{c}(\cos\theta - 1{\cdot}0)\right]\right\} \times \sum_{n=0}^{N-1}\exp(2\pi i k'n). \quad (6)$$

Where $\theta = ma/r_p$ (in radians) and all the other symbols have the same meaning as in the spherical case.

We can conclude from the above derivations that the interference function for a bent lattice is specifically defined by the lattice parameters of the crystal and it therefore must be calculated separately for each bent crystal. This is in contrast to the interference function for undeformed lattices. The new interference function for a bent lattice does not refer to the reciprocal space with the curvelinear coordinates but with its natural coordinates h', k', and l'.

DIFFRACTION EFFECTS OF BENDING ON THE SINGLE CRYSTAL REFLECTIONS

The interference functions, as reformulated, have been computed for several sets of parameters. An orthogonal lattice with parameters $a = 5{\cdot}2$ Å, $b = 9{\cdot}0$ Å, and $c = 10{\cdot}0$ Å (similar to those of a mica) but with a single atom per unit cell† has been considered.

†If the unit cell contains more than one atom then the bending will also cause displacements of the atoms within the unit cell. The above formulation will remain valid provided that the new positions of the displaced atoms within the unit cell are used for the structure factor calculations. Thus the bending of the unit cell can be accounted for in the structure factor without any modifications in the above interference functions.

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We chose hypothetical crystals in the form of a square in the X–Y plane, with an edge (A) of 135 Å, 270 Å, 540 Å, and 1080 Å in order to demonstrate the typical bending effects. Larger linear dimensions require hours of computing time. These small crystallite sizes may be helpful for considering deformation of clay crystallites and mosaic blocks in real crystals. In large crystals the bending may well be accommodated by a smaller deformation of mosaic blocks rather than a uniform deformation of the whole crystal.

In the Z direction the thickness of the crystal has been varied between 10 Å (a single lattice plane) to 100 Å (ten lattice planes). Several radii of curvature (r = 4000, 2000, 1000, 500, and 250 Å) have been considered in order to cover a wide range of bending angles. The bending angle is defined as $\alpha = A/r$ (in radians). The interference function has been computed for each combination of A and r and it has been normalized so that its maximum value is 1·0 corresponding to that of an undeformed lattice. For bending angles of 0·04 rad or larger, it was found that the number of lattice planes in the Z direction does not cause any appreciable differences in the values of the interference function. In fact for a bending angle of 0·135 rad for A = 135 Å and r = 1000 Å the value of the normalized interference function for 10 lattice planes is about 1 per cent different from that of the function for a single lattice plane. The graphs of the interference function given in this report are for a two-dimensional lattice plane.

It is important to note the deviations of the normalized interference function from the normalized interference function of an undeformed lattice. This deviation describes the diffraction effects of bending in a rather simple and graphical manner. The interference function for an undeformed two-dimensional lattice (i.e. with a single unit-cell thickness) is always unity along the c^* direction of hk reciprocal lattice rows, as shown with dashed lines in Fig. 2, 4–6. Deviation of the interference function from this horizontal line, directly gives the effects of bending on the intensity and the profile of the reflections. For a three-dimensional lattice with multiple lattice planes in the Z direction the interference function for unbent crystal will be a symmetrical peak centered at the integer values of l'. As mentioned above there is very little difference in the values of the normalized interference functions for bent two- and three-dimensional lattices. The curves for bent two-dimensional lattices may also be used to a very close approximation for bent three-dimensional lattices. The deviations of these curves from the symmetrical profiles centered at the reciprocal lattice nodes give the diffraction effects of bending in the case of bent three-dimensional lattices. Following this simple approach the interference function has been plotted for different orders and classes of reflections under various conditions of bending. It has been found that the bending models considered do not modify diffraction profiles and intensities along the $[hk0]^*$ directions but along the c^* direction. The properties of interference function are therefore described in the c^* direction for hk and $00l$ reflections in the following paragraphs.

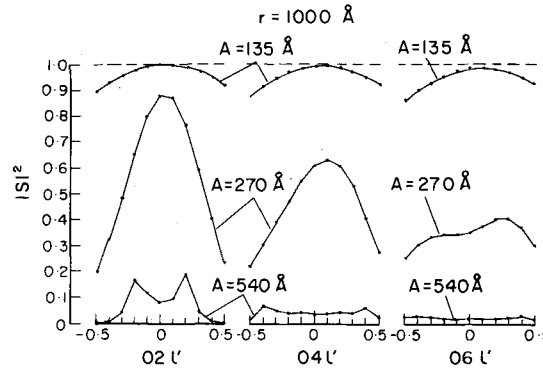


Fig. 2. Profiles of the interference function for a spherically bent crystallite with various linear dimensions (A) and for a radius of curvature of 1000 Å. Dashed lines give the values of the interference function for the unbent crystal.

hk *reflections from spherically bent crystal*

All the hk reflections are similarly affected by the spherical bending of the crystal. As an example, these effects are described for three orders of $0k$ reflections; these are 02, 04 and 06 reflections with increasing Bragg angles. The bending effects can be typically studied for a radius of curvature of 1000 Å in crystallites with linear dimensions A = 135, 270, 540 and 1080 Å. The profiles of the interference functions for these cases are given in Fig. 2. For a crystallite with a linear dimension A = 135 Å and with a radius of curvature of 1000 Å (α = 0·135 rad), the interference function has values very close to unity at the positions l' = 0·0 along the hk rows. The interference function shows, however, appreciable deviation from the dashed lines at other l' positions for all three reflections 02, 04 and 06. There is an asymmetrical broadening of the profile for these reflections. For a crystallite with A = 270 Å, the interference function shows a significant reduction from the value of 1·0. This reduction is about 12 per cent for the 02 reflection, 37 per cent for the 04 reflection, and 65 per cent for the 06 reflection. The profile of the interference function becomes broad and asymmetrical for all these reflections in increasing amount with the order of diffraction. Furthermore the peak positions shift from their normal positions for the higher order reflections. In fact, the maximum for the 04 reflection shifts from l' = 0 to l' = 0·1 and similarly the peak for the 06 reflection appears at l' = 0·3. For a crystallite with a linear dimension of 540 Å, the 02 reflection has lost 80 per cent of its normal intensity. In addition, the profile of the interference function displays now two maxima at l' = −0·2 and l = 0·2. The interference function shows about 96 and 97 per cent reductions in intensity for the reflections 04 and 06 correspondingly. Therefore, these reflections will practically disappear. For a crystallite with a linear dimension of 1080 Å, the function has a value close to zero, even for the 02 reflection; therefore it has

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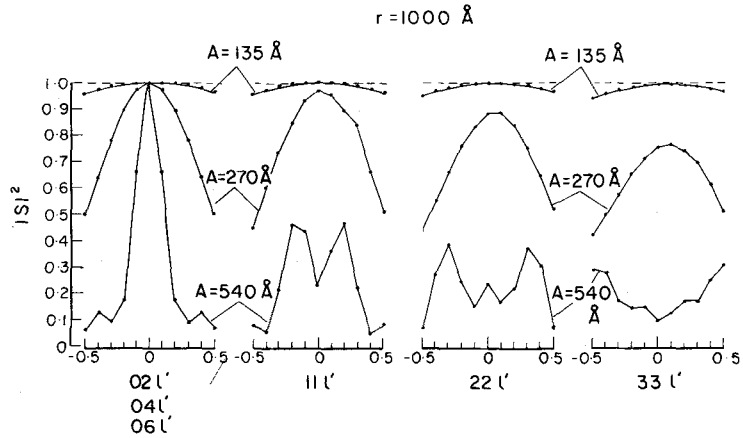


Fig. 4. Profiles of the interference function for a cylindrically bent crystallite with various dimensions (A) and for a radius of curvature of 1000 Å. Dashed lines give the values of the interference function for the unbent crystal.

not been plotted. There will be virtually no more coherent scattering from this crystallite.

Selected area electron diffraction (SAD) patterns of beidellite from Black Jack Mine, Idaho have been studied recently by Güven and Pease (1975). These SAD patterns show features similar to those described for the bending of a crystallite with $A = 270$ Å and $A = 540$ Å. Typical SAD patterns of three beidellite crystallites are given in Fig. 3. These patterns indicate large reductions in intensity with increasing order of diffraction in the directions $0k$, hk, and $h0$. Although these intensity reductions are larger along the b^* than along the other directions, we may still consider a spherical bending for the beidellite crystallites in order to give a qualitative explanation for the observed data. The calculated intensity ratios of the 02/06 and 02/33 reflections for an undeformed beidellite crystallite are both about 6:5, whereas the observed ratios for the 02/06 reflections range between 3:1–5:1 in Figs. 3(a) and 3(b), respectively. Similarly, the observed intensity ratios for the 02/33 reflections range between 2:1–4:1 in Figs. 3(a) and 3(b). In the SAD pattern in Fig. 3(c) all the reflections except 02 are very weak or missing. The large reductions in intensity or the total loss of reflections were shown in Fig. 2 for the interference functions of crystallites with $A = 270$ Å and $A = 540$ Å, and bent to a radius of curvature of 1000 Å. The dimensions of the beidellite crystallites are much larger and beidellites have more atoms per unit cell than the models used in Fig. 2. It would be prohibitively time consuming to calculate the exact corrections for bending effects on the beidellites. The above explanation is, therefore, to be considered as strictly qualitative.

hk *reflections from cylindrically bent crystal*

As seen from equation (6) and also from the geometry of the cylindrical bending, all hk reflections are not affected in the same manner by the deformation. Specifically, the reflections from the set of planes perpendicular to the cylinder axis behave differently from the others. In our model, where the cylinder axis is parallel to the b-axis of the crystal, $0k$ reflections form such special reflections. Therefore, the profile of the interference function will be discussed separately for $0k$ and hk reflections. The effects of the bending are typically displayed in Fig. 4 for the crystallites with linear dimensions of 135 Å, 270 Å, and 540 Å, and with a radius of curvature of 1000 Å.

The profile of the interference function for 02, 04 and 06 reflections are exactly the same. The profile is symmetrical and changes in width only with the linear dimension of the crystallite (Fig. 4). The peak position of the interference function appears exactly at $l' = 0$ or an integer as expected also from an undeformed lattice. The only difference between the diffraction profiles of a bent and unbent crystal is the following: for an unbent two-dimensional lattice the interference function has always the value of unity in the c^* direction of the hk rod. The interference function for a two-dimensional bent lattice, however, behaves as though there are several unit cells in the c^* direction. This is due to the fact that bending of a two-dimensional lattice generates a sequence of several layers.

Other hk reflections behave similar to the 11, 22, and 33 reflections for which the interference function is plotted in Fig. 4. For a crystallite with a linear dimension of 135 Å, all three orders show very small reductions in their intensities. A crystallite size of 270 Å, on the other hand, displays the effects of bending rather clearly. The values of the interference function drops to 0·97 for the 11 reflection, 0·88 for the 22 reflection and to about 0·76 for the 33 reflections. The profiles for all these reflections are asymmetrically broadened and peak positions are displaced to $l' = 0{\cdot}1$ for the 22 and 33 reflections. For a crystallite size of 540 Å the effects of bending on the above reflections are rather drastic. The profile of the 11 reflection displays two maxima at $l' = 0{\cdot}2$ and $l = -0{\cdot}2$ with an average loss of 55 per cent from its normal intensity. The 22 reflection displays three maxima at $l' = -0{\cdot}3$, $l' = 0{\cdot}0$, and $l' = 0{\cdot}3$ with a loss of intensity of about 60 per cent. The profile of the 33 reflection

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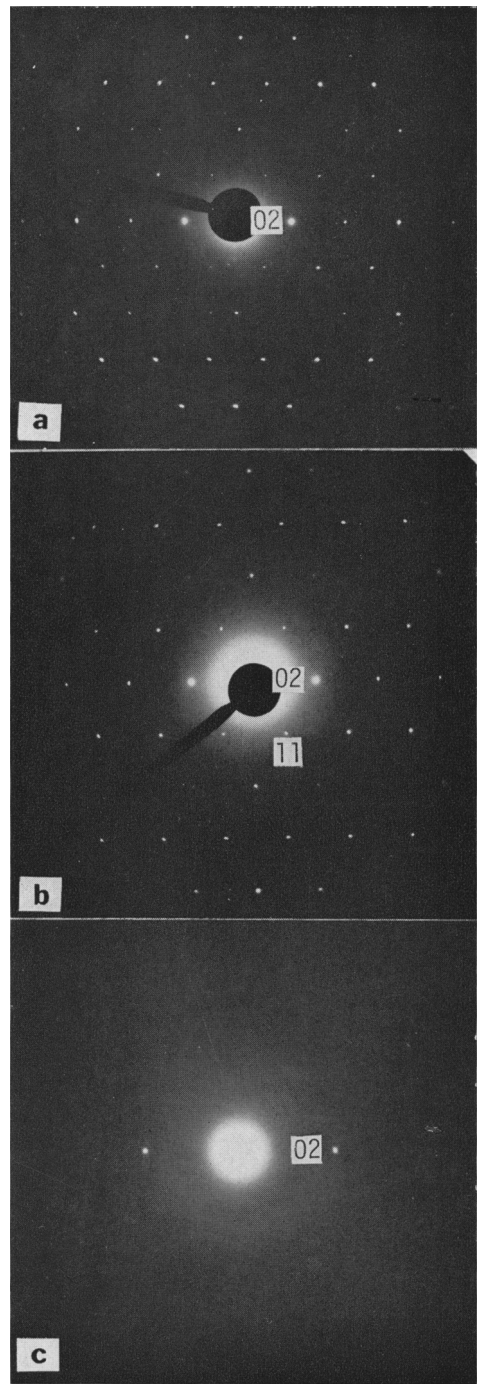


Fig. 3. Selected area electron diffraction patterns of beidellites displaying various degrees of bending.

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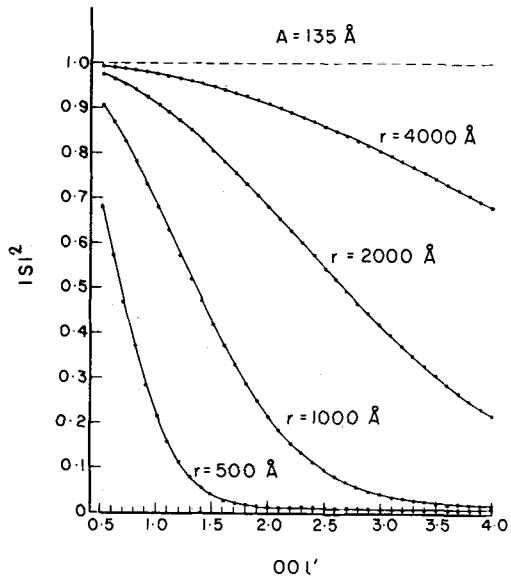


Fig. 5. The interference function for the 00*l* reflections from a spherically bent crystallite with a linear dimension of 135 Å and with different radii of curvature.

becomes rather broad and irregular, with about 90 per cent loss of intensity.

Effects of bending on 00l reflections

This special class of 00*l* reflections undergoes much larger intensity losses and distortions in their profiles for the bending models considered above. The continuous profile of the interference function in the range of $l' = 0{\cdot}5$–$4{\cdot}0$ has been plotted in Fig. 5 for a spherically bent crystal. Cylindrical bending gives also a similar profile for the interference function in the same range. Various radii of curvature (250, 500, 1000, 2000 and 4000 Å) have been considered for a crystallite size of 135 Å. The profile shows a continuous decrease in the value of the interference function with the increasing l' index of the reflection. This reduction is increasing drastically with decreasing radius of curvature i.e. with increasing amount of bending. Thus the behaviour of the interference function predicts anomalous intensity ratios for the different orders of 00*l* reflections and higher background intensity for the bent crystallites. This suggests some caution in interpreting the intensities of basal reflections especially for clay minerals where the diffraction data are often limited to this special class of reflections. Why these reflections undergo so much distortion and loss of intensity can be easily inferred from Fig. 1(b). As seen on the upper right quadrant of the circle in this figure, bending of this model generates a series of lattice planes parallel to 00*l* but with an irregular spacing and hence random phasal relationships between them.

THE PARAMETERS OF BENDING

A few comments should be made on the question of how bending can be defined. The apparent parameters of the bending are the linear dimension (A) of the crystallite and the radius of curvature (r). The ratio (α) of these two parameters is defined as the bending angle (i.e. $\alpha = A/r$). The question arises whether this radio can be used for evaluating the diffraction effects of bending instead of using two parameters A and r. If such a relationship can be derived, this obviously will reduce the computations to a marked degree. In order to explore this possibility the interference function has been evaluated for several sets of A/r values. The results for crystallite sizes of 135 Å and 270 Å for the spherical bending are plotted in Fig. 6. By doubling the edge of a two-dimensional square crystallite, the number of lattice points will be increased four times. Therefore it is expected that the interference functions would show some similarity for the sets 135/1000 and 270/4000; 135/500 and 270/2000; and 135/250 and 270/1000. In fact, Fig. 6 shows that the interference function has similar, but not identical, profiles for the cases 135/1000 and 270/4000; and for 135/500 and 270/2000. The maximum values of the interference function are distinctly different for the above sets. This similarity, however, breaks down when the bending angle is increased. In fact, the pair 135/250 and 270/1000 show completely different profiles for the interference function. Thus the bending must be defined by the two parameters A and r and not simply by their ratio, i.e. with the bending angle (α). This also is the case for cylindrical bending.

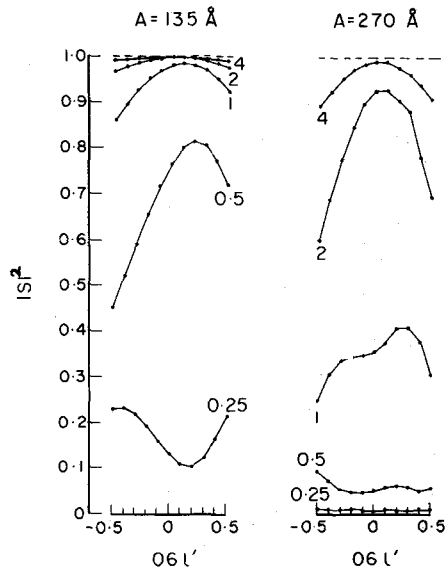


Fig. 6. The variations in interference function for the 06 reflection for different sets of A/r values. Numbers next to the curves give the radii of curvature in thousands of angstroms.

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