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The Diffraction of X-rays by a Cylindrical Lattice. II

By E. J. W. Whittaker

Ferodo Limited, Chapel-en-le-Frith, Stockport, England

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Previous theoretical work on this subject is extended to determine the positions and profiles of the diffuse reflexions from a cylindrical lattice. These are computed in the case when the scattering matter is concentrated at the lattice points, and the necessary formula is derived for the case when an assemblage of atoms is associated with each lattice point. Two of the conclusions reached by Jagodzinski & Kunze are shown to be either erroneous or irrelevant.

1. Introduction

In a previous paper (Whittaker, 1954, hereafter referred to as I) the concept of a cylindrical lattice has been defined, and its relevance to the structure of certain silicates, especially chrysotile, has been pointed out. A circular cylindrical lattice was shown to give two sets of reflexions, one sharp and the other diffuse. The positions, profiles, and intensities of the sharp reflexions were discussed, both for the case when the diffracting matter is concentrated at the lattice points and for the case when an extended electron distribution is present. The diffraction formula required for computation of the profiles of the diffuse reflexions was also derived for the case when the diffracting matter is concentrated at the lattice points, but the form of the reflexions was not examined in detail.

After Part I had been submitted a series of three papers was published by Jagodzinski & Kunze (1954*a*, *b*, *c*) on the 'roll structure' of chrysotile. These authors have derived mathematical expressions which are equivalent to those given in I for the particular case of diffraction by the postulated structure of chrysotile. However, they have not considered explicitly the general concepts of diffraction by cylindrical lattices and they have not examined systematically the effects on the diffraction pattern which are produced by variations in the dimensions of such lattices. In the present paper this general theoretical investigation is therefore continued, with particular reference to the diffuse reflexions. The investigation is made for the idealized case in which the diffracting matter is concentrated at the lattice points (§ 3), and for the important practical case when an assemblage of atoms is associated with each lattice point (§ 4). As a preliminary, however, it is necessary to point out a serious error made by Jagodzinski & Kunze (1954*b*) in the interpretation of their theory (§ 2).

2. Intensity corrections in diffraction by cylindrical lattices

Jagodzinski & Kunze (1954*b*) conclude that the observed intensities of the sharp reflexions from a structure based on a cylindrical lattice must be multiplied by ξ (actually by r^* in their nomenclature, which is ξ/λ in the usual terminology) in order to make them proportional to the squares of the structure factors. This conclusion is also quoted by Jagodzinski & Kunze (1954*c*) in criticism of the use of a Fourier synthesis to refine the chrysotile structure (Whittaker, 1953). The conclusion is at variance with that reached in I of this series.

This difference lies not in the mathematical theory but in the physical interpretation of the result. Expression (13) of I shows that the amplitude of the transform of the structure is indeed proportional to $\xi^{-\frac{1}{2}}$, and therefore that the intensity of the transform in reciprocal space is proportional to ξ^{-1}. Jagodzinski & Kunze appear to equate this intensity to the observed intensity without recognizing that the two are related by a factor analogous to the Lorentz factor in diffraction by a rotating crystal.

An error was also made in I (Whittaker, 1954) in the discussion of this point in relation to expression (6) of I, where it was stated that the intensity recorded in a diffraction experiment would be that contained within a range of Υ equal to the divergence of the

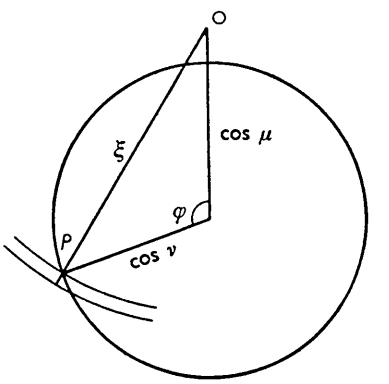

Fig. 1. Section of Ewald sphere at a height $\zeta = l\lambda/c$. The incident beam is inclined at an angle μ to the plane of the section, and the centre of the section is thus at a distance cos μ from the origin O. The radius of the section is cos ν. The sphere intersects a ring of intensity at P which has a width $d\xi$, and a thickness $d\zeta$ perpendicular to the plane.

incident beam, and that the factor ξ^{-1} would be cancelled out on this account. But since the transform under discussion is independent of Υ, the intensity diffracted from every ray of an incident beam will be equal, and the total intensity must therefore be independent of divergence in the beam. However, the following analysis reveals that the conclusion reached was correct although the argument was false.

Fig. 1 shows a section through the Ewald sphere at the level $\zeta = l\lambda/c$ in reciprocal space. The incident beam is inclined at an angle μ to the section, and the elevation of the lth layer line from the equator level is ν. An elementary ring of the transform of the structure, of intensity $|F(\xi, \zeta)|^2$, intersects the sphere at P. If this ring is of radius ξ and cross-section $d\xi d\zeta$, then it follows that the surface area of the sphere which is intersected by the ring is given by

$$\frac{\xi d\xi d\zeta}{\cos\mu\cos\nu\sin\varphi},$$

where φ is the azimuth of the diffracted beam. Hence the diffracted intensity is proportional to

$$|F(\xi, \zeta)|^2 \xi L,$$

where L is the usual Lorentz factor. Since $|F(\xi, \zeta)|^2$ is proportional to the square of the structure factor and inversely proportional to ξ, it follows that the observed intensities after correction for the Lorentz factor are proportional to the squares of the structure factors.

It appears at first sight that this conclusion is at variance with the excellent agreement which Jagodzinski & Kunze obtain between the calculated and observed intensity distribution on the zero layer line. The explanation appears to be as follows. If the observed intensities on the zero layer line are multiplied by ξ instead of by $1/L$, the only variable factor omitted is $\cos\theta$, since here

$$1/L = \sin 2\theta = \xi\cos\theta.$$

But over the range of ξ studied by these authors it is possible to make the approximation

$$\cos\theta \doteq \exp(-k\sin^2\theta)$$

to within 1% by a suitable choice of k. The error is therefore assimilable to the necessarily arbitrary temperature factor assumed.

It is desirable at this stage also to clear up another possible source of misunderstanding which may arise from the papers of Jagodzinski & Kunze. These authors state categorically (1954*a*) that as a result of the cylindrical structure of chrysotile an intensity calculation carried out by normal structure calculation methods gives somewhat usable results only for the basal interferences. When the proof of this statement is offered in the second paper of the series (Jagodzinski & Kunze, 1954*b*) it appears to follow not from the cylindrical structure but from the assumption that the relative displacement of successive layers of the structure in the direction of the cylinder axis may have a random sign. This assumption clearly destroys the regularity of the cylindrical lattice and is therefore not relevant to the present discussion of diffraction by such lattices. It introduces a disorder phenomenon similar to that discussed for normal lattices by Bragg & Howells (1954) and by Cochran & Howells (1954). The assumption is even shown by Jagodzinski & Kunze not to be applicable to the structure of chrysotile, but the above mentioned general categorical statement is nowhere withdrawn.

3. Diffracting matter concentrated at lattice points

Expression (16) of I gives the amplitude of the rays diffracted by a circular cylindrical lattice (omitting the sharp reflexions already considered in I) as

$$\begin{aligned} F(\varrho^*, \Upsilon, z^*) = \frac{2Qgb}{R} \sum_n \exp\left[\frac{2\pi i}{\lambda} ncz^* \sin\beta\right] \\ \times \sum_m \exp\left[\frac{2\pi i}{\lambda}(a_0+ma)z^* \sin\beta\cos\beta\right] \\ \times \sum_\nu \sum_{q=1}^{\infty} i^q \cos q(\varphi_{m,\nu}-\Upsilon) \\ \times J_q\left[\frac{2\pi}{\lambda}(a_0+ma)(\varrho^*-z^*\cos\beta)\sin\beta\right], \quad (1) \end{aligned}$$

using the symbols defined in I. The amplitude on any given layer plane of index l is therefore

$$\begin{aligned} F(\xi, \Upsilon, l) = \frac{2Qgb}{R} \sum_m \exp\left[2\pi i(a_0+ma)\frac{l}{c}\cos\beta\right] \\ \times \sum_\nu \sum_{q=1}^{\infty} i^q \cos q(\varphi_{m,\nu}-\Upsilon) J_q\left[\frac{2\pi}{\lambda}(a_0+ma)\xi\sin\beta\right]. \quad (2) \end{aligned}$$

In a practical diffraction experiment with a fibrous mineral there will be many fibres in the specimen with all possible orientations about the fibre axis. From such a specimen all that can be observed is the distribution of intensity given by

$$I(\xi, l) = \frac{1}{2\pi}\int_0^{2\pi} |F(\xi, \Upsilon, l)|^2 d\Upsilon. \quad (3)$$

This integral may be evaluated in the way used by Fock & Kolpinsky (1940) for diffraction from a single cylindrical layer. We introduce the abbreviations

$$\mathcal{E}(m) = \exp\left[2\pi i(a_0+ma)\frac{l}{c}\cos\beta\right],$$

$$\mathcal{J}(q, m) = i^q J_q\left[\frac{2\pi}{\lambda}(a_0+ma)\xi\sin\beta\right],$$

and let p_m be the number of repeating units in the circumference of the mth cylinder, i.e.

$$p_m = \frac{2\pi}{b}(a_0+ma)\sin\beta\,.$$

Hence

$$F(\xi, \Upsilon, l) = \frac{2Qgb}{R}\sum_m\sum_q \mathcal{E}(m)\mathcal{J}(q, m)\sum_\nu \cos q\left(\frac{2\pi\nu}{p_m}+\varepsilon_m-\Upsilon\right), \quad (4)$$

where ε_m is the azimuth of the initial point on a circle on the mth cylinder. Expression (4) is zero unless $q = Kp_m$ (where K is an integer), when, by substituting in (3) and rearranging, we obtain

$$I(\xi, l) = \frac{2Q^2g^2b^2}{\pi R^2}\sum_m\sum_{m'}\sum_q\sum_{q'}\mathcal{E}(m)\mathcal{E}^*(m')\mathcal{J}(q, m)\mathcal{J}^*(q', m')p_m p_{m'} \times\int_0^{2\pi}\cos q(\varepsilon_m-\Upsilon)\cos q'(\varepsilon_{m'}-\Upsilon)\,d\Upsilon\,. \quad (5)$$

The integral is zero unless $q = q'$, when the expression becomes

$$I(\xi, l) = \frac{2Q^2g^2b^2}{R^2}\left\{\sum_m\sum_q p_m^2|\mathcal{E}(m)|^2|\mathcal{J}(q, m)|^2 + \sum_m\sum_{m'}\sum_q{}_{(m\neq m')} p_m p_{m'}\mathcal{E}(m)\mathcal{E}^*(m')\mathcal{J}(q, m)\mathcal{J}^*(q, m') \times\cos q(\varepsilon_m-\varepsilon_{m'})\right\}. \quad (6)$$

The second term inside the brackets in expression (6) will become zero if it is averaged over a large number of cylindrical fibres in which the ε_m values are randomly distributed. This is a very probable arrangement in a real fibre specimen, and we may therefore neglect this term and expand (6) as

$$I(\xi, l) = \frac{2Q^2g^2b^2}{R^2}\sum_m\sum_{K=1}^{\infty} p_m^2 J_{Kpm}^2(p_m\xi/b^*)\,. \quad (7)$$

In silicate fibres, to which the theory is required to apply, the value of p_m is likely to be in the range 30–120 so that the Bessel functions involved are of very large orders. The properties of such Bessel functions are such that each term in the summation with respect to K is quite negligible for $\xi/b^* < 0{\cdot}9\,K$, and relatively small for $\xi/b^* > K+1{\cdot}0$. We may, therefore, to a first approximation regard each term of this summation as corresponding to a single diffuse reflexion of order K, and it is convenient to put $\xi/b^*=k$, which we regard as a continuous variable whose integral values are denoted by K.

As has been shown in § 2, the observed intensities will be given by $\xi LI(\xi, l)$. It is therefore convenient to compute the function $kI(\xi, l)$, which is proportional to the observed intensities after correction by the Lorentz factor. The summation

$$k\sum_m p_m^2 J_{Kpm}^2(p_m k)$$

has therefore been computed over the ranges $K-0{\cdot}2 < k < K+0{\cdot}5$ and for the values of the parameters a_0 and m given in Fig. 2, it being assumed that

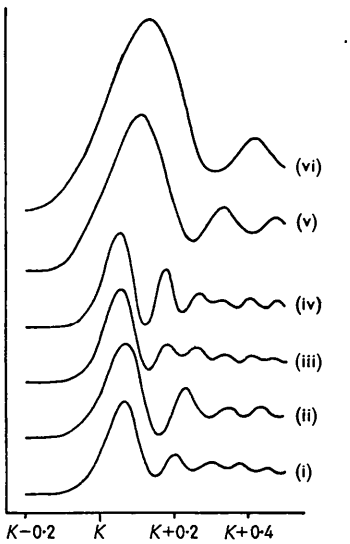

Fig. 2. Curves of $k\sum_m p_m^2 J_{Kpm}^2(p_m k)$ with the parameters

	K	a_0/a	m
(i)	1	4	0–7
(ii)	1	6	0–3
(iii)	1	6	0–7
(iv)	1	10	0–3
(v)	5	4	0–7
(vi)	10	4	0–7

The curves with the same value of K are normalized to the same peak height. Curves (v) and (vi) are to the same scale as curve (i).

$2\pi a = 5b$, which is true for chrysotile. The values of the Bessel functions were obtained from graphs constructed from the data given by Jahnke & Emde (1952). The results are shown in Fig. 2.

It is thus found that the diffuse reflexions from a simple cylindrical lattice (unmodified by the electron scattering function Q) have the following characteristics:

(i) The reflexions are unsymmetrical; they have a sharp 'head' and a long 'tail' extending towards higher values of k.

(ii) The peak of the reflexion is displaced from the integral value of $k = K$ towards higher values by a distance

$$\Delta k = 0{\cdot}84K^{0{\cdot}316}(\bar{p})^{-\frac{2}{3}}\,,$$

where $\bar{p}$ is the arithmetic mean value of p_m for the lattice considered. The peak intensity from a given lattice is proportional to $K^{0{\cdot}314}$ within the range investigated, and the intensity at $k = K$ is constant (within the computational error) at 45% of the peak value independently of K and $\bar{p}$.

(iii) The intensity does not die away altogether at

high values of k; it tends to a constant value of the order of

$$0{\cdot}69/[K^{\frac{1}{2}}(\bar{p})^{\frac{1}{2}}+0{\cdot}81K^{-\frac{1}{2}}(\bar{p})^{-\frac{1}{2}}]$$

of the peak value, for k large.

(iv) The 'tail' contains an oscillatory component which gradually dies away towards higher values of k. The amplitude of this component diminishes as the wall thickness of the cylindrical lattice increases, and also as the internal diameter decreases.

(v) The frequency of the oscillations in the 'tail' increases with the mean diameter of the lattice and diminishes with increasing order K.

(vi) Since (7) is independent of l, all $0Kl$ reflexions with the same value of K are of identical form.

(vii) Since (7) is independent of β, the position and form of the diffuse reflexions are independent of this angle.

4. An assemblage of atoms associated with each lattice point

In a real structure which is based on a cylindrical lattice there will be a distribution of atoms associated with each lattice point. These atoms may, however, be considered to lie at the points of lattices which are similar to (or sub-lattices of) the basic lattice, but with various values of the innermost radius a_0, the circumferential repeat b, and the initial angle ε_m. Since each layer of the structure is now considered to be of finite thickness, b will vary both within any one layer, and also between corresponding levels of different layers except on the neutral surface of the layers. The value of b on the neutral surface therefore constitutes the 'true' value of b for the structure, and it is convenient to define the position of an atom within a layer with reference to an origin on the neutral surface. As we have already found in the preceding section that the diffuse reflexions are independent of β we shall discuss only the case when $\beta = 90°$.

Let the jth atom associated with the νth lattice point of the mth layer have a scattering factor f_j and the cylindrical coordinates

$$\varrho = a_0+ma+x_j\,,$$
$$\varphi = \frac{b\nu}{a_0+ma}+\varepsilon_m+\frac{y_{m,j}}{a_0+ma+x_j}\,,$$
$$z = nc+z_j\,,$$

where $x_j, y_{m,j}, z_j$ are the radial, circumferential, and axial coordinates of this atom referred to an origin in the neutral surface. Then this atom lies on a cylindrical lattice with lattice parameters $a, b_{m,j}, c$, where $b_{m,j}$ is defined by

$$2\pi(a_0+ma+x_j) = p_m b_{m,j}\,.$$

We then proceed in the same way as before, and obtain as the analogue of equation (4)

$$F(\xi, \Upsilon, l) = \frac{2Q}{R}\sum_m\sum_j f_j \exp\left[2\pi i l\frac{z_j}{c}\right]$$
$$\times\sum_q \mathcal{J}(q, m, j)\sum_\nu \cos q\left(\frac{2\pi\nu}{p_m}+\frac{2\pi y_{m,j}}{p_m b_{m,j}}+\varepsilon_m-\Upsilon\right). \quad (8)$$

It then follows exactly as before that

$$I(\xi, l) = \frac{2Q^2}{R^2}\sum_m\sum_K p_m^2$$
$$\times\left\{\left|\sum_j f_j \exp\left[2\pi i l\frac{z_j}{c}\right] J_{Kpm}\left(p_m\frac{b_{m,j}}{b}k\right)\cos 2\pi\frac{Ky_j}{b}\right|^2\right.$$
$$\left.+\left|\sum_j f_j \exp\left[2\pi i l\frac{z_j}{c}\right] J_{Kpm}\left(p_m\frac{b_{m,j}}{b}k\right)\sin 2\pi\frac{Ky_j}{b}\right|^2\right\}. \quad (9)$$

Here we have put

$$y_{m,j}/b_{m,j} = y_j/b$$

since $y_{m,j}/b_{m,j}$ is independent of m, and a quantity y_j can therefore be conveniently defined by this relation.

It is not possible to calculate reflexion profiles from (9) except for a specific structure having known or assumed values of x_j, y_j, z_j, and f_j, and the application of (9) to the calculation of the reflexion profiles of chrysotile will be described in a subsequent paper. It may be pointed out here, however, that the results to be expected from (9) differ from those obtained from (7) in the following particulars:

(i) The various j Bessel functions will have different weights in the summations for different values of l, owing to the factor $\exp(2\pi i l z_j/c)$. Corresponding reflexions on different layer lines will therefore have different profiles, in general.

(ii) Owing to the factor $b_{m,j}/b$ in the argument of the Bessel function the positions of the maxima of the reflexions can no longer be simply predicted. However, the variations in this factor will not be sufficient to upset the conclusion that the maxima will be in the neighbourhood of $k = K$.

(iii) The effect of the atomic coordinates on the positions of the maxima may be to shift them either to greater or smaller values of ξ. We may therefore expect that they will on the average be related to K in the same way as has been found in § 3, but that there will be considerable scatter about the ideal values.

(iv) The profile of a reflexion will approximate to that derived from (7) if the atoms lie in special positions such that the contributions from all the atoms are negligible except for those which lie at or near a single value of x_j.

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The Diffraction of X-rays by a Cylindrical Lattice. III

BY E. J. W. WHITTAKER

Ferodo Limited, Chapel-en-le-Frith, Stockport, England

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Previous papers in this series have dealt with the mathematical theory of diffraction by circular cylindrical lattices. The results have now been confirmed by model optical diffraction experiments, and this method has been used to investigate diffraction by spiral cylindrical lattices and incomplete circular cylindrical lattices.

1. Introduction

In Parts I and II of this series (Whittaker, 1954, 1955) the concept of a cylindrical lattice has been defined, and the diffraction of X-rays by a circular cylindrical lattice has been investigated mathematically on account of its relevance to diffraction by chrysotile fibres and other related minerals. In Part I it was, however, pointed out that a cylindrically curved layer structure might well be expected to adopt a spiral form rather than the form of a set of coaxial circular cylinders. The mathematical theory for diffraction by a spiral cylindrical lattice was at that time still being investigated. However, this has proved intractable and recourse has therefore been taken to the technique of optical diffraction developed by Hanson, Lipson & Taylor (1953) to study the effect in this case. The theory of the importance of spiral cylindrical structures has been more fully developed independently by Jagodzinski & Kunze (1954), who have also proposed an approximate mathematical approach, but the experimental approach described here seems to be more fruitful. In order to facilitate comparison between the diffraction effects from spiral and circular cylindrical lattices, the latter have also been studied in the same way, and the results have confirmed the conclusions already reached in Parts I and II. Since in an actual fibrous specimen it must be anticipated that there will be present broken fibres and incomplete cylindrical layers, the diffraction effects from such structures are also of interest and have been investigated at the same time.

The optical diffraction apparatus developed by Hanson, Lipson & Taylor does not permit the study of diffraction patterns from three-dimensional objects, and it has therefore been necessary to investigate only the diffraction from plane circular and spiral lattices. However, this does not involve any serious limitation, since the diffraction pattern obtained from such a lattice is equivalent to the distribution of intensity on the zero-layer plane in reciprocal space for the corresponding cylindrical lattice. Moreover, we have already shown that, for a structure in which all the scattering matter is concentrated at the lattice points, the distribution of intensity in the diffuse reflexions is identical on all such layer planes, and it is also identical in the sharp reflexions if $\beta = \frac{1}{2}\pi$.

The optical transforms obtained are described in the logical order of increasing complexity, namely the transforms of circular, incomplete circular, and spiral arrays, and under each of these headings the transform of a single element of the array (single circle, spiral turn etc.) is considered before the complete lattice. Finally, comparisons are made in terms which are relevant to the interpretation of X-ray diffraction by fibres.

2. Experimental

The diffraction apparatus used was the actual apparatus described by Hughes & Taylor (1953). The pinhole source used was 10 microns in diameter in order to obtain the highest possible resolution. The masks were prepared with the pantograph punch to a scale of 0·321 mm./Å and each lattice point was represented by a hole 0·5 mm. in diameter. Examples are shown in Fig. 1. Most of the lattices studied had a and b dimensions corresponding to those of the cell of chryso-