Acta Cryst. (1965). **18**, 464

Diffraction Intensities from a Cluster of Curved Crystallites. I. General Theory for One- and Two-Dimensional Cases

By G. B. Mitra

Department of Physics, Indian Institute of Technology, Kharagpur, India

(*Received* 2 *March* 1963 *and in revised form* 12 *May* 1964)

An elementary theory of diffraction by an axially parallel aggregate of curved crystallites has been developed and a general expression for two-dimensional curved crystals has been derived. This expression straightway leads to a corresponding expression for the one-dimensional case. For the extreme cases of zero curvature and of equiangularly spaced atoms arranged on the circumference of a circle, the general expressions, as expected, lead respectively to Bragg's law and to the expression derived by Blackman for a circular lattice. On the basis of the expressions derived, numerical computation of the intensity diffracted at different angles by atoms arranged equiangularly on a circle and on a semicircle, the angular spacing for the two cases being the same, has been carried out from a very small angle of scattering to an anglo larger than the angle corresponding to the first peak which would be obtained if Bragg's law were applicable to the lattices. It is observed that while for the case of the full circle there are a large number of prominent maxima and minima, for the semicircle the most prominent maximum, apart from the one in the zero angle region, is in the neighbourhood of the Bragg angle. In between these two maxima, there are several maxima which are much suppressed. Positions of the peaks and troughs in the two cases are approximately the same.

Introduction

The possibility of curved lattices occurring in nature was first discussed by Pauling (1930). Later X-ray and electron microscope studies (Bates, Sand & Mink, 1950; Noll & Kircher, 1951, 1952; Whittaker, 1953; Taggart, Milligan & Studer, 1954) have confirmed that certain silicate minerals actually have bent lattices. Nye (1949), Cottrell (1949) and Paterson (1954) have also concluded that bent glide lamellae might be present in deformed metals. Tomlin & Ericsson (1960) have suggested that certain types of protein fibres might be formed of curved crystallites. Thus, a study of diffraction intensities from curved crystallites appears to be of wide interest.

Theoretical investigation of this problem has been carried out by Fock & Kolpinsky (1940), Blackman (1951*a*, *b*), Oster & Riley (1952), Whittaker (1954). Jagodzinski & Kunze (1954), Waser (1955), Kunze (1956), Stuart (1959), Fraser, MacRae & Freeman (1959), Burge (1959) and Cowley (1961). All of them have studied different special cases of the problem and the expressions obtained by them do not lead to easy numerical computation. In view of this, there is scope for fresh work in this field and the present attempt has been directed towards obtaining an expression for the intensity of a beam of parallel rays diffracted by an axially parallel aggregate of thin, small, identical crystallites bent along the surface of a cylinder.

Derivation of an expression for diffraction intensity

Let *ABCD* (Fig. 1) represent a layer of identical atoms in the *XY* plane of one of the curved crystallites. The repetition of *ABCD* at regular distances c along the z direction will form the crystallite. In the plane of *ABCD*, the position of an atom P is described by the polar coordinates (ϱ_{mr}, ψ_r) where $\varrho_{mr}=R+mb$, $\psi_r=r\varphi$, R is the radius of the first arc AB, 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, and m and r are integers including zero. The

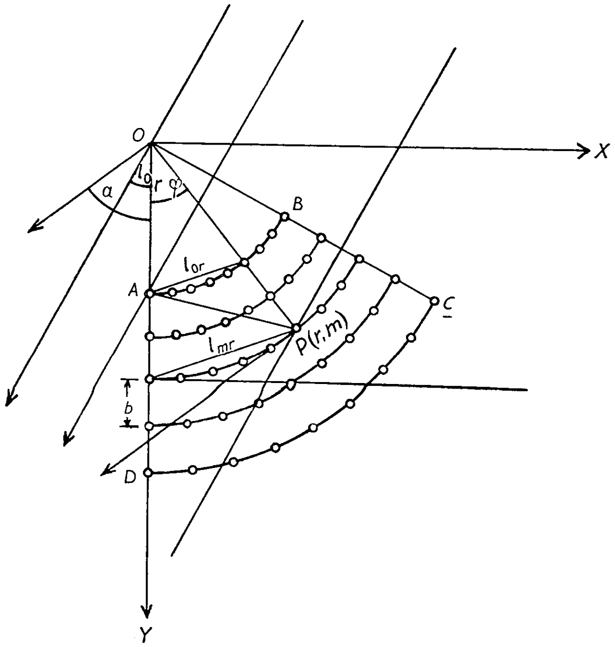

Fig. 1. Diffraction of a parallel beam of X-rays by a curved crystallite.

amplitude of a beam of parallel rays diffracted by this crystallite in the direction $\mathbf{S}=\mathbf{S}_d-\mathbf{S}_i$ (where $\mathbf{S}_i$ and $\mathbf{S}_d$ denote directions of the incident and diffracted rays respectively) will be proportional to

$$A(S)=f(S)\frac{\sin(\pi/\lambda)T\mathbf{C}.\mathbf{S}}{\sin(\pi/\lambda)\mathbf{C}.\mathbf{S}} \times\left\{\left|\sum_r\sum_m \exp\{-(2\pi/\lambda)i(\boldsymbol{\rho}_{mr}-\boldsymbol{\rho}_0)\mathbf{S}\}\right|\right\} \quad (1)$$

where $f(\mathbf{S})$ is the atomic scattering factor in the direction $\mathbf{S}$, T is the number of layers in the z direction and λ the wavelength of the diffracted beam. The evaluation of A thus depends on the evaluation of the quantity G given by

$$G(\mathbf{S})=\sum_r\sum_m \exp\{-(2\pi/\lambda)i(\boldsymbol{\rho}_{mr}-\boldsymbol{\rho}_0).\mathbf{S}\}\,. \quad (2)$$

Let us, for the time being, forget about the z direction and consider a random aggregate of two-dimensional crystallites each identical with $ABCD$ and lying in the same plane as $ABCD$. Let the incident and diffracted rays make angles α_0 and α with the Y axis as shown in Fig. 1. Let each layer be composed of M concentric arcs, each arc containing N atoms. Then equation (2) can be written

$$\begin{aligned} G(S)=&\sum_{r=0}^{N-1}\sum_{m=0}^{M-1}\exp\left(-(2\pi/\lambda)i[(R+mb)\{\cos(r\varphi+\alpha)\right.\\ &\left.-\cos(r\varphi+\alpha_0)\}-R(\cos\alpha-\cos\alpha_0)]\right) \quad (3)\\ =&\sum_{r=0}^{N-1}\sum_{m=0}^{M-1}\exp\left((2\pi/\lambda)i[2R\sin\tfrac{1}{2}r\varphi\{\sin(\tfrac{1}{2}r\varphi+\alpha)\right.\\ &-\sin(\tfrac{1}{2}r\varphi+\alpha_0)\}-mb\{\cos(r\varphi+\alpha)\\ &\left.-\cos(r\varphi+\alpha_0)\}]\right)\,. \quad (4)\end{aligned}$$

When R becomes very large, $\varphi\to 0$ and $\sin\frac{1}{2}r\varphi\to\frac{1}{2}r\varphi$, $l_{mr}\to l_{0r}=ar$ (Fig. 1) where a is the repeat distance between two neighbouring atoms on the first arc ($m=0$), so that $R=a/\varphi$ and equation (4) can be written

$$G(S)=\sum_{r=0}^{N-1}\sum_{m=0}^{M-1}\exp\left((2\pi/\lambda)i[\{ar(\sin\alpha-\sin\alpha_0)\}-\{bm(\cos\alpha-\cos\alpha_0)\}]\right) \quad (4a)$$

which represents the amplitude of X-rays scattered by a two-dimensional rectangular Bravais lattice of repetition distances a and b respectively. This is as is expected.

Equation (3) can be written

$$G(S)=\exp\{(4\pi/\lambda)iR\sin\theta\sin(\theta+\alpha_0)\}\times\sum_{r=0}^{N-1}\sum_{m=0}^{M-1}\exp\{(4\pi/\lambda)i(R+mb)\sin\theta\sin(r\varphi+\theta+\alpha_0)\}\,, \quad (5)$$

where

$$\alpha-\alpha_0=2\theta\,. \quad (6)$$

Utilizing the well known relation (Sneddon, 1956)

$$\exp(ix\sin\theta)=\sum_{p=-\infty}^{\infty}J_p(x)\exp ip\theta$$

where $J_p(x)$ is the pth order Bessel function of the first kind with argument x, we may write equation (5) in the form

$$\begin{aligned} G(S)=&\exp\{(4\pi/\lambda)iR\sin\theta\sin(\theta+\alpha_0)\}\\ &\times\sum_{r=0}^{N-1}\sum_{m=0}^{M-1}\sum_{p=-\infty}^{\infty}J_p((4\pi/\lambda)\sin\theta\{R+mb\})\\ &\times\exp\{ip(r\varphi+\theta+\alpha_0)\}\\ =&\exp\{(4\pi i/\lambda)R\sin\theta\sin(\theta+\alpha_0)\}\\ &\times\sum_{m=0}^{M-1}\sum_{p=-\infty}^{\infty}J_p((4\pi/\lambda)\sin\theta\{R+mb\})\\ &\times(\sin Np\tfrac{1}{2}\varphi/\sin p\tfrac{1}{2}\varphi)\exp\{ip(\theta+\alpha_0+\overline{N-1}\tfrac{1}{2}\varphi)\}\,. \quad (7)\end{aligned}$$

The measured intensity of the beam diffracted in a direction making an angle 2θ with the incident beam will be proportional to the average value of GG^* (where G^* is the complex conjugate of G) the averaging process being carried over all values of α_0 from 0 to 2π and the given value of θ. The measured intensity in the direction 2θ for such a cluster of two-dimensional curved crystallites will then be proportional to

$$\begin{aligned} I(\mu)=&\langle|GG^*|\rangle\\ =&N^2\sum_{m=0}^{M-1}\sum_{n=0}^{M-1}J_0(\mu\{R+mb\})J_0(\mu\{R+nb\})\\ &+2\sum_{p=1}^{\infty}\left[\sum_{m=0}^{M-1}\sum_{n=0}^{M-1}J_p(\mu\{R+mb\})J_p(\mu\{R+nb\})\right]\\ &\times\sin^2 Np\tfrac{1}{2}\varphi/\sin^2 p\tfrac{1}{2}\varphi\,, \quad (8)\end{aligned}$$

where

$$\mu=(4\pi/\lambda)\sin\theta\,.$$

Writing

$$\left.\begin{aligned} Q&=2\pi/N\varphi\\ h&=2a\sin\theta/\lambda\\ k&=2b\sin\theta/\lambda\end{aligned}\right\} \quad (9)$$

we find easily that equation (8) can be written

$$\begin{aligned} I(hk)=&N^2\sum_{m=0}^{M-1}\sum_{n=0}^{M-1}J_0(QN\{h+mk\varphi\})J_0(QN\{h+nk\varphi\})\\ &+2\sum_{p=1}^{\infty}\left[\sum_{m=0}^{M-1}\sum_{n=0}^{M-1}J_p(QN\{h+mk\varphi\})J_p(QN\{h+nk\varphi\})\right]\\ &\times\sin^2 Np\tfrac{1}{2}\varphi/\sin^2 p\tfrac{1}{2}\varphi\,. \quad (10)\end{aligned}$$

The case of a single arc

Let us consider the average intensity $I(h)$ from a cluster of identical single arcs each lying in the same plane as the others and each oriented at random with respect to the axis. Equation (10) for such a case can be written

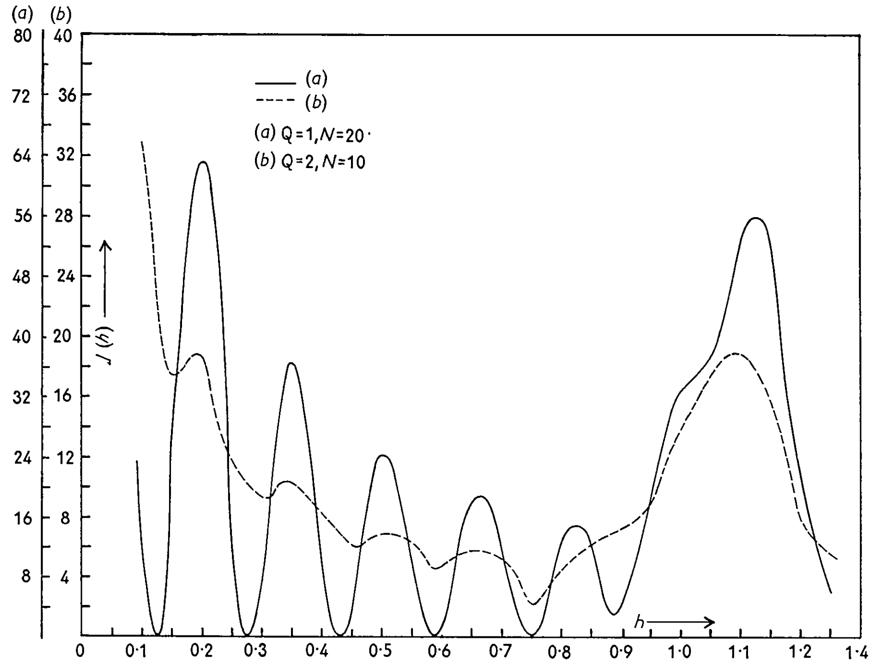

Fig. 2. Relative intensity at different angles of deviation of X-rays diffracted by an axially parallel aggregate of linear crystallites each consisting of (*a*) 20 atoms arranged equiangularly on the circumference of a circle, (*b*) 10 atoms arranged equiangularly on half the circumference of the same circle, so that angular and linear spacings between two consecutive atoms in the two cases are same.

$$I(h)=N^2J_0^2(QNh)+2\sum_{p=1}^{\infty}J_p^2(QNh)\,(\sin^2 N\tfrac{1}{2}p\varphi/\sin^2 p\tfrac{1}{2}\varphi)\,. \qquad (11)$$

For $Q=1$,

$$I(h)=N^2J_0^2(Nh)+2\sum_{p=1}^{\infty}J_p^2(Nh)\,(\sin^2 p\pi/\sin^2 p(\pi/N)\,. \qquad (12)$$

The product within the summation sign of equation (12) will have appreciable values only for $p=nN$, n being an integer. Hence, equation (12) can be written

$$I(h)=N^2J_0^2(Nh)+2N^2\sum_{n=1}^{\infty}J_{nN}^2(Nh)\,. \qquad (13)$$

This is the same as equation (4) of Blackman (1951*b*), which is valid for N atoms arranged equiangularly on the circumference of a circle. Since this case is identical with the case with $Q=1$, we find that equation (11) automatically leads to equation (4) of Blackman (1951*b*).

Fig. 2 shows the plots of $I(h)$ against h for two cases *viz.* (*a*) $Q=1$, $N=20$ and (*b*) $Q=2$, $N=10$. Thus φ for these two cases is the same and hence for the same radius of curvature, a, and therefore h will be same for both cases. Computations were carried out with Bessel functions of order up to 30, when even for the maximum argument the functions became negligibly small. It is observed that while for the case of the full circle ($Q=1$), there are a large number of maxima and minima, for the case of the semicircle ($Q=2$), there is a main maximum at about $h=1\cdot1$, preceded by a large number of suppressed peaks. Positions of the peaks and troughs in the two cases are, however, observed to agree approximately. It will be interesting to follow how the intensity distribution changes with increasing Q and how it is modified for two- and three-dimensional cases. These points will be discussed in several forthcoming publications.

The author is highly indebted to Prof. A. J. C. Wilson for attracting his attention to the problem and to the referees for pointing out some errors in the original manuscript.

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Kristall- und Molekülstruktur des *syn*-Methyldiazotatkaliums CH_3N_2OK

Von R. Huber, R. Langer und W. Hoppe

Abteilung für Röntgenstrukturforschung am Max-Planck-Institut für Eiweiss- und Lederforschung, München und Physikalisch-Chemisches Institut der Technischen Hochschule, München, Abteilung für Strukturforschung, Deutschland

(*Eingegangen am* 25. *März* 1964 *und wiedereingereicht am* 30. *April* 1964)

The crystal structure of potassium *syn*-methyldiazotate has been determined by two-dimensional heavy-atom methods and refined by three-dimensional Fourier- and least-squares computations. The final R index is 8·4% for 1230 reflexions. The space group is $C2/c$ with unit-cell dimensions $a=12·49$, $b=9·97$, $c=6·61$, $\beta=81·5°$. There is one molecule per asymmetric unit. The methyl hydrogen atoms have been located.

The molecule is found in the *cis*-diazotate form and is planar within the limits of the analysis. The N–O bond length 1·306 Å is unusually short.

Einleitung

In einer früheren Arbeit (Müller, Hoppe, Hagenmaier, Haiss, Huber, Rundel & Suhr, 1963) haben wir kurz über Ergebnisse einer zweidimensionalen Röntgenkristallstrukturanalyse berichtet, welche die Bestimmung der Molekülstruktur des *syn*-Methyldiazotatkaliums zum Ziele hatte.

In der vorliegenden Arbeit werden die Röntgenuntersuchungen, die zuerst mit zweidimensionalen, später auch mit dreidimensionalen Methoden durchgeführt wurden, im einzelnen beschrieben.

Experimentelles

Das *syn*-Methyldiazotatkalium kristallisiert aus flüssigem Ammoniak in dünnen Nadeln, aus Dimethylsulfoxyd in Prismen von *ca.* ½ mm Kantenlänge. Die Kristalle waren uns von E. Müller zur Verfügung gestellt worden, wofür wir auch an dieser Stelle unseren besten Dank aussprechen.

Die ausserordentlich luft- und feuchtigkeitsempfindlichen Kristalle wurden unter trockenem Stickstoff in Markkapillaren eingeschmolzen. Nach Präzessionsaufnahmen ergaben sich die Gitterkonstanten zu

$$a=12{,}49\pm0{,}02,\ b=9{,}97\pm0{,}02,\ c=6{,}61\pm0{,}02\ \text{Å}$$
$$\beta=81°\,30'\pm5'\ .$$

Entsprechend der hohen Genauigkeit der Parameterbestimmung wurden die Gitterkonstanten mit besonderer Sorgfalt gemessen (Aufbelichtung eines NaCl-Einkristalldiagrammes auf den gleichen Präzessionsfilm). Die Dichte ergab sich nach der Schwebemethode (Mischungen von getrocknetem Benzol und Methylenjodid unter Stickstoff) zu $\varrho=1{,}60$ g.cm^{-3} (theoretische Dichte bei 8 Formeleinheiten $\varrho=1{,}61$ g.cm^{-3}).

Auf Grund der Auslöschungen (hkl) für $h+k=2n+1$, $(h0l)$ für $l=2n+1$, kommen die Raumgruppen Cc (azentrisch, vierzählige Punktlage) und $C2/c$ (zentrosymmetrisch, achtzählige Punktlage) in Frage. Im Laufe der Analyse stellte sich die zentrosymmetrische Raumgruppe als die richtige heraus.

$$\text{Punktlagen:}\ (0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},0)+x,y,z;\ \bar{x},\bar{y},\bar{z}$$
$$\bar{x},y,\tfrac{1}{2}-z;\ x,\bar{y},\tfrac{1}{2}+z\ .$$

Für die Intensitätsaufnahmen wurden Kriställchen mit den Kantenlängen 0,5, 0,2, 0,2 mm verwendet, deren Absorption bei Verwendung von Mo $K\alpha$-Strahlung ($\mu=11{,}0$ cm^{-1}) vernachlässigbar gering war. Die Intensitäten wurden photographisch vermessen (Präzessionsaufnahmen und Weissenberg–Mehrfachfilm-Aufnahmen mit Zwischenlage von 15 μ starken Kupferfolien, Photometrierung mit einem an unserem Institut entwickelten integrierenden Photometer). Da der Kristall einen hohen Temperaturfaktor be-