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Diffraction Effects in X-ray Fourier Syntheses Due to Non-observed 'Weak Reflexions'

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A crystal structure in which displacements of certain atoms suddenly occur at long, regular intervals gives strong X-ray reflexions only in the close vicinity of reciprocal-lattice points, corresponding to the period of the basic sublattice. If the remaining reflexions, which may be very weak, are not detectable by the experimental method applied, then larger diffraction effects can appear in the Fourier calculations of the electron-density function based on the observed X-ray data.

Introduction

In connexion with the determination of the crystal structure of a tungsten oxide of composition $W_{20}O_{58}$ (β tungsten oxide), recently performed at this Institute (Magnéli, 1950*a*, *b*), a very peculiar diffraction effect was observed in the Fourier syntheses. This effect will be discussed here for a model linear structure and also for the case actually observed.

A linear model

Let a one-dimensional lattice of identity period a contain a number, say eight, of scattering units ('atoms') arranged as follows (cf. Fig. 1 (*d*)):

$$x_1=\tfrac{1}{15}a,\quad x_2=\tfrac{3}{15}a,\quad x_3=\tfrac{5}{15}a,\quad x_4=\tfrac{7}{15}a,$$
$$x'_1=a(1-\tfrac{1}{15}),\quad x'_2=a(1-\tfrac{3}{15}),\quad x'_3=a(1-\tfrac{5}{15}),$$
$$x'_4=a(1-\tfrac{7}{15}).$$

This lattice is evidently centro-symmetrical, and the interatomic spacing is $\tfrac{2}{15}a$ except for the atoms indexed 4 and 4′, where it is $\tfrac{1}{15}a$, thus representing a recurrent displacement. The identity period of the 'sublattice' is $\tfrac{2}{15}a$.

The scattering power of the atom being f, the structure factor of the nth-order reflexion will be given by

$$F(n)=\sum_i f\cos 2\pi n\frac{x_i}{a}.$$

In order to suppress the influence of the termination of the Fourier series a convergence factor ('temperature factor') $e^{-\alpha(n/a)^2}$ is introduced (Bragg & West, 1930). The lattice may then be represented by the series

$$\rho(x)=\frac{1}{a}\sum_n\left[F(n)\,e^{-\alpha(n/a)^2}\right]\cos 2\pi n\frac{x}{a}. \qquad (1)$$

For the numerical calculations a, f and α are given the arbitrary values 1, 1 and 2 respectively, the n/a (or $\sin\theta/\lambda$) dependence of the scattering power being implied in the convergence factor. The Fourier coefficients of (1) will thus acquire the values given in Fig. 2. In this reciprocal representation the larger values occur only close to the reciprocal-lattice points of the substructure of identity period $\tfrac{2}{15}a$. If the highest wave number obtainable with the applied

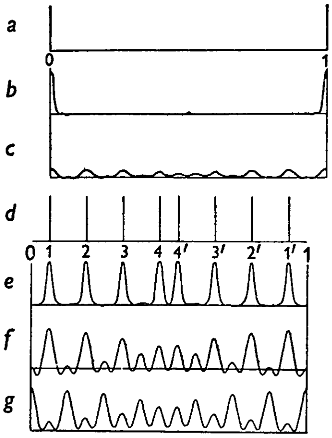

Fig. 1. (*a*) A linear lattice containing one atom in the unit period. (*b*) The corresponding ρ function derived on the basis of wave numbers up to 40. (*c*) The ρ function obtained when using the reflexions of 0th, 7th, 8th and 15th order only. (*d*) A linear lattice, the atoms of which are uniformly distributed with the exception of one pair of atoms (4 and 4′). This shorter distance thus represents the dislocation of the atoms, occurring after long periods. (*e*) The corresponding ρ function calculated by summation over all wave numbers up to 40. (*f*) The ρ function obtained when omitting all weak interferences (|Fourier coefficients| > 4). (*g*) The Patterson function derived on the basis of the same reflexions as were used in (*f*).

radiation is 40, it will correspond to a wave-length slightly longer than $\frac{1}{20}a$, thus allowing a reliable reproduction of the lattice. A calculation of the ρ function on the basis of all these Fourier coefficients gives accordingly the curve illustrated in Fig. 1 (*e*). It is evident that the influence of the termination of the series at $n=40$ is practically insignificant.

However, if, in studying a spectrum such as the one mentioned above, the method of recording the interferences is not sensitive enough to reveal the existence of the weaker ones, this will correspond to the omission of a great number of terms in the Fourier series and cause considerable diffraction effects. This case may be studied by investigating the diffraction image given by one single atom, which, for convenience, is placed at the origin of the unit period (Fig. 1 (*a*)). The Fourier coefficients will now be represented by the product of the scattering factor f and the converging factor $e^{-\alpha(n/a)^2}$. Summation over all values of n of course will give a curve showing a single maximum within the period (Fig. 1 (*b*)). If the summation is restricted to the wave numbers which correspond to the highest values of the Fourier coefficients in Fig. 2, the function will take the form illustrated in Fig. 1 (*c*) (calculated for $|F(n)\,e^{-\alpha(n/a)^2}|>4$). The heavy peaks of Fig. 1 (*b*) are now replaced by a series of major or minor maxima occurring at every fifteenth of the identity period. This diffraction image may be described as consisting of two interpenetrating systems of maxima, the magnitudes of which show a steady decrease as x increases from zero for one system and decreases from a for the other. The spacing between the peaks of each system is $\frac{2}{15}a$.

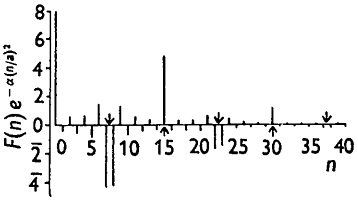

Fig. 2. Fourier coefficients derived for the linear lattice reproduced in Fig. 1 (*d*). The intersection points between the reciprocal-lattice planes of the substructure and the n axis are indicated by arrows.

If only the major Fourier coefficients are considered, every atom in the primary linear lattice will be the origin of a diffraction image such as the one now described. By superimposing the suitably displaced curves for all the atoms ($x=\frac{1}{15}a$, $\frac{3}{15}a$, etc.), the corresponding function for the complete lattice is thus obtained (Fig. 1 (*f*); this curve may of course also be derived from (1) by summation over the proper wave numbers). It is remarkable that from this point of view the peak corresponding to any one atom owes its size, for the most part, to contributions from the diffraction fringes of the other atoms of the lattice. The function may be described in an analogous way as was the 'one-atom curve' mentioned above. Here, however, each of the interpenetrating systems of maxima corresponds to a set of adjacent, uniformly distributed atoms of the lattice, and to a number of accessory 'ghost maxima'.

The wave numbers used in the last summation, namely, $n=0$, 7, 8 and 15, to some extent correspond to the zero-, first- ($n=7$ and 8) and second- ($n=15$) order reflexions when using a radiation of $\frac{15}{2}$ times the wave-length of that assumed in the preceding discussion. From this point of view, the 'effective wave-length' by far exceeds the interatomic distances; it also seems quite natural that the calculated function does not give a true image of the arrangement of the atoms but a series of diffraction fringes.

The derivation of the Patterson function is analogous to that of the electron-density function, except that the squares of the Fourier coefficients of the latter enter as coefficients into the Patterson series. The strong reflexions will thus have a far more dominating influence here, and omission of the weak ones will not cause serious distortion of the curve. This is evident from Fig. 1 (*g*), showing the Patterson function as calculated using the wave numbers $n=0$, 7, 8 and 15. The magnitudes of the maxima are in approximate agreement with those required by the assumed lattice, i.e.

$$A:B:C:D:E:F:G:H=8:1:7:2:6:3:5:4.$$

The observed case of β tungsten oxide

The case of β tungsten oxide actually investigated (Magnéli, 1950 *b*) is closely analogous to the structure model discussed above. A preliminary treatment of the structure could be made by assuming it to contain only one kind of atom, since the scattering power of oxygen is very small in comparison with that of tungsten.

The single crystals of the oxide used when taking the Weissenberg photographs formed extremely thin needles, and in spite of ample exposure very weak patterns were obtained. Reflexions with low values of the structure factor were thus not recorded. Fig. 3 illustrates the appearance of the reciprocal-lattice plane *h*0*l*.* The concentration of all the observed reflexions close to reciprocal-lattice points corresponding to a simple cubic lattice of metal atoms (cf. a lattice of ReO_3 type) gave the clue to the problem of finding the signs of the various structure factors $F(h0l)$. The projection of the ρ function thus calculated is schematically reproduced in Fig. 4 (*a*). The maxima are arranged on two interpenetrating systems of square networks, mutually related by the centrosymmetry of the figure. There is a continuous decrease in the magnitude of the peaks as z increases from zero for one system and decreases from unity for the other.

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* Similar X-ray photographs are given by an intermediate phase in the system molybdenum trioxide–tungsten trioxide (Magnéli, 1949). An investigation of the structure of this compound is in progress.

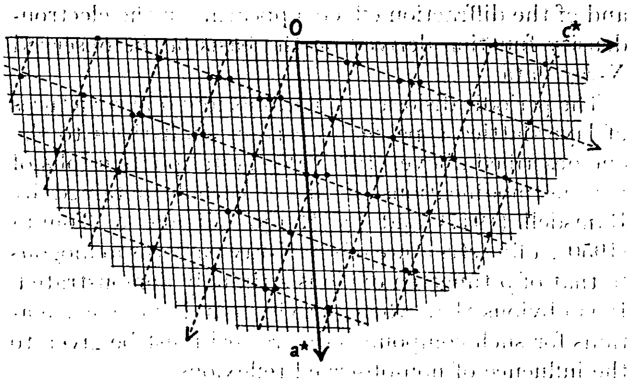

Fig. 3. The reciprocal-lattice plane $h0l$ of β tungsten oxide. Lattice points of observed reflexions are represented by dots. The networks corresponding to the substructure and the real structure are indicated by broken and full lines respectively.

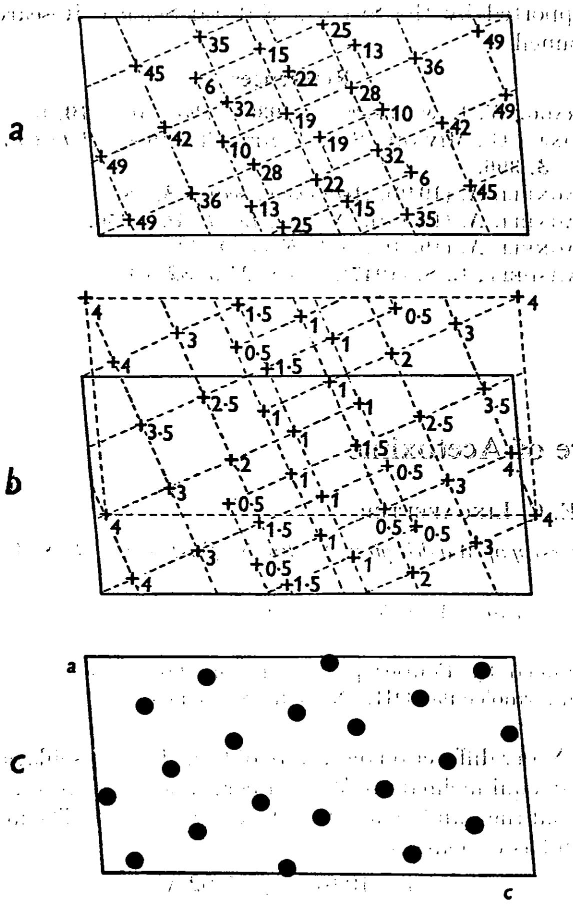

Fig. 4 (a) Schematic representation of the projection parallel to the b axis of the ρ function of β tungsten oxide. The figures denote the heights of the maxima above the fairly smooth background. The maxima are arranged on two interpenetrating systems of square networks, indicated by broken lines. (b) The diffraction image for one tungsten atom calculated on the basis of only those wave numbers which correspond to observed reflexions of β tungsten oxide. The heights of the maxima are given on the same scale as those of Fig. 4 (a). (For convenience the atom was placed at the origin of an auxiliary cell, indicated by broken lines.) (c) The tungsten positions of β tungsten oxide.

In order to get a more detailed understanding of the origin of these maxima, the diffraction image of one tungsten atom has been derived as for the 'one-atom curve' of the linear model mentioned above. The resulting projection is illustrated in Fig. 4 (b). The heavy peak, corresponding to a true image of the atom, is broken up into a multitude of diffraction maxima, distributed as are the maxima of the original projection. The latter are evidently built up of contributions from the diffraction maxima originating from all the metal atoms constituting the lattice.

It was assumed that the twenty highest maxima of the ρ projection correspond to tungsten positions (Fig. 4 (c)). This assumption was fully verified by the fair agreement found to exist between calculated and observed structure-factor values (cf. Fig. 5) and by the complete conformity between the projection of the ρ function derived on the basis of the observed data (Fig. 4 (a)) and the corresponding projection obtained from the calculated $F(h0l)$ values, when omitting those below the limit of visibility.

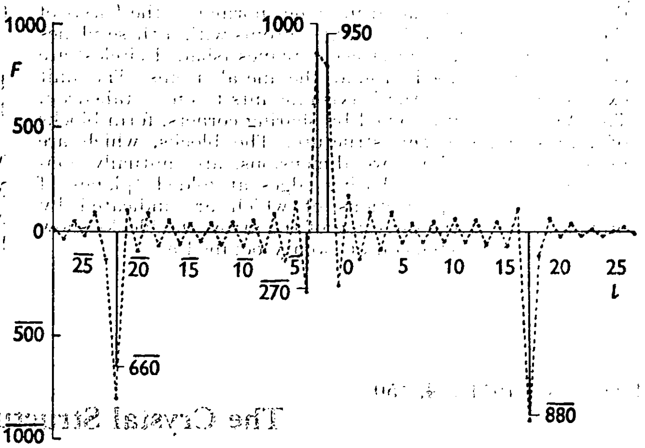

Fig. 5. Comparison between observed and calculated structure factors for reflexions $30l$ of β tungsten oxide. The observed values are indicated by heavy lines, and the calculated values, marked with small rings, are connected by broken lines. The intensity of the reflexion $30\bar{4}$ is at the limit of visibility in the Weissenberg photograph.

The structure of β tungsten oxide thus arrived at is illustrated in Fig. 6. The sites of the oxygen atoms, which are too light to give considerable contributions to the X-ray reflexions, have been derived from comparisons with previously known oxide structures and from spatial considerations. The lattice consists of blocks, infinitely extended in two dimensions, of almost ideal ReO_3 structure. Adjacent blocks are cemented by folded planes and show a mutual displacement of the atoms. This dislocation is connected with the different ways of joining the fundamental structure elements of WO_6 octahedra, which within the blocks have corners in common, but share edges at the border planes.

This dislocation of the metal atoms, suddenly occurring after long periods, is evidently the cause of the peculiar X-ray pattern given by β tungsten oxide, and of the diffraction effects appearing in the electron-density function derived on the basis of the observed X-ray data.

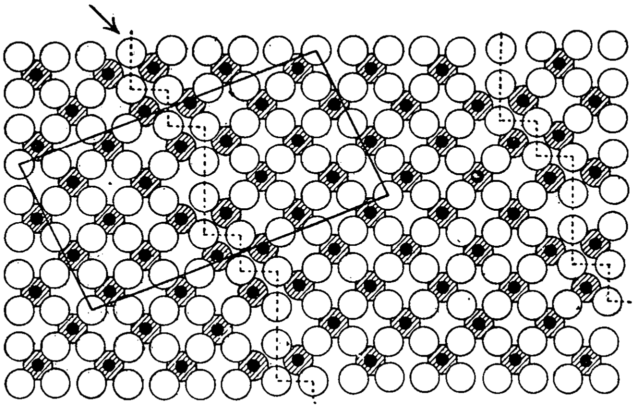

Fig. 6. The structure of β tungsten oxide. The tungsten atoms (black circles) are situated in planes normal to the b axis of the monoclinic unit cell. Oxygen atoms within these planes (open circles) and in interjacent planes (shaded circles) are octahedrally grouped around the metal atoms. The unit extension parallel to the b axis amounts to one octahedron. The WO_6 octahedra, joined by sharing corners, form blocks of almost regular $D0_9$ structure. The blocks, which are infinitely extended in two dimensions, are mutually connected by octahedra, sharing edges at folded 'planes of dislocation', the projections of which are indicated by broken lines. In the direction of the arrow the blocks show a characteristic extension of twenty octahedra.

The periodic dislocation of atoms found in structures of layer-lattice type shows certain similarities to the one described above. In single-crystal photographs of various modifications of silicon carbide obtained by Ramsdell (1947) and by Honjo, Miyake & Tomita (1950), a fine structure of the X-ray patterns analogous to that of β tungsten oxide is strikingly demonstrated. It is obvious that when carrying out Fourier calculations for such compounds due regard must be given to the influence of non-observed reflexions.

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The Crystal Structure of Acetoxime

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The crystal structure of acetoxime has been determined by Fourier projections on (001). The structure consists of sheets of planar trimers having intermolecular OH...N hydrogen bonds.

Introduction

Since investigations of acetoxime in the melt and in solution (Caughlan, 1941) indicate association to a higher degree than dimers, the crystal structure has been investigated in order to determine the degree of association in the solid state as well as the configuration of the molecule.

Preliminary crystallographic data

Because of the appreciable vapor pressure of acetoxime at room temperature, suitable crystals were readily grown by sublimation. However, for the same reason, it was found necessary to enclose the crystals with a thin film of formvar (Roth & Harker, 1948).

X-ray diffraction data were obtained from oscillation and equi-inclination Weissenberg photographs taken about the a and c axes of the hexagonal lattice. The unit cell has dimensions

$$a_0 = 10{\cdot}61, \quad c_0 = 7{\cdot}02\,\text{A}.$$

and contains 6 molecules. (Calculated density, 1·057 g.cm.$^{-3}$; observed, 1·045 g.cm.$^{-3}$.) Copper radiation ($K\alpha = 1{\cdot}5418$ A.) was used and the camera diameter was calibrated with NaCl ($a_0 = 2{\cdot}8197$ A.).

The only extinction observed was ($00l$) for l odd. This, combined with the Laue symmetry $C6/m$, indicated the space groups $C6_3$ or $C6_3/m$. The excellent cleavage parallel to (001), the exceptionally high intensity of the ($00l$) diffractions, and the identity in the intensity dis-