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Some apparent periodic errors in the crystal lattice of the molecular complexes of 4:4′-dinitrodiphenyl with 4-iodo- and 4-bromodiphenyl

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[Plate 23]

Oscillation photographs from crystals of the complexes of 4:4′-dinitrodiphenyl with 4-bromo- and 4-iododiphenyl show a mixture of sharp and diffuse spots. When the oscillation is about the *c*-axis the spots on every seventh layer-line are observed to be sharp, those on all the other lines being diffuse. The diffuseness varies from line to line, but in all cases corresponds to an elongation of the maxima of the interference function in the reciprocal-lattice space in the b^*-direction. The spacing of the diffuse layer-lines in the *c*-axis photographs from the complex with 4-bromodiphenyl is anomalous, and the positions of the lines correspond to those of optical ghosts accompanying the sharp layer-lines, such as would be expected if a fundamental spacing of 3·69 A were periodically distorted, the period of the distortion being rather less than $3\frac{1}{2}$ times that of the fundamental spacing. The diffuseness of the spots suggests that the structure also contains faults in the *b*-direction. A suggested explanation of the effects in terms of the structure is put forward.

In the second part of the paper, a mathematical discussion of diffraction by a simplified model, consisting of a lattice with a periodic error in spacing in the *c*-direction, and faults consisting of sudden random changes in the phase of a periodic error in lattice planes perpendicular to the b^*-axis, is discussed, and it is shown that the diffraction pattern given by such a structure exhibits features similar to those observed.

INTRODUCTION

The crystal structures of a number of molecular complexes of 4:4′-dinitrodiphenyl with other 4- and 4:4′-substituted diphenyl compounds have been investigated by one of us (Saunder 1946, 1947). Although the compounds examined vary considerably both in crystal symmetry and in the ratio of the two components of the complex, the underlying structure is undoubtedly of the same general type for all of them. The typical arrangement may be taken as that in the complex of 4:4′-dinitrodiphenyl with 4-hydroxydiphenyl in the ratio of three molecules of the first to one of the second, the structure of which has been fully determined (Saunder 1946). Two of the complexes examined, those with 4-bromo- and 4-iododiphenyl, give X-ray photographs showing certain peculiarities, which are of considerable interest from the optical point of view, and which it is the purpose of this paper to discuss.

A general idea of the type of structure to which all complexes of the kind considered approximate may be given as follows. The dinitrodiphenyl molecules form layers in face-centred array, as shown in figure 1. In any given crystal, the molecules will not in general lie exactly in these idealized planes, but they never depart greatly from them. Suppose a series of such planes to lie one above the other with a spacing of about 3·7 A. The dinitrodiphenyl molecules in any one layer are denoted by *A* in figure 1, and those in any row parallel to *a* are so placed that a gap is left between adjacent nitro groups. When a series of superposed layers is considered, it will be seen that these gaps produce a set of tubular cavities, also in face-centred array, running through the structure. The characteristic molecules of the complex, in the cases to be considered, the 4-bromo- and 4-iododiphenyl molecules, occupy these tubular cavities. They are seen end-on in figure 1, and are denoted by *B*. The general

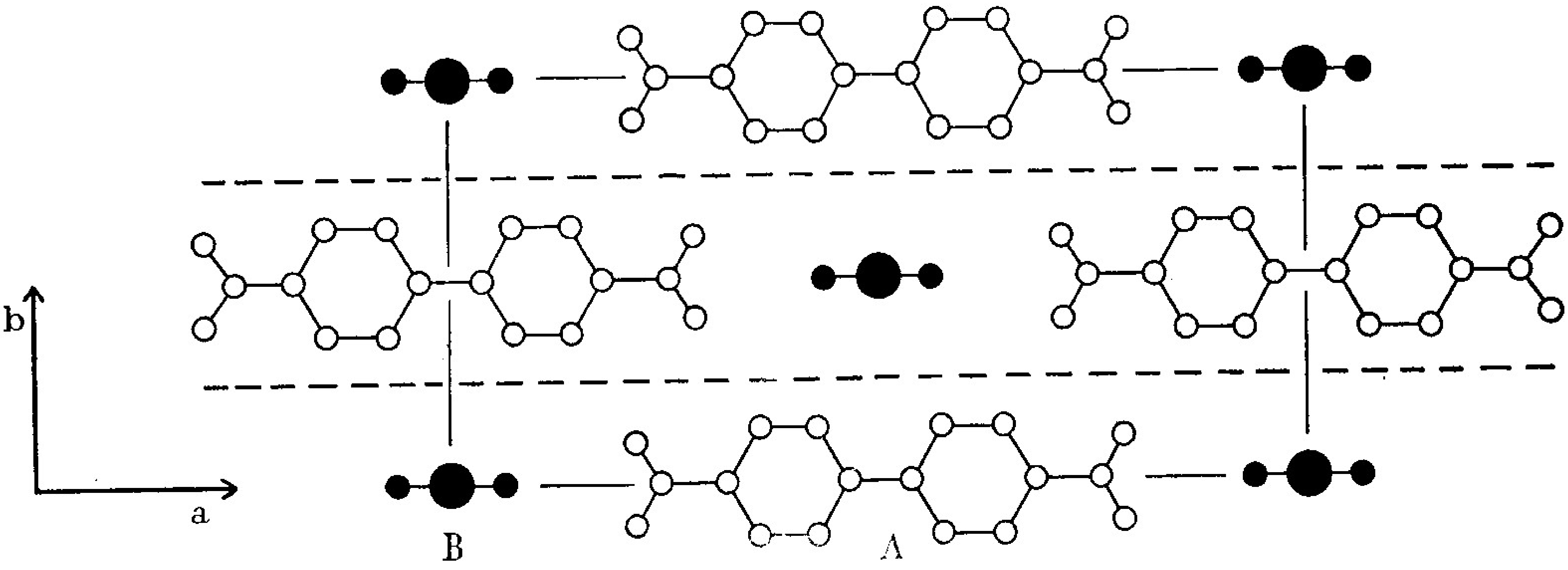


FIGURE 1. Projection along *c* on to the *ab*-plane of the idealized structure of the complexes of 4:4′-dinitrodiphenyl with 4-iodo- and 4-bromodiphenyl. In the distance *c* there are two iodo- or bromodiphenyl molecules (*B*), seen end-on. Each dinitrodiphenyl molecule (*A*) represents seven molecules one above the other, separated by *c*/7.

direction of the long axes of these *B* molecules is perpendicular to the planes containing the *A* molecules. In the only structure fully worked out, mirror planes of symmetry lie perpendicular to the planes of *A* molecules, and contain their long axes and also the planes of the benzene rings of the *B* molecules. This exact arrangement is not found in all the complexes, although it is probably also that of the iodo- and bromo-complexes discussed here, but the departure from it never seems to be large.

The ratio of the number of *A* to the number of *B* molecules varies from complex to complex, but appears to depend on the length of the *B* molecules, rather than on chemical considerations; and, indeed, it has been found possible to predict the ratio from a knowledge of this length (Rapson, Saunder & Stewart 1947). In general, the *A* molecules do not lie exactly in planes, nor is the direction of the length of the *B* molecules perpendicular to that of the lengths of the *A* molecules, and on account of these and other departures from the ideal structure outlined above, the actual symmetry of the crystals may differ widely from case to case, but consideration of the actual structures shows the departure from the ideal type to be relatively slight, and oscillation photographs taken about structurally equivalent axes are extraordinarily similar for all the complexes.

THE COMPLEXES WITH 4-IODO- AND 4-BROMODIPHENYL

The preparation and chemical analysis of these complexes has been described by Rapson *et al.* (1947). The molecular ratio of dinitrodiphenyl to iodo- and bromodiphenyl is found to be 7 : 2 in each case, so that the complexes may be represented by the formulae

$$(IC_6H_4C_6H_5)_2\,(O_2NC_6H_4C_6H_4NO_2)_7 \quad \text{and} \quad (BrC_6H_4C_6H_5)_2\,(O_2NC_6H_4C_6H_4NO_2)_7.$$

Details of the crystallographic determinations will be found in a previous paper (Saunder 1947). The crystal symmetry is monoclinic. As will be seen later, the arrangement of the spots in oscillation photographs from the bromo-complex is in some respects abnormal, but with the iodo-complex the positions of the spots on the photographs are normal and show the dimensions of the unit cell to be

$$a = 20{\cdot}0\,\text{A}, \quad b = 9{\cdot}5\,\text{A}, \quad c = 25{\cdot}8;\text{A} \quad \beta = 100^\circ.$$

The space-group may be C_m, C_2, or $C_{2/m}$, but there is reason to think that of these C_m is the most likely, which is the same as that for the complex with 4-hydroxydiphenyl, the structure of which has been fully determined. Detailed comparison of the intensities of the more important spectra given by this compound with those given by the iodo-complex, and comparison of the cell dimensions, the refractive indices, and the diffuse spectra due to thermal vibrations, leads to the conclusion that the structures of the two crystals must be extremely similar.

If the abnormalities in the spectra from the bromo-complex are for the moment disregarded, all the remarks given above may be taken as applying to it also, the dimensions of the two unit cells being the same within the limits of error of the photographs taken.

DISCUSSION OF THE OSCILLATION PHOTOGRAPHS

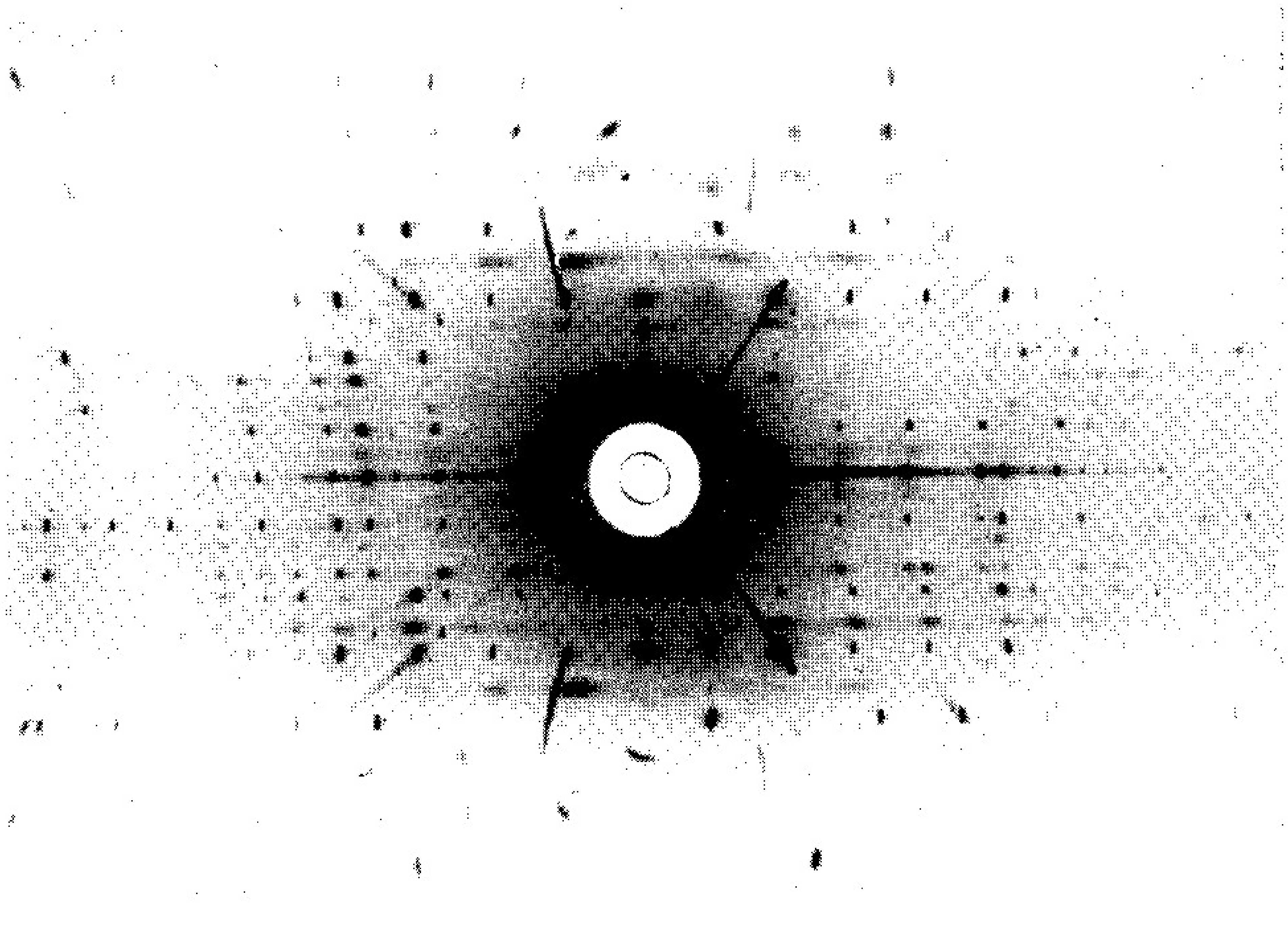
In the crystals of these complexes, the planes most closely corresponding with the idealized planes containing the A molecules in figure 1 are the (001) planes, and if the planes of A molecules were regularly spaced the distance between successive planes would be 3·69 A. If the structure consisted only of such regularly spaced planes of A molecules, a rotation photograph taken about the c-axis would show widely spaced layer-lines corresponding to this distance. In the actual complex with iododiphenyl, the pattern repeats itself every seven layers of A molecules, there being two B molecules in this distance, so that intermediate layer-lines make their appearance dividing the distance between the layer-lines due to the A molecules into seven equal parts, thinking in terms of the reciprocal-lattice space. Actual oscillation photographs taken about the c-axis show the layer-lines corresponding to this larger spacing, $7 \times 3{\cdot}69$ A; their appearance is, however, abnormal. The 0th, 7th and 14th layer-lines, corresponding to a spacing of 3·69 A, which on an ideal structure would be given by the layers of A molecules alone, are sharp and clear, but all the intermediate layer-lines show spots that are more or less diffuse, with elongations along the layer-lines. The diffuseness of the spots on any one line appears to be about the same, but it varies markedly from line to line. There is no trace of diffuseness in the *A* layer-lines, which are in every way normal. A photograph from the bromo-complex is reproduced in figure 2, plate 23. Alternations of sharp and diffuse layer-lines have also been observed by Powell & Huse (1943) from molecular complexes of picryl chloride with hexamethylbenzene, and from several other complexes of a similar type. They have ascribed these to faults in the regular sequence of atomic planes in structure.

Oscillation photographs about the *b*-axis show sharp and diffuse spots also (see figure 4, plate 23), and in every case the diffuse spots are those that would lie on the intermediate layer-lines in photographs about the *c*-axis. On the photographs taken with rotations about the *b*-axis the diffuse spots are elongated transversely to the layer-lines, as would, of course, be expected from the *c*-axis photographs, but the elongated spots are not always centred on the layer-lines, but show marked displacements above and below them. The degree of this displacement appears to be a property of the individual crystal, since it varies in photographs obtained from different specimens.

A careful study of photographs taken with oscillations about different axes shows the elongation of the maxima of the interference function about the corresponding points in the reciprocal-lattice space to be parallel to b^*. An elongation in this direction would be produced by a crystal having only a small extension in the *b* direction, but this would make all the spots equally diffuse, which is not observed here. The explanation of the diffuseness is therefore probably to be sought in faults of the nature of those discussed by Wilson (1942), which are superposed on the framework of a fundamentally regular lattice structure. A possible type of fault which might account for the effect will be considered later.

ABNORMALITIES OBSERVED IN PHOTOGRAPHS FROM THE COMPLEX WITH 4-BROMODIPHENYL

Photographs taken with oscillations about the *c*-axis with the bromo- and iodo-complexes are at first sight very similar (figures 2 and 3, plate 23, respectively). Both show the sharp 0th, 7th and 14th layer-lines, and the diffuse intermediate ones. Careful inspection shows, however, that in the photograph from the bromo-complex the spacing of the intermediate layer-lines is not uniform, when considered in terms of the reciprocal-lattice space, but that the lines are arranged in groups, themselves evenly spaced, about the sharp layer-lines. So far as the position of the lines alone is concerned, the arrangement is exactly that to be expected of a series of optical ghosts accompanying the sharp layer-lines, such as would appear if a set of planes of regular spacing 3·69 A had been modified by a periodic error of spacing repeating itself in a distance 12·7 A in the direction of the *c*-axis, that is to say, with two repetitions in a distance a little less than that corresponding to seven layers of the *A* molecules. Had the error repeated itself *exactly* twice in seven layers, the ghost



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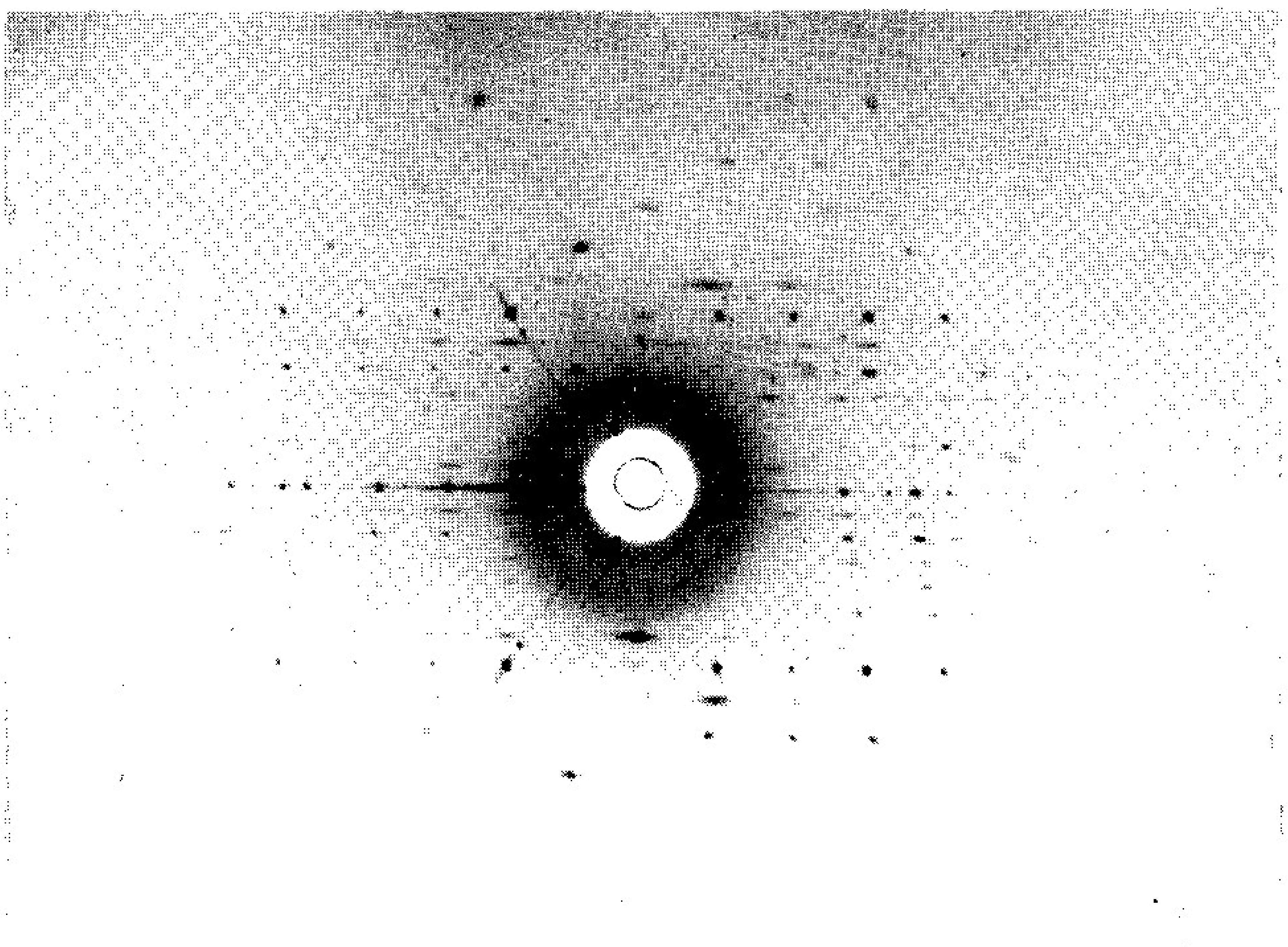

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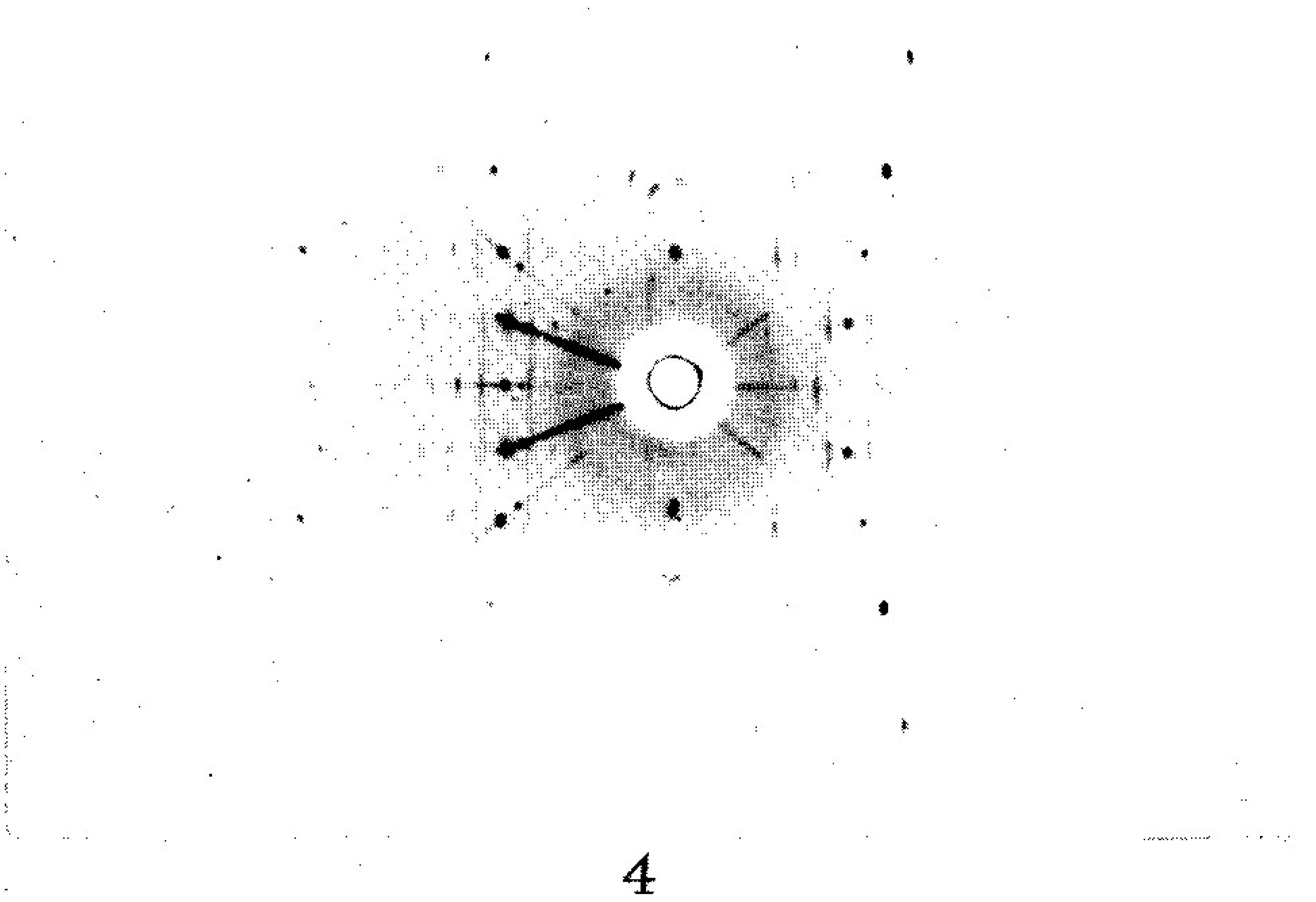

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layer-lines would have exactly divided the spacing between the zero layer-line and the 7th layer-line, and between the 7th and 14th layer-lines, as in fact they do within the errors of measurement in the case of the iodo-complex.

On the actual photographs from the bromo-complex the departure from regularity is very plain to the eye. The measured spacings of the layer-lines in the reciprocal-lattice space, as determined by means of the Bernal chart, and using Cu K_α radiation, are shown diagrammatically in figure 5. The notation used in the figure has the following significance. Let n be the order of a spectrum from a series of regularly spaced planes. Suppose these planes to be displaced periodically, a complete period of the displacement occurring every Q planes. Then additional spectra of order $n \pm m/Q$ make their appearance, and these are the optical ghosts. Any spectrum is denoted by the symbol (n, m), the spectra from the undisturbed planes being those of order $(n, 0)$. When the planes are periodically displaced, the spectra of order $(n, 0)$ still appear, but those with $m \neq 0$ also appear. In the photographs from the bromo-complex, the positions of the layer-lines correspond to a value of Q rather less than $3\frac{1}{2}$.[†]

The *positions* of the irregularly spaced layer-lines are explained in detail by the assumption of a periodic error in spacing. According to this view, the layer-lines, in the order in which they occur in the photograph, are $(0, 0)$, $(1, \bar{3})$, $(0, 1)$, $(1, \bar{2})$, $(0, 2)$, $(1, \bar{1})$, $(0, 3)$, $(1, 0)$, $(0, 4)$, $(1, 1)$, $(2, \bar{2})$ and $(0, 5)$, $(1, 2)$, $(2, \bar{1})$, $(1, 3)$, $(2, 0)$, ... As a working hypothesis, the occurrence of the B molecules at regular intervals might be supposed to impose a variation of spacing on the sheets of A molecules. It is significant that the error period in the case of the bromo-complex, as determined by direct measurement from the photographs, is 12·7 A, which is the length, as closely as can be determined from the available data, to be expected for the molecule of 4-bromodiphenyl; and twice this length, which is 25·4 A, is rather less than $7 \times 3{\cdot}69$, which is 25·8 A. The length to be expected for the molecule of 4-iododiphenyl is 12·9 A, and twice this is equal to 25·8 A. The periodic error then becomes part of the regularly repeating pattern of the crystal, and the ghost layer-lines become ordinary layer-lines.

On the view that the intermediate layer-lines are ghost spectra due to a periodic error in a fundamental spacing, the ghosts accompanying the zero layer-line, the spectra $(0, \pm m)$, would be expected to be very weak, although not in principle absent, while in the actual photograph these spectra are quite strong. It must, however, be remembered that the structure contains the regularly spaced B mole-

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[†] After this paper had been sent for publication photographs were taken from the complex of 4:4′-dinitrodiphenyl with 4-chlorodiphenyl. The irregularity of the spacing of the layer-lines is even more marked than in the case of the complex with the bromo-compound, as had in fact been anticipated. The lines again form groups about the zero and seventh layer-lines, and are consistent with an error period of 12·3 A and ratio of the dinitro constituent to the chloro constituent of 3·3:1. Photographs from the corresponding fluoro-compound are perfectly normal, all spots being sharp, the ratio of the constituents being now 3:1. The photographs resemble extremely closely those from the complex with 4:4′-hydroxydiphenyl. It is hoped to publish further details of these cases in a subsequent paper.

cules, which, considered alone, would give a set of spectra in the positions of the spectra $(0, \pm m)$ so that in any case these would be expected to occur.

Another point requiring consideration is the diffuseness of the lines. The existence of diffuse ghost spectra must be explained, the diffuseness of which, moreover, varies with the order m of the ghost. It is plain that the crystals of these complexes are not simple enough for an exact quantitative explanation of the observed effects to be possible. All that can be attempted with much hope of success is to produce a simplified model that will give spectra exhibiting the same general type of properties as those actually observed. In the second half of the paper an attempt will be made to do this.

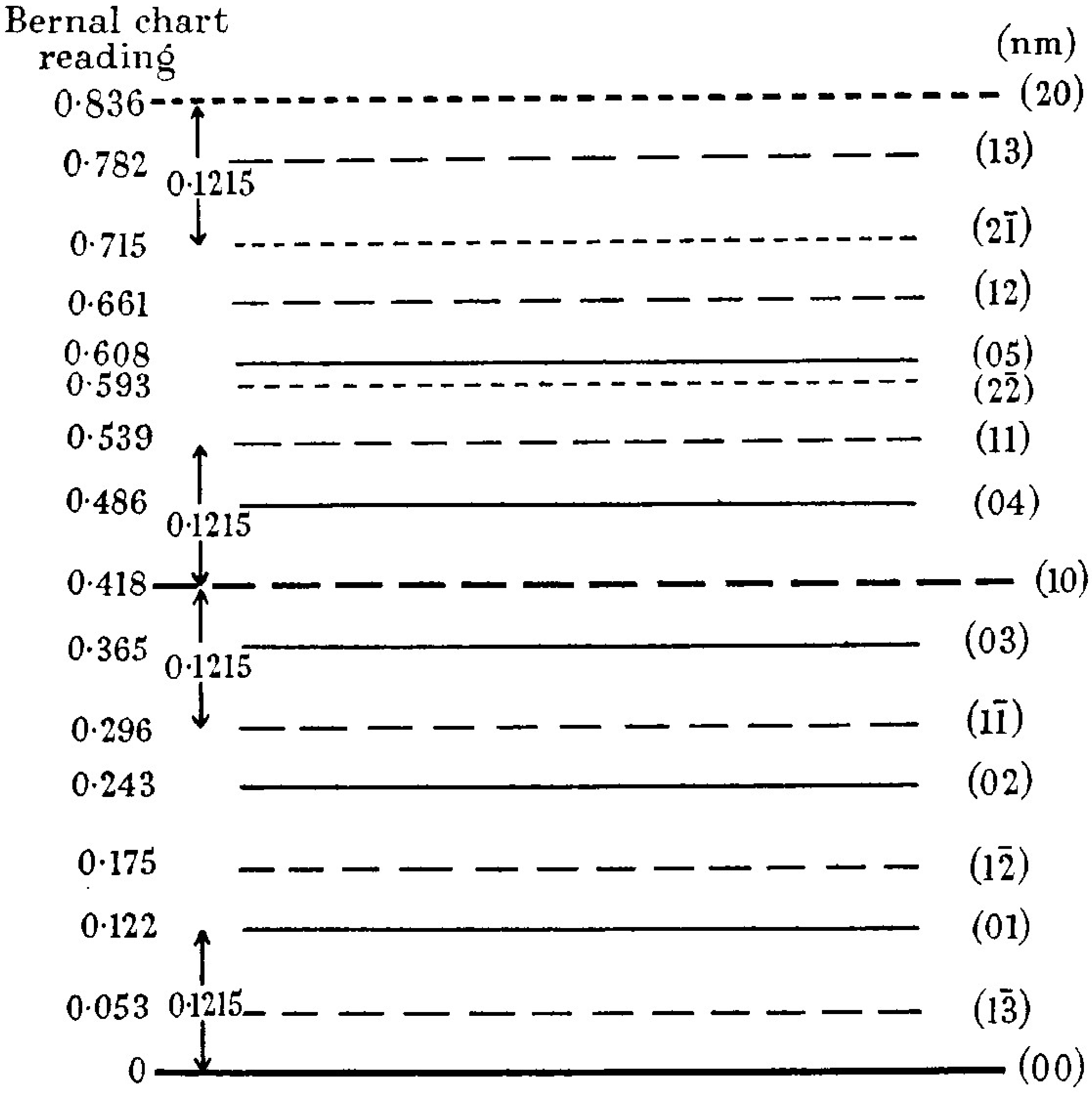

FIGURE 5. Scale representation of the layer-lines as they appear on a rotation diagram for a rotation about the c-axis with the complex with 4-bromodiphenyl.

THEORETICAL: THE DISCUSSION OF AN IDEALIZED MODEL

Assume the crystal to consist of layers of A molecules, all exactly alike, placed one above the other in the array represented in figure 1, and this array will be assumed to persist coherently throughout the crystal. Through this structure the chains of B molecules pass transversely to the A planes, and parallel to the c-axis of the crystal. Suppose the B molecules lying in any one chain to maintain an unchanged regular sequence through the crystal. The dotted lines in figure 1 are the traces of planes dividing the crystal into a series of slabs parallel to the planes

(010). In any one such slab the structure is supposed to be without faults, corresponding atoms in the different B chains all having the same c co-ordinates, so that the consequent periodic displacements of the A planes are all in phase. Suppose, however, that in different slabs there are relative displacements of the B molecules, so that in passing from one slab to the next there may be a sudden change in the c co-ordinates of corresponding B molecules. It will be assumed that there is a certain probability that within any distance measured parallel to b such a sudden change, or fault, may occur. Making the simplest possible assumption, it is seen that there are two possible sets of co-ordinates for the B molecules. It will then be necessary to work out in the manner described by Wilson (1942) the probability that two slabs separated by a given distance shall have the same or different c co-ordinates, and thence to calculate the interference function for the crystal, remembering at the same time that the B molecules introduce periodic variations in the spacing of the A molecules, which will vary in phase according to the occurrence of faults in the slabs. Consideration is given first to the scattering due to the A molecules alone, with the periodic errors imposed on their spacing by the B molecules, neglecting for the time being the scattering by the B molecules themselves. For this purpose, the model will be still further simplified, each unit of the structure being replaced by a scattering point.

SCATTERING BY A PERIODICALLY DISTORTED POINT-LATTICE WITH FAULTS

Consider a point-lattice that is parallelepipedal in form, having N_1, N_2 and N_3 points parallel to a, b and c respectively. The position relative to the origin of a point in the lattice when it is undistorted is given by the vector

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}, \tag{1}$$

u, v, w being integers.

Suppose a periodic error of the c spacing to be introduced, which for the sake of simplicity will be taken as sinusoidal in character, the c co-ordinate of a point being given by $[w + q\cos\{2\pi cg(w+\phi_v)\}]\,\mathbf{c}$. Here, g is the *frequency* of the periodic disturbance, the number of times it occurs in unit distance, so that $cg = 1/Q$, Q being the number of c spacings within which a complete period of the error occurs. The maximum amplitude of the displacement, expressed as a fraction of c, is q, and ϕ_v is a phase constant, which depends on v, and has the same value so long as v is constant, that is to say, over any (010) plane. According to this simple assumption, it will later be supposed that ϕ_v may have the values 0 or ϕ but no other value.

Consider first scattering by a single b-plane of points, with v constant and $\phi_v = \phi$. The vector position of a point on such a plane may now be written

$$\mathbf{r}_v = u\mathbf{a} + v\mathbf{b} + [w + q\cos\{2\pi cg(w+\phi)\}]\,\mathbf{c}. \tag{2}$$

Let $\mathbf{s}_0$ and $\mathbf{s}$ be unit vectors in the directions of incidence and scattering, and let

$$\mathbf{S} = \mathbf{s} - \mathbf{s}_0, \quad |\,\mathbf{S}\,| = 2\sin\theta, \tag{3}$$

2θ being the angle of scattering. One may then write for the amplitude scattered by a single plane v, in terms of that scattered by a single unit,

$$A_v = \sum_{u=0}^{u=N_1-1} \sum_{w=0}^{w=N_3-1} \exp\{2\pi i(\mathbf{S}\,.\,\mathbf{r}_v)/\lambda\}. \tag{4}$$

The scattering in terms of a distribution in the reciprocal-lattice space may now be expressed in the usual way, writing

$$\mathbf{S}/\lambda = \xi\mathbf{a}^* + \eta\mathbf{b}^* + \zeta\mathbf{c}^*, \tag{5}$$

which gives, using (2) and the properties of reciprocal vectors,

$$A_v = \exp(2\pi iv\eta) \sum_u \exp(2\pi iu\xi) \sum_w \exp 2\pi i[w\zeta + q\zeta\cos\{2\pi cg(w+\phi)\}]. \tag{6}$$

A_v is now expressed as a function of ξ, η and ζ, and it gives the amplitude scattered in the direction $\mathbf{s}$ when the conditions of incidence and scattering are such that the extremity of the vector $\mathbf{S}/\lambda$ lies at the point $(\xi a^*, \eta b^*, \zeta c^*)$ in the reciprocal-lattice space, that is to say, when the sphere of reflexion passes through this point.

Carrying out the summation with respect to u, (6) may be written in the form

$$A_v = \exp(2\pi iv\eta)\frac{\exp(2\pi iN_1\xi) - 1}{\exp(2\pi i\xi) - 1}\sum_{w=0}^{w=N_3-1} \exp 2\pi i[w\zeta + q\zeta\cos\{2\pi cg(w+\phi)\}]. \tag{7}$$

The summation with respect to w may be handled by a method employed by Kochendörfer (1939) in a paper on the effect of periodic errors in lattices. Now use an expansion in terms of Bessel functions,

$$\exp(ipx) = J_0(p) + 2\sum_{m=1}^{m=\infty} i^m J_m(p)\cos mx, \tag{8}$$

from which follows immediately

$$\exp[2\pi iq\zeta\cos\{2\pi cg(w+\phi)\}] = \sum_{m=-\infty}^{m=\infty} i^{|m|}J_{|m|}(2\pi q\zeta)\exp(2\pi imcgw)\exp(2\pi imcg\phi), \tag{9}$$

a result that follows at once if the cosines are expressed in the exponential form.

The sum with respect to w in (7) can now be written

$$\sum_w = \sum_{m=-\infty}^{m=\infty} i^{|m|}J_{|m|}(2\pi q\zeta)\exp(2\pi imcg\phi)\sum_{w=0}^{w=N_3-1}\exp\{2\pi iw(\zeta+mcg)\}. \tag{10}$$

The sum over w on the right-hand side of (10) is a geometrical progression of a type occurring in the theory of the ordinary diffraction grating, and is equal to

$$\frac{\exp\{2\pi iN_3(\zeta+mcg)\} - 1}{\exp\{2\pi i(\zeta+mcg)\} - 1} = \exp\{\pi i(N_3-1)(\zeta+mcg)\}\frac{\sin\{\pi N_3(\zeta+mcg)\}}{\sin\{\pi(\zeta+mcg)\}}. \tag{11}$$

The expression (11) has maxima equal to N_3 whenever $\zeta + mcg$ is a whole number, and these maxima are exceedingly sharp if N_3 is large, while, under the same conditions, the subsidiary maxima that occur between the main maxima are negligible.

Considered as a function of ζ therefore, (11) has sharp maxima when $\zeta = l \pm mcg$, l being an integer, and is otherwise of negligible magnitude, a result that will be used later.

Now write (6) in the form

$$A_v = \exp(2\pi i v\eta)\frac{\exp(2\pi i N_1\xi)-1}{\exp(2\pi i\xi)-1}F_v, \tag{12}$$

where $F_v = \sum_w$, and is given by (10); and for the whole crystal the amplitude scattered in the direction considered is

$$A = \sum_v A_v = \frac{\exp(2\pi i N_1\xi)-1}{\exp(2\pi i\xi)-1}\sum_{v=0}^{v=N_2-1} F_v \exp(2\pi i\eta v). \tag{13}$$

The corresponding intensity, expressed in terms of the scattering by a single point, and considered as a function of ξ, η and ζ, is called the interference function for the piece of crystal considered. Its value is

$$I_0(\xi,\eta,\zeta) = |A|^2 = \frac{\sin^2(\pi N_1\xi)}{\sin^2(\pi\xi)}\sum_v\sum_{v'} F_v F_{v'}^* \exp\{2\pi i\eta(v-v')\}, \tag{14}$$

or, if $v' = v+n$,

$$I_0(\xi,\eta,\zeta) = \frac{\sin^2(\pi N_1\xi)}{\sin^2(\pi\xi)}\sum_v\sum_n F_v F_{v+n}^* \exp\{-2\pi i n\eta\}. \tag{15}$$

Now F_v can have one of two possible values, one being that given by (10) and the other the corresponding value with $\phi = 0$. These two values may be called F_ϕ and F_0 respectively. Let I_n be the average value of $F_v F_{v+n}^*$ for two b planes separated by n planes, and let M be the number of times this particular separation occurs. Then

$$I_0(\xi,\eta,\zeta) = \frac{\sin^2(\pi N_1\xi)}{\sin^2(\pi\xi)}\sum_n M I_n \exp(-2\pi i n\eta). \tag{16}$$

In the case of a parallelepipedal lattice, $M = N_2 - |n|$, and n can run from $N_2 - 1$ to $-(N_2-1)$. Thus

$$I_0(\xi,\eta,\zeta) = \frac{\sin^2(\pi N_1\xi)}{\sin^2(\pi\xi)}\sum_{n=-(N_2-1)}^{n=N_2-1} I_n(N_2-|n|)\exp(-2\pi i n\eta). \tag{17}$$

The next step is to calculate the average value I_n, and to do this the method given by Wilson (1942, 1943) in dealing with the effects of faults in alloy structures is applied. Assume that there are two possible values of F_v, F_0 and F_ϕ, and that a fault may occur at any b plane of such a kind that the value of F_v changes from one possible value to the other. Let $P(n)$ be the probability that the plane $v+n$ is like the plane v, and let αds be the probability that a fault occurs between bs and $b(s+ds)$. Consider a plane (2) at a distance $b(s+ds)$ from a plane (1). The plane (2) may be like plane (1) because the plane at a distance bs is like plane (1) and no fault occurs in the further distance bds; or because the plane at a distance bs is unlike plane (1) and a fault occurs in the further distance bds which once more makes plane (2) like plane (1). The probability that plane (2) is like plane (1) is therefore the sum of the probabilities of these two mutually exclusive types of event. Thus

$$P(s+ds) = P(s)(1-\alpha ds)+\{1-P(s)\}\alpha ds = P(s)-2\alpha P(s)\,ds+\alpha ds. \tag{18}$$

But since ds is small, then

$$P(s+ds) = P(s)+(dP(s)/ds)\,ds, \tag{19}$$

whence, by comparing (18) and (19),

$$dP(s)/ds = -2\alpha P(s)+\alpha,$$

which, on integration, remembering that $P(0) = 1$, gives

$$P(s) = \tfrac{1}{2}(1+e^{-2s\alpha}), \tag{20}$$

or, since s gives the distance expressed as a multiple of the lattice spacing b,

$$P(n) = \tfrac{1}{2}\{1+\exp(-2\,|\,n\,|\,\alpha)\}. \tag{21}$$

The average value of $F_v F^*_{v+n}$, I_n, may be written in the form

$$\begin{aligned} I_n &= \tfrac{1}{2}F_0[P(n)\,F_0^*+\{1-P(n)\}\,F_\phi^*]+\tfrac{1}{2}F_\phi[P(n)\,F_\phi^*+\{1-P(n)\}\,F_0^*] \\ &= \tfrac{1}{2}P(n)\{|\,F_0\,|^2+|\,F_\phi\,|^2\}+\tfrac{1}{2}\{1-P(n)\}\{F_0F_\phi^*+F_\phi^*F_\phi\}. \end{aligned} \tag{22}$$

Now

$$F_0 = \sum_{m=-\infty}^{m=\infty} i^{|m|}J_{|m|}(2\pi q\zeta)\sum_{w=0}^{w=N_3-1}\exp\{2\pi i w(\zeta+mcg)\} = \sum_m B_{0m}(\zeta), \tag{23}$$

$$F_\phi = \sum_{m=-\infty}^{m=\infty} i^{|m|}J_{|m|}(2\pi q\zeta)\exp(2\pi imcg\phi)\sum_{w=0}^{w=N_3-1}\exp\{2\pi i w(\zeta+mcg)\} = \sum_m B_{\phi m}(\zeta). \tag{24}$$

Each of these expressions is a function of ζ with very narrow maxima, and the only terms in $|\,F_0\,|^2$ and $|\,F_\phi\,|^2$ that are appreciable are those of type $|\,B_{0m}(\zeta)\,|^2$ or $|\,B_{\phi m}(\zeta)\,|^2$, while in $F_0F_\phi^*$ or $F_0^*F_\phi$ the only terms of appreciable value are those of the types $B_{0m}(\zeta)\,B^*_{\phi m}(\zeta)$ or $B^*_{0m}(\zeta)\,B_{\phi m}(\zeta)$. Neglecting all other terms, and using (11), then

$$\tfrac{1}{2}\{|\,F_0\,|^2+|\,F_\phi\,|^2\} = \sum_{m=-\infty}^{m=\infty} J^2_{|m|}(2\pi q\zeta)\frac{\sin^2\{\pi N_3(\zeta+mcg)\}}{\sin^2\{\pi(\zeta+mcg)\}} = \sum_m S_m, \tag{25}$$

$$\tfrac{1}{2}\{F_0F_\phi^*+F_0^*F_\phi\} = \sum_m S_m\cos(2\pi mcg\phi). \tag{26}$$

By (22), (25), (26) and (21), therefore,

$$\begin{aligned} I_n &= \sum_m [P(n)\,S_m+\{1-P(n)\}\,S_m\cos(2\pi mcg\phi)] \\ &= \tfrac{1}{2}\sum_m [S_m\{1+\cos(2\pi mcg\phi)\}+\exp(-2\,|\,n\,|\,\alpha)\,S_m\{1-\cos(2\pi mcg\phi)\}] \\ &= \sum_m S_m\{\cos^2(\pi mcg\phi)+\exp(-2\,|\,n\,|\,\alpha)\sin^2(\pi mcg\phi)\}. \end{aligned} \tag{27}$$

Equation (17) now becomes

$$I_0(\xi,\eta,\zeta) = \frac{\sin^2(\pi N_1\xi)}{\sin^2(\pi\xi)} \sum_{n=-(N_2-1)}^{n=N_2-1} \sum_{m=-\infty}^{m=\infty}$$

$$\times S_m\{\cos^2(\pi mcg\phi) + \exp(-2\,|\,n\,|\,\alpha)\sin^2(\pi mcg\phi)\}(N_2-|\,n\,|)\exp(-2\pi in\eta). \tag{28}$$

Now write

$$\sum_{n=-(N_2-1)}^{n=N_2-1} (N_2-|\,n\,|)\exp(-2\pi in\eta) = N_2 + 2\sum_{n=1}^{n=N_2-1}(N_2-|\,n\,|)\cos 2\pi n\eta \tag{29}$$

$$= \frac{\sin^2(\pi N_2\eta)}{\sin^2(\pi\eta)}; \tag{29a}$$

for (29) is an alternative form of the ordinary grating formula (29*a*). The right-hand side of (29) is a Fourier series of N_2 terms, and the greater N_2 the sharper are the periodic maxima in η. This gives a clue to the nature of the second term in (28), which contains the summation

$$D(\eta) = N_2 + 2\sum_{n=1}^{n=N_2-1}(N_2-|\,n\,|)\exp(-2\,|\,n\,|\,\alpha)\cos 2\pi n\eta. \tag{30}$$

This again is a Fourier series, with maxima for the same values of ζ as those for which (29) is a maximum. The coefficients are, however, multiplied by the factor $\exp(-2\,|\,n\,|\,\alpha)$, which decreases rapidly with increasing $|\,n\,|$ if α is appreciable. The effect of this is to broaden the maxima; for the terms of higher order, to which the sharpening of the maxima is due, become ineffective. This sum is therefore denoted by $D(\eta)$ to indicate that its maxima are relatively diffuse.

Using (25), (29*a*) and (30), (28) may now be written in the form

$$I_0(\xi,\eta,\zeta) = \frac{\sin^2(N_1\pi\xi)}{\sin^2(\pi\xi)} \sum_{m=-\infty}^{m=\infty} J^2_{|m|}(2\pi q\zeta)\frac{\sin^2\{\pi N_3(\zeta+mcg)\}}{\sin^2\{\pi(\zeta+mcg)\}}$$

$$\times\left\{\frac{\sin^2(\pi N_2\eta)}{\sin^2(\pi\eta)}\cos^2(\pi mcg\phi) + D(\eta)\sin^2(\pi mcg\phi)\}\right\}. \tag{31}$$

When $m = 0$,

$$I_0(\xi,\eta,\zeta) = J_0^2(2\pi q\zeta)\frac{\sin^2(\pi N_1\xi)}{\sin^2(\pi\xi)}\frac{\sin^2(\pi N_2\eta)}{\sin^2(\pi\eta)}\frac{\sin^2(\pi N_3\zeta)}{\sin^2(\pi\zeta)}, \tag{32}$$

an expression giving sharp maxima when $\xi = h$, $\eta = k$ and $\zeta = l$, h, k, l being integers. These are in fact the ordinary lattice maxima, which are in the same positions as those given by the undistorted lattice and are just as sharp. The *intensities* are, however, modified by the factor $J_0^2(2\pi q\zeta)$, which may be written $J_0^2(2\pi lq)$ for the sharp maxima, and this becomes smaller with increasing l, the rate of decrease depending on q, the maximum distortion.

THE GHOST SPECTRA

In addition to the main maxima, other maxima occur when

$$\zeta \pm |m| cg = l, \quad \text{or} \quad \zeta = l \pm |m| cg = l \pm |m|/Q,$$

where Q is the number of repetitions of the undisturbed spacing in one repetition of the periodic distortion. These extra maxima are the ghost spectra, a group of which, corresponding to different values of m, for the same value of l accompanies each main maximum. The ghost maxima are sharp in ξ and ζ, but their sharpness in η is governed by the factor

$$\frac{\sin^2(N_2\pi\eta)}{\sin^2(\pi\eta)}\cos^2\left(\frac{\pi m\phi}{Q}\right) + D(\eta)\sin^2\left(\frac{\pi m\phi}{Q}\right),$$

and so is a function of m, the order of the ghost, and not of the order of the main spectrum that the ghost accompanies. The first term of this factor is sharp if N_2 is large, but the second term is much more diffuse if α, the probability of a fault, is appreciable. The two terms, however, make different relative contributions for different values of m. For small $m\phi/Q$, the first term will be preponderant and the second will have small values, but, as $m\phi/Q$ grows, the importance of the second or diffuse term increases and that of the first or sharp term diminishes. For still larger values of $m\phi/Q$ the relative importance of the terms may be once more reversed. The form of the factor suggests that the spots on the ghost layer-lines might show sharp nuclei with relatively diffuse wings, and on the photographs from the bromo- and iodo-complexes a number of such spots are in fact to be seen, which may perhaps be some confirmation of the view that the effects observed are due to an irregularity of the same general nature as that discussed.

The intensities of the ghost maxima for the simple lattice with a sinusoidal displacement are determined by the factor $J_m^2(2\pi q\zeta)$, which for $m \neq 0$ is small for small values of ζ. So long as $2\pi q\zeta$ is not too large, $J_m(2\pi q\zeta)$ is proportional to ζ^m. The ghosts of higher order are therefore unimportant for the low orders of main spectra, but become more important for the higher orders, even when the distortion is sinusoidal. The ghosts accompanying the zero-order spectrum will be expected to be faint, since they are given by the values of $J_m^2(2\pi mq/Q)$, which will be small unless the maximum displacement is large. The zero-order ghosts are not in principle absent, as the approximate treatment of periodic errors, given, for example, by Daniel & Lipson (1943), seems to indicate.

The assumption of a sinusoidal distortion has been made for the sake of simplicity. It is clear that the actual distortion, although periodic, cannot be sinusoidal. It would, in fact, be more accurate to represent it by a Fourier series of the type $c\sum_k q_k \cos(2\pi kcgw)$, instead of by $cq\cos(2\pi cgw)$. If no limitations to small displacements are imposed, the algebra in this case becomes rather heavy. If, however, it is assumed that q_k is always small, it is easy to show that the kth order ghost accompanying any main maximum has an amplitude proportional to q_k, the kth Fourier coefficient of the series representing the periodic displacement. If the displacement is not small, matters are more complicated, and the amplitude of the kth order ghost does not depend on q_k alone, but it appears still to be true that the value of q_k exercises the determining influence.

THE SPECTRA DUE TO THE B MOLECULES

In the actual photographs, the ghosts accompanying the zero layer-line are strong, much stronger than would be expected from the analysis given above. It must be remembered, however, that this refers only to the effect of the A molecules of the underlying lattice, distorted, it is supposed, by the B molecules, the scattering by which has so far been neglected. In the actual photographs, the scattering by the B molecules is of course recorded. The structure must be considered as a whole. Before doing so, however, the scattering from the B molecules alone will be considered, assuming the same probability of faults in the structure as was assumed above. Consider, as before, the amplitude scattered by the B molecules lying in a single (010) plane, corresponding to a given value of v. Write this in the two possible forms

$$A_v = R_1(\xi)\,R_3(\zeta)\exp(2\pi i v\eta),$$

$$A_{v'} = R_1(\xi)\,R_3(\zeta)\exp(2\pi i v'\eta)\exp(2\pi i\phi\zeta), \tag{33}$$

$R_1(\xi)$ and $R_3(\zeta)$ being the amplitude factors obtained by summing over u and w respectively. It must be remembered that the frequency in $R_3(\zeta)$ is that corresponding to the repetition of the B molecules, that is to say it is g, the frequency of the periodic error assumed in calculating the effect of the distorted lattice of A molecules. Just as before, one writes for the interference function due to the B molecules alone

$$I_B(\xi,\eta,\zeta) = \sum_v\sum_n |R_1(\xi)|^2\,|R_3(\zeta)|^2\,F_v F^*_{v+n}\exp(-2\pi i n\eta), \tag{34}$$

where F_v and F_{v+n} are now either $+1$ or $\exp(2\pi i\phi\zeta)$.

Now introduce the probability of a sudden change from one type of F to the other, just as before. This gives for the average value of $F_v F^*_{v+n}$

$$I_n = \cos^2(\pi\phi\zeta) + \exp(-2\,|n|\,\alpha)\sin^2(\pi\phi\zeta), \tag{35}$$

and, following exactly the same argument as that given above in deriving (31), then

$$I_B(\xi,\eta,\zeta) = |R_1(\xi)|^2\,|R_3(\zeta)|^2\left\{\frac{\sin^2(\pi N_2\eta)}{\sin^2(\pi\eta)}\cos^2(\pi\phi\zeta) + D(\eta)\sin^2(\pi\phi\zeta)\right\}. \tag{36}$$

If ζ has the same significance as in the discussion of the scattering by the A molecules, its maxima, and so the layer-lines in a rotation photograph about the c axis, occur when $\zeta = \pm m/Q$, for the c^* spacing of the B reciprocal lattice is $1/Q$ of that of the A lattice. Equation (36) shows therefore that the B molecules alone would produce a set of layer-lines having the same positions, and the same variation of diffuseness with order, as those predicted for the ghost spectra of zero order. The relatively strong spectra actually observed in these positions can therefore mainly be ascribed to this cause, the true ghosts being those accompanying the higher orders.

In the case of the iodo-complex, in which the spacing of the sheets of A molecules and the period of the distortion appear to be commensurable, and which is thus to be considered only as a degenerate case of a structure with a periodic error, the higher orders of these $(0, m)$ spectra produced by the B molecules will always coincide with ghost spectra (n, m) accompanying higher orders. In the case of the bromo-complex, in which the two periodicities appear not be to commensurable, this will not be so, and some doubling of the layer-lines might therefore be expected. There is some evidence that it does actually occur. Reference to figure 5 will show that the layer lines $(0, 5)$ and $(2, \bar{2})$ lie very close together. The layer line $(0, 5)$ is faint, and no $(0, 6)$, or higher orders, are observed at all, but there are one or two spots on the line $(0, 5)$ visible on the actual photographs which quite definitely do not lie on the line $(2, \bar{2})$. Doubling between $(0, 4)$ and $(2, \bar{3})$ is also to be expected, but is not observed in the photographs. It is, however, perhaps significant that this layer-line, and some of the other lines of higher order, are broadened in the c-direction, which might indicate an incipient doubling of the lines. Corresponding lines in the photographs from the iodo-complex are not thus broadened.

DIFFRACTION BY TWO LATTICES WITH INCOMMENSURABLE SPACINGS BUT WITH A DEFINITE PHASE RELATIONSHIP

In the above discussion, it has been assumed that the interference function can be built up by adding together the effects of the A and B molecules, considered separately. This, of course, is an over-simplification. Interference effects occur that depend on the juxtaposition of the two types of molecule, and these may be very important if the two periodicities are commensurable, so that the two structures, taken together, constitute a single repeating pattern. It is necessary to consider this point in more detail.

The simple case of reflexion from two sets of parallel planes, one set with a spacing a_1, the other with a spacing a_2, will now be discussed. Let f_1 and f_2 be the structure factors of a single plane of each set, which may conveniently be supposed as complex, to take into account any phase difference due to the relative positions of the sets of planes. Let θ be the glancing angle of reflexion from the planes. Then the phase difference between waves reflected from successive planes of the two sets are respectively μa_1 and μa_2, where $\mu = (4\pi \sin\theta)/\lambda$. If in the piece of crystal considered there are N_1 planes of one set and N_2 planes of the other, the amplitude reflected in the direction θ may be written

$$A = f_1 \sum_{n=0}^{n=N_1-1} \exp(in\mu a_1) + f_2 \sum_{m=0}^{m=N_2-1} \exp(im\mu a_2)$$

$$= f_1 \exp\{\tfrac{1}{2}(N_1-1)\mu a_1\} \frac{\sin(\frac{1}{2}\mu N_1 a_1)}{\sin(\frac{1}{2}\mu a_1)} + f_2 \exp\{\tfrac{1}{2}(N_2-1)\mu a_2\} \frac{\sin(\frac{1}{2}\mu N_2 a_2)}{\sin(\frac{1}{2}\mu a_2)}. \quad (37)$$

The intensity I is equal to $|A|^2$, which gives

$$I \doteq |f_1|^2 \frac{\sin^2(\frac{1}{2}\mu N_1 a_1)}{\sin^2(\frac{1}{2}\mu a_1)} + |f_2|^2 \frac{\sin^2(\frac{1}{2}\mu N_2 a_2)}{\sin^2(\frac{1}{2}\mu a_2)} + 2|f_1||f_2| \frac{\sin(\frac{1}{2}\mu N_1 a_1)}{\sin(\frac{1}{2}\mu a_1)} \frac{\sin(\frac{1}{2}\mu N_2 a_2)}{\sin(\frac{1}{2}\mu a_2)} \cos[\tfrac{1}{2}\mu\{(N_1-1)a_1-(N_2-1)a_2\}-\delta], \tag{38}$$

where δ is given by $f_1 f_2^* = |f_1||f_2|e^{i\delta}$, and is the phase difference between waves reflected from the first planes of the two sets. If these planes are at a distance d apart, $\delta = \mu d$.

The first two terms in (38) give the sum of the intensities produced by the two sets of planes acting independently. The effect of their interaction is given by the third term. Considered as functions of θ, the two factors involving sines have very sharp maxima when N_1 and N_2 are large, and the value of the last term will therefore be inappreciable unless both factors have principal maxima for the same value of θ. If a_1 and a_2 are commensurable, so that $p_1 a_1 = p_2 a_2$, p_1 and p_2 being integers, this will occur for a number of values of θ. If p_1 and p_2 have no common factor, the first coincidence will be between the spectrum of order p_2 due to the planes a_1 with that of order p_1 due to the planes a_2; and the next will be between the spectra of order $2p_2$ and $2p_1$, and so on. It is plain that these coincidences produce no spectra in positions other than those already given by the two sets of planes considered independently, but they will modify the intensities of certain of these, because there is a definite phase relationship between the two sets of planes. When the spacings are commensurable $(N_1-1)a_1 = (N_2-1)a_2$ in any block of crystal that contains a number of complete repetitions of the pattern, so that the cosine factor in the last term of (38) becomes simply $\cos\delta$.

To take a very simple example, the (111) planes of diamond may be considered to consist of two sets of planes with $a_1 = a_2$, one set being displaced relative to the other through a distance $a_1/4$. The spectra due to the two independent sets of planes now coincide for all orders, but since $\delta = 0$ for the zero order, $\pi/2$ for the first, π for the second, $3\pi/2$ for the third, 2π for the fourth, and so on, it will be seen that the intensities of these spectra are respectively $4f^2$, $2f^2$, 0, $2f^2$, $4f^2$, and so on. It is clear that this is merely a slight modification of the ordinary method of calculating the intensity from the structure factor.

If the spacings are not commensurable, coincidences will not occur, and if N_1 and N_2 are large, the last term of (38) will always be negligible, and the spectra observed will be just those due to the two sets of planes considered independently. In the case considered in this paper, one set of planes has been assumed, the A planes, to have a periodic *variation* of spacing of the same period as the spacing of the other set, the B planes, and this produces, in addition to the two sets of spectra given by the two sets of planes independently without error of spacing, the sets of ghost spectra accompanying the spectra due to the A planes. The effects observed with the bromo-complex appear to be adequately explained by this type of assumption. If the two periodicities are commensurable, as appears to be the case with the iodo-complex, the problem can be treated as a case of a repeating pattern, with a definite structure factor, which can be considered as a degenerate case of a structure with a periodic error. In the case actually dealt with, the pattern does not repeat itself exactly at all, so that ordinary methods of structure-factor calculation are not applicable.

The treatment of the problem given here must be regarded only as an attempt to produce a model that shall show effects of the same general type as those observed. It has not been found possible to account in detail for the patterns obtained from the actual crystals. No really satisfactory explanation of the fact that, in the oscillation photographs taken about the *b*-axis, the diffuse spots are not always centred exactly on the layer-lines has been found, although it seems almost certainly to be connected with some imperfection in the crystals on a scale larger than those considered here.

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DESCRIPTION OF PLATE 23

FIGURE 2. The complex with 4-bromodiphenyl: 15° rotation about the *c*-axis. Rays initially incident along a^*.

FIGURE 3. The complex with 4-iododiphenyl: 15° rotation about the *c*-axis. Rays initially incident along a^*.

FIGURE 4. The complex with 4-iododiphenyl: 15° rotation about the *b*-axis. Rays initially incident along a^*.

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