Herrn Prof. Dr Rüdorff danke ich für wertvolle Diskussionen und apparative Unterstützung.

Literatur

BRODERSEN, K. & RÜDORFF, W. (1954). *Z. anorg. Chem.* **275**, 141.
BRODERSEN, K. & RÜDORFF, W. (1955). *Z. Naturforsch.* 9b, 164.
FEHÉR, F. (1941). *Z. Elektrochem.* **47**, 369.
Gmelin Kraut's Handbuch der anorganischen Chemie, (1914). Band V(2), S. 531.
LIPSCOMB, W. N. (1951*a*). *Acta Cryst.* **4**, 156.
LIPSCOMB, W. N. (1951*b*). *Acta Cryst.* **4**, 266.
MACGILLAVRY, C. H. & BIJVOET, J. M. (1936). *Z. Kristallogr.* A, **94**, 240.
NIJSSEN, L. & LIPSCOMB, W. N. (1952). *Acta Cryst.* **5**, 604.
RÜDORFF, W. & BRODERSEN, K. (1952). *Z. anorg. Chem.* **270**, 145.
RÜDORFF, W. & BRODERSEN, K. (1953). *Z. anorg. Chem.* **274**, 323.
VERWEEL, H. J. & BIJVOET, J. M. (1931). *Z. Kristallogr.* **77**, 122.
WIDMAN, R. (1910). *Z. anorg. Chem.* **68**, 1.

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

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The previous theoretical work presented in this series is extended to cover diffraction by regular circular cylindrical lattices with an oblique generating lattice, and by helical circular cylindrical lattices.

1. Introduction

The discussion of diffraction by cylindrical lattices in previous papers in this series (Whittaker, 1954, 1955*a*, *b*) has been confined to those cases in which the two-dimensional lattice inscribed on the cylindrical layers is primitive and rectangular and has one axis oriented perpendicular to the cylinder axis. A particular case of diffraction by a helical structure has also been discussed by Jagodzinski & Kunze (1954). Now that the possible types of cylindrical lattices have been enumerated and classified (Whittaker, 1955*c*), the discussion is extended to diffraction by regular cylindrical lattices with an oblique generating lattice, and by those belonging to the helical series. The results for a regular circular cylindrical lattice with a centred generating lattice are readily deduced from the previous discussion of cylindrical structures containing more than one scattering centre associated with each lattice point (Whittaker, 1954, 1955*a*), and they have also been given in a recent paper by Waser (1955). They are therefore not discussed further, but some points of interest which arise in connexion with centred helical lattices are pointed out.

2. The anorthic cylindrical lattice of the first kind

The geometrical characteristics of this lattice type have been defined previously (Whittaker, 1955*c*). Consideration of diffraction by such a lattice completes the diffraction theory for regular circular cylindrical lattices, since the monoclinic lattice of the second kind constitutes a special case obtained by putting $\beta = \frac{1}{2}\pi$. The coordinate systems used are the same as those defined in Part I (Whittaker, 1954).

The coordinates of the lattice point denoted by the set of integers m, ν, n are

$$\varrho = \varrho_m = a_0+ma\ ,$$
$$\varphi = \varphi_{m,\nu,n} = \frac{b\nu+nc\cos\alpha}{(a_0+ma)\sin\beta}+\varepsilon_m\ ,\dagger$$
$$z = z_n = nc\sin\alpha\ ,$$

† The quantity denoted by ε_m is the value of φ for the initial point of the mth cylinder and on the level $n = 0$. This quantity was denoted by δ_m in Part I and by ε_m in Part II. The latter convention is followed here, especially as δ_m is a convenient symbol for another parameter used in the description of helical lattices (Whittaker, 1955*c*).

where α is the oblique angle included between the axes of the generating lattice. Proceeding in exactly the same way as in Part I, we therefore obtain

$$F(\varrho^*, \Upsilon, z^*) = \frac{Qgb}{R} \sum_m \sum_n \sum_\nu \exp\left(\frac{2\pi i}{\lambda} ncz^* \sin\alpha \sin\beta\right)$$
$$\times \exp\left[\frac{2\pi i}{\lambda}(a_0+ma)z^* \sin\beta \cos\beta\right]$$
$$\times J_0\left[\frac{2\pi}{\lambda}\xi(a_0+ma)\sin\beta\right]$$
$$+\frac{2Qgb}{R}\sum_{q=1}^{\infty}\sum_m \sum_n \sum_\nu \exp\left(\frac{2\pi i}{\lambda} ncz^* \sin\alpha \sin\beta\right)$$
$$\times \exp\left[\frac{2\pi i}{\lambda}(a_0+ma)z^* \sin\beta \cos\beta\right]$$
$$\times i^q \cos q(\varphi_{m,\nu,n}-\Upsilon)J_q\left[\frac{2\pi}{\lambda}\xi(a_0+ma)\sin\beta\right]. \quad (1)$$

The first part of (1), which involves the zero-order Bessel function, is identical with the formula obtained in Part I for the sharp $h0l$ reflexions, apart from the replacement of c by $c \sin\alpha$, which is in fact still the axial spacing between successive circles of points. This term therefore requires no further discussion.

The second part of (1) differs from the corresponding formula discussed in Part II in that the summation with respect to n cannot be taken outside the other summations because n is involved in $\varphi_{m,\nu,n}$. However, the same considerations lead to the restriction

$$q = Kp_m$$

and to the same elimination of cross terms in the square of the modulus, and we therefore obtain

$$I(\xi, l) = \frac{2Q^2g^2b^2}{R^2}\sum_K \sum_m p_m^2 J^2_{Kp_m}(p_m k)$$
$$\times \sum_n \sum_{n'} \exp\left[\frac{2\pi i}{\lambda} cz^*(n-n')\sin\alpha \sin\beta\right]$$
$$\times \cos\left[2\pi\frac{Kc}{b}(n-n')\cos\alpha\right]. \quad (2)$$

The summation over n and n' is more conveniently expressed in the form

$$\tfrac{1}{2}\sum_n \sum_{n'} \exp\left[2\pi ic(n-n')\left(\frac{z^*}{\lambda}\sin\alpha\sin\beta+\frac{K}{b}\cos\alpha\right)\right]$$
$$+\tfrac{1}{2}\sum_n \sum_{n'} \exp\left[2\pi ic(n-n')\left(\frac{z^*}{\lambda}\sin\alpha\sin\beta-\frac{K}{b}\cos\alpha\right)\right].$$

It is therefore non-zero, and has the usual profile, only near the values of z^* given by

$$z^* = \frac{\lambda l}{c\sin\alpha\sin\beta} \pm \frac{K\cot\alpha}{b\sin\beta}.$$

The diffuse $0Kl$ reflexions are thus identical in profile with those discussed in Part II, but they occur in pairs symmetrically placed above and below the layer lines defined by the sharp $h0l$ reflexions. The separation of the pairs is the same for all the layer lines but is proportional to the index K and also to $\cot\alpha$.

3. The anorthic cylindrical lattice of the second kind

Consideration of the diffraction by such a lattice suffices for all the helical circular lattices, since the results for the other three types may be obtained by inserting the appropriate special values of α and β. The nomenclature of the geometrical parameters of the helical lattice follows that previously defined by the author (Whittaker, 1955c). In order to avoid ambiguity, however, it is necessary to adopt a sign convention for the angle δ_m between the b axis and a plane perpendicular to the cylinder axis, and also for N, the order of the helix. The convention adopted is that these parameters are positive if the helices formed by the b and c axes are of opposite hand and negative if they are of the same hand. The positive directions of these axes are taken to include the obtuse angle α. With these conventions, the νth lattice point on the nth row of the generating lattice of the mth cylinder has the coordinates

$$\varrho = \varrho_m = a_0+ma,$$
$$\varphi = \varphi_{m,\nu,n} = \frac{2\pi\nu}{p_m}\cos^2\delta_m(1+\tan\delta_m\cot\alpha)$$
$$-\frac{2\pi n}{N}\sin^2\delta_m(1-\cot\delta_m\cot\alpha)+\varepsilon_m,$$
$$z = z_{m,\nu,n} = t\cos^2\delta_m\left(n+\frac{N\nu}{p_m}\right)(1+\tan\delta_m\cot\alpha)+\frac{\varepsilon_m}{2\pi}Nt.$$

The diffracted amplitude is therefore given by an expression of exactly the same form as (1) with the appropriate value of $z_{m,\nu,n}$ replacing $nc\sin\alpha$ in the first exponential factor in each summation.

For brevity we put

$$\cos^2\delta_m(1+\tan\delta_m\cot\alpha) = T$$

and

$$\sin^2\delta_m(1-\cot\delta_m\cot\alpha) = U.$$

Then in the term involving the zero-order Bessel function the summations with respect to n and ν may be separated (within the summation with respect to m). They are

$$\sum_n \exp\frac{2\pi i}{\lambda}z^*ntT\sin\beta \quad (3)$$

and

$$\sum_\nu \exp\frac{2\pi i}{\lambda p_m}z^*N\nu tT\sin\beta. \quad (4)$$

Expression (3) is appreciable only near

$$z^* = l\lambda/tT\sin\beta,$$

and hence (4) is zero unless Nl is a multiple of p_m. In the case of a fibrous silicate we are interested only in values of Nl less than about 10 and p_m greater than 30. Hence, within these practical limits, the term involving the zero-order Bessel function is relevant only to the zero layer line. Here it will give rise to sharp $h00$ reflexions identical with those discussed in Part I.

In the term involving higher-order Bessel functions the summations involving n and ν may be put into the form

$$\begin{aligned}&\tfrac{1}{2}\exp\left(\frac{iz^*}{\lambda}\varepsilon_m Nt\sin\beta+iq\varepsilon_m-iq\Upsilon\right)\\ &\qquad\times\sum_n\exp\left[2\pi in\left(\frac{z^*}{\lambda}tT\sin\beta-q\frac{U}{N}\right)\right]\\ &\qquad\times\sum_\nu\cos\left[2\pi\frac{T\nu}{p_m}\left(q+z^*\frac{Nt}{\lambda}\sin\beta\right)\right]\\ &+\tfrac{1}{2}\exp\left(\frac{iz^*}{\lambda}\varepsilon_m Nt\sin\beta-iq\varepsilon_m+iq\Upsilon\right)\\ &\qquad\times\sum_n\exp\left[2\pi in\left(\frac{z^*}{\lambda}tT\sin\beta+q\frac{U}{N}\right)\right]\\ &\qquad\times\sum_\nu\cos\left[2\pi\frac{T\nu}{p_m}\left(q-z^*\frac{Nt}{\lambda}\sin\beta\right)\right].\end{aligned}\qquad(5)$$

The usual considerations then show that one or other of these expressions is non-zero only when

$$q = Kp_m \mp Nl$$

and

$$z^* = \frac{l\lambda}{t\sin\beta}\pm\frac{K\lambda}{b\sin\beta}\sec\delta_m\cot(\alpha+\delta_m)\,,$$

i.e.

$$\zeta = \frac{l\lambda}{t}\pm\frac{K\lambda}{b}\sec\delta_m\cot(\alpha+\delta_m)\,,$$

where the upper signs refer to the first half of the expression (5).

When $K = 0$ the reflexions lie on the layer lines to be expected from a structure with an axial repeat of t. The expression for their amplitude is given by

$$F(\varrho^*,\Upsilon,l) = \frac{Qgb}{R}i^{Nl}\exp(iNl\Upsilon)\times\sum_m p_m\exp\left(2\pi\frac{il}{t}\varrho_m\cos\beta\right)J_{Nl}\left(\frac{2\pi}{\lambda}\xi\varrho_m\sin\beta\right).\qquad(6)$$

This result differs from that for the sharp reflexions from a regular cylindrical lattice only in that it contains a phase factor outside the summation (which will not affect the intensity) and that it contains the Bessel function of order Nl instead of zero. The latter difference will have a negligible effect except close to $\xi = 0$, where the meridional reflexions will be split into two as has already been discussed by Jagodzinski & Kunze (1954).

When $K \neq 0$ the reflexions occur in pairs above and below the layer lines, as in the case discussed in § 2, but these pairs of reflexions are dissimilar, since they depend on terms involving Bessel functions of different orders, Kp_m+Nl and Kp_m-Nl. The two reflexions in each pair therefore have similar profiles but lie at slightly different values of ξ. Also, since the separation of the members of the pair depends on δ_m as well as on α, the contributions to the reflexions from each cylindrical layer of the lattice lie in general at slightly different values of ζ. If the resolution in a diffraction experiment is sufficient and if the values of δ_m for the different layers present in a macroscopic specimen are sufficiently different (which will depend on the value of N and the distortions in the layers) the oscillations of the Bessel functions will no longer be smoothed out, and the $0Kl$ reflexions will contain a fine structure. This will consist of two sets of fringes, one running parallel to the ξ axis corresponding to the separation of the reflexions from different cylindrical layers, and the other inclined at a small angle to the ζ axis, corresponding to the varying positions of the maxima and minima of $J^2_{Kp_m\pm Nl}(kp_m/\sin(\alpha+\delta_m))$ in terms of k, as a function of m.

No simplification of the above phenomena occurs if we put $\alpha = \frac{1}{2}\pi$. However, if we postulate appropriate distortions in the cylindrical layers to make

$$\alpha+\delta_m = \tfrac{1}{2}\pi$$

on all such layers, then we obtain the special case which has been treated previously by Jagodzinski & Kunze (1954). In this case the reflexions are all confined to the same layer lines, and the profile of an $0Kl$ reflexion is given by

$$\frac{Q^2g^2b^2}{R^2}\sum_m p_m^2\{J^2_{Kp_m-Nl}(p_mk)+J^2_{Kp_m+Nl}(p_mk)\}\,.\qquad(7)$$

Fig. 1 shows the form of a single term of (7) for several values of Nl (half-integral values are included for a reason which will appear in § 4). It is evident that the profiles of $0Kl$ reflexions from such a lattice will exhibit a marked dependence on l, unlike the corresponding reflexions from a regular cylindrical lattice.

4. Centred lattices

If the generating lattice is centred it may in general be considered to consist of two congruent interpenetrating lattices with a relative displacement. A phase difference in the rays diffracted by the two lattices is thereby introduced and leads to the usual extinction of reflexions with $K+l$ odd. This has been formally proved by Waser (1955). The analysis breaks down, however, if the lattice is helical and the value of N is half-integral. In these circumstances the lattice may still be resolved into two interpenetrating mutually displaced lattices of a sort, but neither of these is a helical lattice in the sense in which this term has been defined, and the above diffraction theory cannot be applied to them separately. The lattice must therefore be considered as a whole.

If N is half-integral it follows that p_m is also half-integral, but there are $2p_m$ lattice points in every nth row of unit cells of the generating lattice. With this slight change in the significance of n, and with the

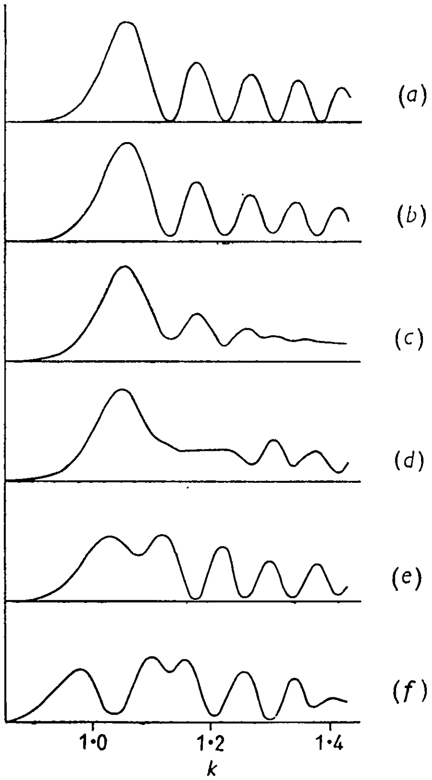

Fig. 1. $J^2_{pm-Nl}(kp_m)+J^2_{pm+Nl}(kp_m)$ for $p_m = 65$ and the following values of Nl: (a) 0; (b) 0·5; (c) 1·0; (d) 1·5; (e) 2·5; (f) 5·0. In order to correspond strictly with the diffracted intensity from a single layer of a helical cylindrical lattice, p_m should be half-integral when Nl is half-integral; but no appreciable difference is produced in the curves by a change of 0·5 in p_m.

summation with respect to ν extended to cover the range $1 \leqslant \nu \leqslant 2p_m$, all the formulae of § 3 are valid, and the conditions for the diffracted amplitude to be non-zero remain true. (When it is non-zero the amplitude is, of course, double that from a primitive lattice; analytically this arises from doubling the range of the summation over ν.) However, the condition

$$q = Kp_m \mp Nl$$

includes the condition that $K+l$ be even, since only integral values of q are involved in the expansion

$$\exp\,(ix\cos\theta) = J_0(x)+\sum_{q=1}^{\infty} i^q \cos q\theta J_q(x)\;.$$

The restriction on the indices therefore arises analytically from a restriction on the orders of the Bessel functions, instead of in the usual way by the cancelling of trigonometric terms of opposite sign. Physically, of course, the restriction arises in precisely the same way as usual.

It is evident on general grounds that centred cylindrical lattices of the type c_n (Whittaker, 1955c) will diffract in exactly the same way as a primitive lattice, except that $h00$ reflexions will occur only when h is a multiple of n.

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References

Jagodzinski, H. & Kunze, G. (1954). *Neues Jb. Miner. Mh.* p. 137.
Waser, J. (1955). *Acta Cryst.* 8, 142.
Whittaker, E. J. W. (1954). *Acta Cryst.* 7, 827.
Whittaker, E. J. W. (1955a). *Acta Cryst.* 8, 261.
Whittaker, E. J. W. (1955b). *Acta Cryst.* 8, 265.
Whittaker, E. J. W. (1955c). *Acta Cryst.* 8, 571.

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

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Determination of the absolute configuration of optically active complex ion $[Coen_3]^{3+}$ by means of X-rays.

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The absolute configuration of optically active tris-ethylene-diamine cobalt (III) complex ion has been determined using the absorption-edge technique (Bijvoet, Peerdeman & van Bommel, 1951). Hitherto unrecorded double salts having the composition 2D-$[Coen_3]Cl_3.NaCl.6H_2O$ and 2L-$[Coen_3]Cl_3.NaCl.6H_2O$ (en: ethylenedi-