NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2448

X-RAY DIFFRACTION BY BENT CRYSTAL LAMELLAE

By Hans Ekstein

Armour Research Foundation

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SUMMARY

Bent crystal lamellae may consist of individual blocks, spaced somewhat irregularly and having a mutual angular disorientation. In this case, the X-ray intensities of the individual blocks will simply be added. As long as the blocks are not too small, no effect on integrated intensity or line width of a Debye-Scherrer line is to be expected.

Alternatively, the lamella may be perfectly regular in its structure, except for the elastic deformation. In this case, the amplitudes rather than the intensities must be added.

It is shown that these two possibilities lead substantially to the same result: No intensity change or line broadening may be expected from moderate bending.

INTRODUCTION

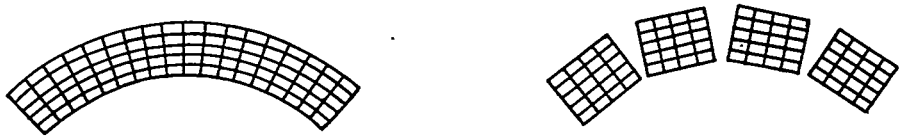
It is well-known that any deviation from strict periodicity in the crystal lattice produces a diffraction pattern different from that of the undistorted crystal. Considerable attention has been given to the correlation between observed "anomalous" patterns and the distortions of crystal lattices. The simplest assumption leading to a theoretical description is that the original perfect crystal is broken up into small blocks, each of which is perfect in its structure, and that these blocks diffract incoherently. Internal stresses can be taken into account by allowing the blocks to be homogeneously deformed to varying degrees.

Observations of severely distorted solids cannot be explained by this simple assumption alone. Therefore, other types of distortion have been investigated, which are sometimes rather arbitrary. One of the most plausible types of inhomogeneous distortion is the bending of crystal lamellae. The usual picture of a plastically deformed crystal shows thin crystal lamellae which are elastically bent (see reference 1).

Buerger's theory of the formation of crystals assumes bent lamellae, the intervals between them being filled by misplaced atoms.

It is possible that the bent lamellae are not really elastically deformed lattices but consist of blocks which are separated by a "boundary" layer of irregularly placed atoms. In this case, bending would be a special case of block arrangement. It seems interesting, however, to inquire whether different effects can be produced if the whole crystal lamella is "coherent" in the sense that the contributions of small sections add their amplitudes rather than their intensities for the resultant scattering. More specifically, the question is whether a bending with a negligibly small strain can produce either a change of integrated intensity of a Debye-Scherrer line or a broadening.

Intuitively, it would seem that there should not be much difference between the diffraction by a bent lamella and that by an array of irregularly spaced blocks arranged in a circle as shown below.



An analysis confirming this intuitive view was made by the Armour Research Foundation under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics. This report is part of a cooperative project with Dr. Stanley Siegel.

SUM FORMULA

Consider a simple lattice with primitive translations $\underline{a}_1$, $\underline{a}_2$, and $\underline{a}_3$ so that the radius vector of a nucleus in the undistorted lattice is

$$\underline{a}_n = n_1\underline{a}_1 + n_2\underline{a}_2 + n_3\underline{a}_3 \tag{1}$$

and the reciprocal lattice vectors are

$$\underline{A}_m = m_1\underline{A}_1 + m_2\underline{A}_2 + m_3\underline{A}_3 \tag{2}$$

By an elastic deformation, the atoms are displaced from their equilibrium positions so that their new positions are

$$\underline{r}_n = \underline{a}_n + \underline{u}(\underline{a}_n) \tag{3}$$

An incident plane wave of wave vector $\underline{k}_o$ is diffracted in the direction $\underline{k}$. The diffracted amplitude is proportional to

$$\Psi = F(R) \sum_n \exp \left\{ 2\pi i \underline{R} \cdot \left[\underline{a}_n + \underline{u}(\underline{a}_n) \right] \right\} \tag{4}$$

where

$$\underline{R} = \underline{k} - \underline{k}_o \tag{5}$$

is the radius vector in the Fourier space and $F(\underline{R})$ is the form factor. From the qualitative considerations, it is known that the function Ψ will be large only near the points $\underline{A}_m$. In this case, the sum in equation (4) can be transformed conveniently into another sum of terms, each of which is noticeably different from zero only in the neighborhood of one point $\underline{A}_m$. For approximate calculations, one sole term of this sum may be used to determine the amplitude near a given point $\underline{A}_m$. Consider the sum

$$S(\underline{r}) = \sum_n \varphi(\underline{a}_n + \underline{r}) \tag{6}$$

where $\underline{a}_n$ stands for any lattice point. For values of $\underline{r}$ inside the first unit cell

$$x_1, x_2, x_3 \leq 1 \tag{7}$$

where

$$\underline{r} = x_1\underline{a}_1 + x_2\underline{a}_2 + x_3\underline{a}_3 \tag{8}$$

In this interval, let $S(\underline{r})$ be represented by a Fourier sum:

$$\sum_{\underline{n}} \varphi(\underline{a}_n + \underline{r}) = \sum_{\underline{m}} \exp\left(2\pi i \underline{A}_m \cdot \underline{r}\right) q_m \tag{9}$$

If the volume of the unit cell is designated by v,

$$q_m = \frac{1}{v} \iiint_{(1)} \exp\left(-2\pi i \underline{A}_m \cdot \underline{r}\right) \sum_{\underline{n}} \varphi(\underline{a}_n + \underline{r}) \, dv$$

$$= \frac{1}{v} \sum_{\underline{n}} \iiint_{(1)} \varphi(\underline{a}_n + \underline{r}) \exp\left(-2\pi i \underline{A}_m \cdot \underline{r}\right) dv \tag{10}$$

where the integration is extended over the first unit cell. By a change of coordinates

$$\underline{r} \longrightarrow \underline{a}_n + \underline{r} \tag{11}$$

Equation (10) becomes, since the product $\underline{A}_m \cdot \underline{a}_n$ is an integer,

$$q_m = \frac{1}{v} \sum_{\underline{n}} \iiint_{(n)} \varphi(\underline{r}) \exp\left(-2\pi i \underline{A}_m \cdot \underline{r}\right) dv \tag{12}$$

where the integration is extended over the nth unit cell, that is

$$\left.\begin{aligned} n_1 \leqq x_1 \leqq n_1 + 1 \\ n_2 \leqq x_2 \leqq n_2 + 1 \\ n_3 \leqq x_3 \leqq n_3 + 1 \end{aligned}\right\} \tag{13}$$

Equation (12) can be written:

$$q_m = \frac{1}{v}\int_\infty \varphi(\underline{r}) \exp\left(-2\pi i \underline{A}_m \cdot \underline{r}\right) dv \tag{14}$$

the integration being extended over the infinite space. In particular, if $\underline{r} = 0$, equations (9) and (14) give:

$$\sum_n \varphi(\underline{a}_n) = \sum_m \int_\infty \varphi(\underline{r}) \exp\left(-2\pi i \underline{A}_m \cdot \underline{r}\right) dv \tag{15}$$

This transformation can be considered as a three-dimensional generalization of Poisson's sum formula (reference 2).

INTEGRATED INTENSITY

In order to apply the sum formula (15) to the sum formula (4), take

$$\varphi(\underline{r}) = \exp\left\{2\pi i \underline{R} \cdot \left[\underline{r} + \underline{u}(\underline{r})\right]\right\} \tag{16}$$

inside the crystal and $\varphi = 0$ outside the crystal. Equation (4) becomes

$$\Psi \approx F(R) \sum_m \int \exp\left\{2\pi i \left[\left(\underline{R} - \underline{A}_m\right) \cdot \underline{r} + \underline{R} \cdot \underline{u}(\underline{r})\right]\right\} dv \tag{17}$$

If the distortion of the crystal is not too severe, the "spots" about the reciprocal lattice points $\underline{A}_m$ will not overlap, so that in the surrounding of one particular point $\underline{A}_l$, Ψ becomes:

$$\Psi^{(l)} = F(R) \int \exp\left\{2\pi i \left[\left(\underline{R} - \underline{A}_l\right) \cdot r + \underline{R} \cdot \underline{u}(\underline{r})\right]\right\} dv \tag{18}$$

Without further specifying the form of the displacement function $\underline{u}(\underline{r})$, it is possible to derive the "integrated intensity" of a Debye-Scherrer line from equation (18). This term is not quite unambiguous. If a great number of identically shaped and distorted crystals, distributed randomly, is irradiated by a plane wave, the intensity will essentially be accumulated about the Debye-Scherrer positions. "Integrated intensity" then means the integral of the intensity extended over "the neighborhood" of the Debye-Scherrer line. But, since "neighborhood" cannot be given a precise meaning, the usual definition is equivalent to the integral from $-\infty$ to $+\infty$ of <u>one</u> contribution of the form of equation (18). Obviously, this definition is meaningful only if the intensity between the lines, that is, the overlap, is negligibly small.

This definition is not in agreement with that used in the theory of thermal scattering, where a definite distinction can be made between "the line" and the background surrounding it.

If the above definition of "integrated intensity" is used, it can be shown (reference 3) that it is proportional to the integral of the square modulus of $\Psi^{(l)}$, extended over the infinite Fourier space. If, as usual, $F(\underline{R})$ is considered a slowly variable function and is replaced by $F_l = F(\underline{A}_l)$, the integrated intensity of the lth line is

$$I_l \propto \int_\infty \Psi^{(l)}(\underline{R})\Psi^{(l)*}(\underline{R})\,dV$$

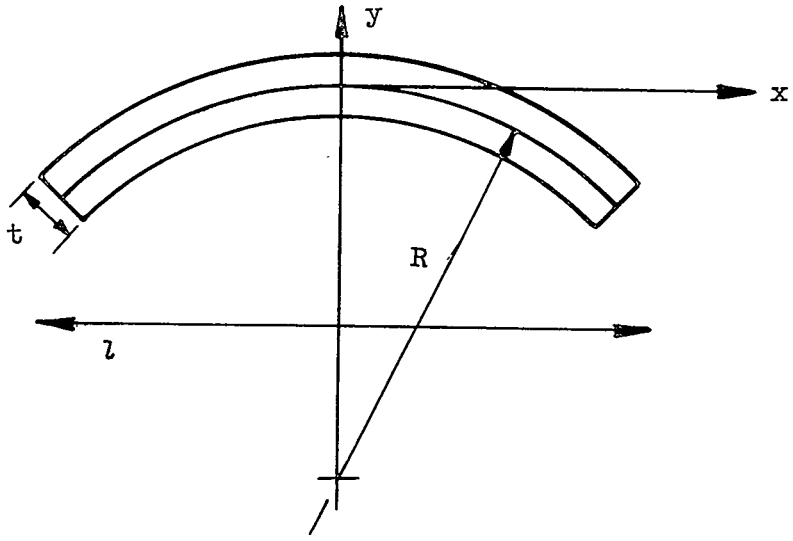
$$\int_\infty dV \iint \exp\left\{-2\pi i\underline{A}_l \cdot (\underline{r} - \underline{r}') + 2\pi i\underline{R} \cdot \left[\underline{r} + \underline{u}(\underline{r}) - \underline{r}' - \underline{u}(\underline{r}')\right]\right\} dv\,dv'$$

$$= \int dv = W \tag{19}$$

where W designates the crystal volume. It follows, in general, that <u>a moderate elastic distortion does not change the integrated intensity of Debye-Scherrer lines</u>. This conclusion holds, of course, only as long as the crystals are small enough so that the kinematic theory can be applied, which has been assumed implicitly.

DIFFRACTED AMPLITUDE

Let the crystal lamella be bent about an axis parallel to the z-direction as shown in the following diagram.



The components of the elastic displacement are

$$\left.\begin{aligned} u &= \frac{yx}{R} \\ v &= \frac{-x^2}{2R} \\ w &= 0 \end{aligned}\right\} \qquad (20)$$

where R is the radius of curvature. Let the dimensions of the lamella be l, t, and w in the x-, y-, and z-directions, respectively.

From equation (18),

$$\Psi^{(l)} = F_l \int_{-w/2}^{w/2} \exp\left[2\pi i(Z - Z_l)z\right] dz \times$$

$$\int_{-t/2}^{t/2} \exp\left[2\pi i y(Y - Y_l)\right] dy \times$$

$$\int_{-l/2}^{l/2} \exp\left\{2\pi i\left[x\left(X - X_l + \frac{Xy}{R}\right) - Y\frac{x^2}{2R}\right]\right\} dx$$

$$= F_l \frac{\sin \pi w(Z - Z_l)}{\pi(Z - Z_l)} \times$$

$$\int_{-t/2}^{t/2} dy \exp\left[2\pi i y(Y - Y_l) + \frac{R}{2Y}\left(X - X_l + \frac{Xy}{R}\right)^2\right] \times$$

$$\int_{-l/2}^{l/2} \exp\left\{-\frac{\pi i Y}{R}\left[x - \frac{R}{Y}\left(X - X_l + \frac{Xy}{R}\right)\right]^2\right\} dx \qquad (21)$$

where X_l, Y_l, and Z_l are the components of $\underline{A}_l$. To make the notation clearer, the variables may be expressed in terms of a lattice parameter a_o which might be, for instance, $|a_1|$. Let

$$\left.\begin{aligned} x &= ua_o \qquad l = Na_o \qquad X = \frac{p}{a_o} \qquad R = \rho a_o \\ y &= va_o \qquad t = Ma_o \qquad Y = \frac{q}{a_o} \qquad X - X_l = \frac{s}{a_o} \\ & \qquad\qquad\qquad Y - Y_l = \frac{r}{a_o} \end{aligned}\right\} \qquad (22)$$

and $\Psi^{(l)}$ becomes:

$$\Psi_l = a_o^2 F_l \frac{\sin \pi w(Z - Z_l)}{\pi(Z - Z_l)} \cdot U \tag{23}$$

where

$$U = \int_{-M/2}^{M/2} dv \exp\left\{2\pi i\left[vr + \frac{\rho}{2q}\left(s + \frac{pv}{\rho}\right)^2\right]\right\} \times$$

$$\int_{-N/2}^{N/2} \exp\left\{-\frac{\pi i}{\rho}\left[u - \frac{\rho}{q}\left(s + \frac{pv}{\rho}\right)\right]^2\right\} du$$

$$= \sqrt{\frac{\rho}{2q}} \exp\left(\frac{2\pi i \rho s^2}{2q}\right) \int_{-M/2}^{M/2} dv \exp\left\{2\pi i\left[v\left(r + \frac{sp}{q}\right) + \frac{v^2 p^2}{2q\rho}\right]\right\} \times$$

$$\int_A^B \exp\left(-\frac{i\pi u^2}{2}\right) du \tag{24}$$

where

$$\left.\begin{aligned} A &= \sqrt{\frac{2q}{\rho}}\left[-\frac{N}{2} - \frac{\rho}{q}\left(s + \frac{pv}{\rho}\right)\right] \\ B &= \sqrt{\frac{2q}{\rho}}\left[\frac{N}{2} - \frac{\rho}{q}\left(s + \frac{pv}{\rho}\right)\right] \end{aligned}\right\} \tag{25}$$

DIFFRACTED INTENSITY

Of special interest is that case where the strain is small so that the block hypothesis would predict no substantial intensity outside the Debye-Scherrer lines. The thickness t should not be larger than about 10^3 atomic distances a_o, if the kinematic theory is to be valid.

But t should not be much smaller than $10^3 a_o$ if broadening as a result of small size is to be avoided. Therefore, M will be assumed to be of the order of a thousand.

If strains are related to the position of the Debye-Scherrer line in the usual way (i.e., considering each strained crystal as an isolated diffractor), then a strain $\epsilon = \Delta d/d$ of about 10^{-5} would be hardly noticeable. At the boundary

$$y = \frac{t}{2} = \frac{Ma_o}{2}$$

and if it is assumed that the strain in the X-direction is

$$\epsilon = \frac{\partial u}{\partial x} = \frac{y}{R} \approx 10^{-5}$$

the following relations are obtained

$$R \approx \frac{Ma_o}{2} \times 10^5$$

or

$$\rho = \frac{R}{a_o} \approx 10^8$$

that is, the radius of curvature equals about 10^8 atomic distances or it is of the order of 1 centimeter. The X-ray lines ordinarily observed have Miller indices of the order of unity; therefore, the components of the reciprocal lattice vectors in the region under consideration will be at most of the order $1/a_o$. The quantities p and q defined in equation (22) cannot, therefore, be larger than of the order of unity ($p \approx q \approx 1$ or smaller). Consider the surrounding of a lattice point A_l for which $X_l \approx Y_l \approx 1/a_o$ and, therefore, $p \approx q \approx 1$. Then the integral $\int_A^B$ in equation (24) is practically independent of v, and U can be written:

$$U = \exp\left(\frac{\pi i \rho s^2}{2q}\right)\sqrt{\frac{\rho}{2q}}\int_{-M/2}^{M/2} \exp\left[2\pi i v\left(r + \frac{sp}{q}\right)\right] dv - \int_A^B \exp\left(-\frac{i\pi u^2}{2}\right) du \tag{26}$$

where

$$\left.\begin{aligned} A &\approx \sqrt{\frac{2q}{\rho}}\left(-\frac{N}{2} - \frac{\rho s}{q}\right) \\ B &\approx \sqrt{\frac{2q}{\rho}}\left(\frac{N}{2} - \frac{\rho s}{q}\right) \end{aligned}\right\} \tag{27}$$

In the exponent of the first integral of equation (26) the small quantity $v^2p^2/2q\rho$ has been omitted.

The first integral in equation (26),

$$\int_{-M/2}^{M/2} \exp\left[2\pi i v\left(r + \frac{sp}{q}\right)\right] dv = \frac{\sin \pi M\left(r + \frac{sp}{q}\right)}{\pi\left(r + \frac{sp}{q}\right)}$$

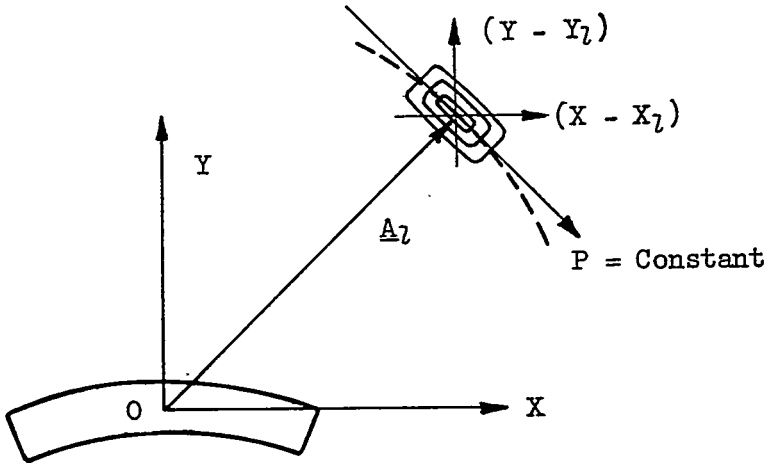
$$= \frac{\sin \pi t\left[Y - Y_l + \frac{(X - X_l)X}{Y}\right]}{\left[Y - Y_l + \frac{(X - X_l)X}{Y}\right]a_o}$$

$$\approx \frac{\sin \pi t\left[Y - Y_l + \frac{(X - X_l)X_l}{Y_l}\right]}{a_o\left[Y - Y_l + \frac{(X - X_l)X_l}{Y_l}\right]} \tag{28}$$

since X and Y change little in the neighborhood of the lattice point. If a new variable in Fourier space

$$P = Y - Y_l + \frac{X_l}{Y_l}\left(X - X_l\right) \tag{29}$$

is defined so that the lines P = Constant are straight lines normal to the vector $\left(X_l, Y_l\right)$, as shown below, it can be seen that the direction



P = Constant is tangential to the sphere $|R| = |A_l|$.

The intensity is, by equations (4), (23), (26), (28), and (29):

$$I \propto |F_l|^2 a_o^2 \left[\frac{\sin \pi w\left(Z - Z_l\right)}{\pi\left(Z - Z_l\right)}\right]^2 \left(\frac{\sin \pi t P}{\pi P}\right)^2 \left|\int_A^B \exp\left(-\frac{i\pi u^2}{2}\right) du\right|^2 \tag{30}$$

where A and B depend on the coordinate $X - X_l = s/a_o$ only, if Y is again considered nearly constant. The quantity $\left|\int_A^B\right|^2$ is usually represented by Cornu's spiral, and it is sufficient to discuss its properties qualitatively.

If $(X - X_l)$ is small, then by equation (27) the limits A and B are of the order of $N/\sqrt{\rho}$. As an example, take N of the order of 10^6; that is, the dimension of the lamella in the X-direction is about 1/10 millimeter. In this case, $A \approx -100$ and $B \approx 100$ if $(X - X_l)$ is small. In this range, the quantity $\left|\int_A^B\right|^2$ has the nearly constant value 2. The value of this square modulus begins to decrease rapidly as soon as one of its limits becomes of the order of unity. This will happen when

$$|s| \approx \frac{N}{\rho}$$

or, if as above $N \approx 10^6$ and $\rho = 10^8$ are chosen, when $|s|$ reaches the order 10^{-2}. The intensity "spot" about the reciprocal lattice point $\underline{A}_l$ consists then of the product of three functions:

$\left[\sin \pi w(Z - Z_l)/\pi(Z - Z_l)\right]^2$ which limits its extent in the Z-direction;

$(\sin \pi tP/\pi P)^2$ which in a section Z = Constant makes the intensity decrease rapidly in a direction parallel to the lattice vector $\underline{A}_l$; and a function of $(X - X_l)$ which is sensibly constant up to a certain value (e.g., 10^{-2}) and then decreases rapidly. The preceding schematic diagram shows the spot in a section Z = Constant near $Z = Z_l$. In our example, the spot is about 10 times longer in the direction normal to $\underline{A}_l$ than in the direction of A_l. Since the length of the spot is tangential to the sphere |R| = Constant (i.e., θ = Constant for a Debye-Scherrer picture), no line broadening is to be expected.

The distribution of intensity is of the same type as that to be expected from the block hypothesis: The actual spot can be imagined to be produced by a smearing out of the original rectangular spot about $\underline{A}_l$, as the crystals are slightly rotated about the Z-direction.

A discussion of the cases $X_l \approx 0$ and $Y_l \approx 0$ leads qualitatively to the same result and will not be reproduced here.

CONCLUSIONS

A bent crystal lamella may consist of individual blocks, spaced somewhat irregularly and having a mutual angular disorientation. In this case, for calculation of X-ray intensities, the intensities of the individual blocks will simply be added. As long as the blocks are not too small, no effect on integrated intensity or line width of a Debye-Scherrer line is to be expected.

Alternatively, the lamella may be perfectly regular in its structure, except for the elastic deformation. In this case, the amplitudes rather than intensities must be added.

It is shown that the two possibilities lead to substantially the same result: No intensity change or line broadening may be expected from moderate bending.

Armour Research Foundation
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