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## EXTRAORDINARY DIFFRACTION OF X-RAYS

By L. W. McKEEHAN

The term "Extraordinary Diffraction" is here proposed for the directed emission of characteristic X-rays from the atoms of a crystal placed in a narrow beam of X-rays containing sufficiently short wave-lengths. The theory here presented was developed in attempting to explain the occurrence, on photographs taken for the crystal analysis of iron, nickel, and copper, of spots, evidently diffraction images of the source, at places, and in positions, quite inexplicable by the ordinary theory of X-ray diffraction in crystals. Before admitting the explanation here offered attempts were made to explain the observed effects by postulates less radical in their implications than those finally adopted, but it was found, for example, that no number of successive reflections within a single crystal, or within a twinned pair, could be made to account for the observed effects. The new physical hypothesis given below does permit an explanation of the new phenomena, and that, at present, is its sole justification.

The effects of "extraordinary diffraction" are always associated with the effects of what may, for distinction, be termed "ordinary diffraction." It seems clearest, therefore, to present the analysis in a form covering both sorts of diffraction at once, there being, of course, nothing novel in the results so predicted for the ordinary case.

In order to avoid the wholly formal complexity inseparable from equations applying to the completely general case of a triclinic crystal, the analysis will be undertaken for the simplest possible crystal, in which the mean positions of the atom-centers are the points of a simple cubic space-lattice, and in which the atoms are all alike. There is no known crystal as simple as this, but crystals of potassium chloride approach it closely, and the crystals of many metals, including those which clearly show the new effects, can be regarded as composed of two or four interpenetrating arrangements of exactly this type. Further to simplify the mathematical expressions involved, the incident X-rays will be taken as forming a plane-parallel beam, and the dimensions of the crystal will be taken as negligibly small in comparison with the radius of the sphere, centered at the crystal, on which the diffraction effects are studied. To simplify the description of these effects it will be supposed that they produce a photographic record, so that it will be appropriate to speak of spots, lines, bands, and the like. The modifications due to non-parallelism of the incident beam, to lack of circular symmetry in it, and to the finite extent of the source of primary X-rays, will be discussed only qualitatively.

Take the origin,  $O$ , at any point of the space-lattice, and lay the axes of  $X$ ,  $Y$ , and  $Z$  along the edges of that one of the eight cubical cells which meet at  $O$  which includes the prolongation of the incident ray through  $O$ . Let the orientation of the crystal with respect to this incident ray be unrestricted, so that its direction-cosines  $l_1$ ,  $m_1$ ,  $n_1$ , in addition to being all positive as required by the choice of axes, are restricted only by the geometrical requirement that  $l_1^2 + m_1^2 + n_1^2 = 1$ . Let  $a$  be the parameter of the space-lattice, so that adjacent points along each of the three axes are separated by this interval.

Assume (1) that the incident beam contains wave-trains long in comparison with their wave-length  $\lambda_1$ , and (2) that each diffracted beam consists of wave-trains long in comparison with their wave-length  $\lambda_2$ . The wave-lengths  $\lambda_1$  and  $\lambda_2$  are, in the practically important cases, of the same order of magnitude as  $a$ .

Assume (3) that at a time  $t = \tau + \frac{n\lambda_2}{c}$  after the time  $t = 0$  when some particular wave of a primary wave-train had phase  $\phi_1$  at the lattice-point  $P$ , that a secondary wave, if emitted from  $P$  as a result of the primary wave having passed through it at time  $t = 0$ , will have phase  $\phi_2$  at a distance  $n\lambda_2$  from  $P$ . In the last assumption  $\phi_1$  may be called the primary phase at excitation,  $\tau$  the delay between excitation and emission, and  $\phi_2$  the secondary phase at emission. The integer  $n$  is introduced to obviate the awkwardness of talking about the phase at the origin of a divergent beam, and  $c$  is the velocity of propagation in vacuo. Assume (4) that the values of  $\phi_1$ ,  $\tau$ ,  $\phi_2$  do not depend upon the coordinates  $x$ ,  $y$ ,  $z$ , of  $P$ , nor upon events at other lattice-points, and (5) that the variations among the individual values of  $\phi_1$ ,  $\frac{c\tau}{\lambda_1}$ ,  $\frac{c\tau}{\lambda_2}$ ,  $\phi_2$  are small in comparison with  $2\pi$ . Assume (6) that secondary waves from  $P$  have appreciable amplitude in directions considerably inclined to the prolongation of the incident ray.

The only assumption which can be dropped in the case of ordinary diffraction is the first and this is therefore the new physical hypothesis here advanced. The third assumption can be suitably modified for the ordinary case so as to eliminate reference to a primary wave-train, the origin of time being changed to the instant when a particular singularity of the incident disturbance reaches the point  $P$ . In ordinary diffraction, also,  $\lambda_1 = \lambda_2$ ; in extraordinary diffraction  $\lambda_1 < \lambda_2' < \lambda_2$ , where  $\lambda_2'$  is the wave-length of the absorption limit corresponding to the emission of the characteristic wave-length  $\lambda_2$ .

It is possible that the fifth assumption could be better expressed by requiring rigorous constancy of  $\phi_1$ ,  $\tau$ , and  $\phi_2$ , if these quantities were defined with respect to points  $P'$ ,  $P''$ , near  $P$ , where the absorbing and the emitting mechanisms concerned were at the times  $t = 0$  and  $t = \tau$ . As written above the phase differences, due to thermal agitation displacing atom-centers from the lattice-points, have been included in  $\phi_2 - \phi_1$ .

The elementary theory of diffraction now states that appreciable energy in the form of secondary waves will only be emitted

in those directions along which, at great distances, the secondary waves from all the points of the space-lattice agree in phase. These directions do not depend upon the mean values of  $\phi_1$ ,  $\phi_2$ , and  $\tau$ , so that all three of these quantities may conveniently be put equal to zero in discussing the geometry of emission. Referring to Fig. 1, which diagrammatically represents the incident and

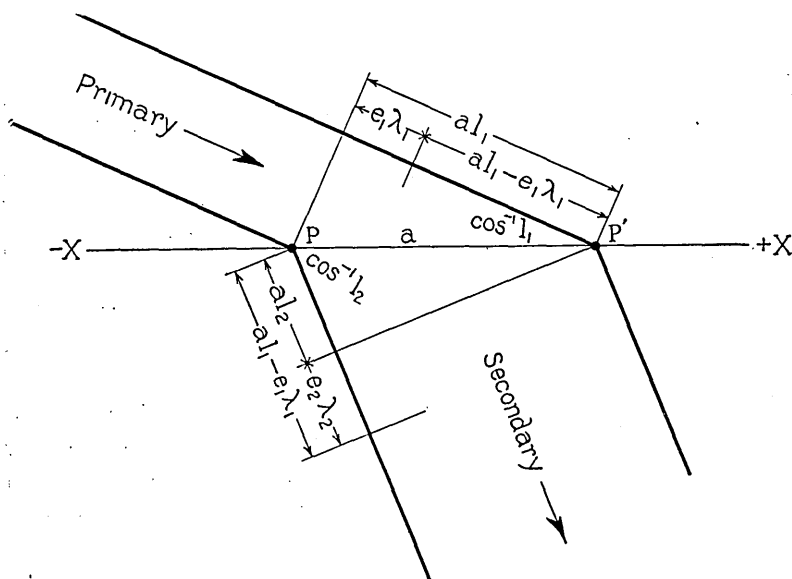


Fig. 1

*Extraordinary Diffraction at Two Atom-Centers.*

diffracted rays and wave-fronts near two adjacent atoms on the X-axis, it will be seen that the direction-cosines of the emitted secondary rays are given by

$$\left. \begin{aligned} l_2 &= l_1 - \frac{e_1 \lambda_1}{a} - \frac{e_2 \lambda_2}{a}, \\ m_2 &= m_1 - \frac{f_1 \lambda_1}{a} - \frac{f_2 \lambda_2}{a}, \\ n_2 &= n_1 - \frac{g_1 \lambda_1}{a} - \frac{g_2 \lambda_2}{a}. \end{aligned} \right\} \dots\dots\dots (a)$$

In these equations  $l_2, m_2, n_2$  are not limited as to sign, but  $l_2^2 + m_2^2 + n_2^2 = 1$ . The quantities,  $e_1, f_1, g_1$  are integers positive, negative, or zero, which may be called the orders of incidence with respect to the three axes, and  $e_2, f_2, g_2$  are integers which may similarly be called the orders of diffraction with respect to the axes. It will be noted that Fig. 1 is drawn for the special case  $n_1 = g_1 = g_2 = 0$ . In the general case the diffracted ray will not lie in a plane determined by the incident ray and one of the three axes.

For ordinary diffraction, putting  $\lambda_1 = \lambda_2 = \lambda$  and  $h = e_1 + e_2$ ,  $k = f_1 + f_2$ ,  $l = g_1 + g_2$ , where  $h, k, l$  are, of course, integers,

$$\left. \begin{aligned} l_2 &= l_1 - \frac{h\lambda}{a}, \\ m_2 &= m_1 - \frac{k\lambda}{a}, \\ n_2 &= n_1 - \frac{l\lambda}{a}. \end{aligned} \right\} \dots\dots\dots (b)$$

These formulas, as they should, represent the directions of the transmission ( $h = k = l = 0$ ), of specular reflection in the various lattice-planes ( $h, k, l$  mutually prime) and of so-called reflection in higher orders (in order  $w$  if  $h, k, l$  have  $w$  as highest common factor). Examination shows that  $h, k, l$  are, in fact, the Miller indices of the reflecting planes in the last two cases. The appropriate wave-length for any particular choice of  $l_1, m_1, n_1$  and  $h, k, l$  is found by eliminating  $l_2, m_2, n_2$ . This gives

$$\lambda = \frac{2a(l_1h + m_1k + n_1l)}{h^2 + k^2 + l^2} = \frac{2a\Sigma(l_1h)}{\Sigma(h^2)} \dots\dots\dots (b')$$

In the case of extraordinary diffraction no simplification of the general formulas (a) is possible, and, using notation similar to that in (b')

$$\lambda_1 = \frac{1}{\Sigma(e_1^2)} \left[ a\Sigma(l_1e_1) - \lambda_2\Sigma(e_1e_2) \pm \sqrt{a\Sigma(l_1e_1) - \lambda_2\Sigma(e_1e_2) - \lambda_2\Sigma(e_1^2)[\lambda_2\Sigma(e_2^2) - 2a\Sigma(l_1e_2)]} \right] \dots (a')$$

The ambiguity of signs is resolved by the condition  $\lambda_1 < \lambda_2$ . In both

cases the number of real diffracted rays for a given range in  $\lambda_1$  is limited by the condition that  $l_2, m_2, n_2$  must be real and must lie between  $+1$  and  $-1$ . The ray for which  $e_1=f_1=g_1=e_2=f_2=g_2=0$  is coincident with the prolongation of the incident ray for all values of  $\lambda_1$  and  $\lambda_2$  and for amorphous as well as crystalline arrangements.

It is fairly obvious that the general case of extraordinary diffraction permits values of  $l_2, m_2, n_2$  not possible in the special case of ordinary diffraction, but an arbitrary numerical example may serve to make this clearer.

$$\begin{aligned}\text{Let } a &= 3.60 \times 10^{-8} \text{ cm} & e_1 &= 1, f_1 = 0, g_1 = 0, \\ & & e_2 &= 0, f_2 = -1, g_1 = 0 \\ & & l_1 &= \frac{4}{5}, m_1 = \frac{3}{5}, n_1 = 0\end{aligned}$$

It is seen that  $h=l, k=-1, l=0$ .

In the case of ordinary diffraction, by (b')

$$\lambda = 0.720 \times 10^{-8} \text{ cm}$$

and by (b)

$$l_2 = \frac{3}{5} \qquad m_2 = \frac{4}{5} \qquad n_2 = 0$$

The ray has clearly been reflected in the (110) plane. In the case of extraordinary diffraction we must take a value of  $\lambda_2$ , e.g.,  $\lambda_2 = 0.600 \times 10^{-8}$  cm. Substituting in (a') gives

$$\lambda_1 = 0.569 \times 10^{-8} \text{ cm}$$

and using this in (a) gives

$$l_2 = 0.642, \qquad m_2 = 0.767, \qquad n_2 = 0.$$

It will be found that both  $\lambda_1$  and  $\lambda_2$  must be less than  $\lambda$  and that the extraordinary ray therefore diverges less from the transmitted ray than does the ordinary ray. This is generally true.

The observed effects depend upon the range of wave-lengths present in the incident beam, and upon the number of crystals dealt with. If there is one crystal, fixed in position, and a wide range of incident wave-lengths, the ordinary diffraction gives the familiar spot-pattern (Laue pattern). The extraordinary diffraction gives additional spots which in the usual experimental arrangements wherein  $\lambda_1$  is very much less than  $\lambda_2$  would be relatively faint. The spots of the ordinary pattern are formed by beams of various wave-lengths, those of the extraordinary pattern by beams all of a single wave-length or of a few definite

values corresponding to the strong lines in the characteristic X-ray spectra of the elements present. This case has not been experimentally tested.

If the crystal is rotated about any line as an axis the spots of the pattern move along paths which are, in general, curved. If attention is confined to a single direction of emission, and if the axis of rotation is perpendicular to this direction and to the incident ray, the conditions are those obtaining in the ordinary X-ray spectrometer. The customary orientations of the crystal are those in which the axis of rotation lies in one of its important planes. That both ordinary and extraordinary diffraction occurs in this case is apparently shown in results recently reported by Clark and Duane<sup>1</sup> for the case of *KI* crystals. The peak *X* which they obtain would be an extraordinary diffraction maximum in the sense of this analysis. Its location with respect to the ordinary maxima would, of course, depend upon the fixed sum of the angles of incidence and diffraction which would not, as in the ordinary case, be equal.

If the incident radiation is monochromatic there are no diffracted spots of either sort except for particular values of  $l_1, m_1, n_1$ , and no extraordinary diffraction for any direction of incidence if  $\lambda_1 > \lambda_2'$ . This case is of no practical importance, but if the single crystal is replaced by a great number, oriented at random these particular values of  $l_1, m_1, n_1$  occur and the ring-pattern (Hull or Debye-Scherrer pattern) is obtained. Both ordinary and extraordinary patterns can occur. It was, in fact, phenomena observed in this case that led to the explanation here offered.

Both the ordinary and extraordinary spots obtained in the last mentioned type of experiment are, if the individual crystals are not too small, replicas of the source in the aspect which it

<sup>1</sup> Clark, G. L., Duane, Wm., N. A. S. Proc. 8, pp. 90-96; May, 1922.

There is a curious error in this paper at the point where the spacing for lattice-planes making an angle of  $17^\circ.84$  with the planes (100) is calculated, apparently by the formula  $d = a \sin 17^\circ.84$ . There are no lattice planes with low indices inclined at this angle to the (100) planes of a cubic space-lattice and if we find integral values of  $h$  and  $k$  such that  $\tan 17^\circ.84 = h/k$  the spacing of these planes ( $h\ k\ 0$ ) would be given by

$$d = \frac{a}{\sqrt{h^2 + k^2}} = \frac{a}{h} \sin 17^\circ.84.$$

presents to the crystals, i.e., narrow elliptical outlines. The extraordinary spots are distinguishable from the ordinary spots, however, by several peculiarities. They are not so sharply defined, which may be attributed to the comparative rarity of atoms which emit characteristic X-rays as compared with those which merely scatter the incident beam. The greater complexity of the process in extraordinary diffraction may also account for greater variability in  $\phi_1$ ,  $\phi_2$ , and  $\tau$ , and consequent diffuseness in that case. The extraordinary spots can be inclined at greater angles to the lines joining them with the trace of the incident rays upon the film. This is due to the greater complexity in the extraordinary case of the expressions for  $l_2$ ,  $m_2$ ,  $n_2$  which causes the direction of emission to vary less directly with the direction of incidence. The extraordinary spots frequently form parallel groups which are in fact characteristic emission spectra where the different values of  $\lambda_2$  have been resolved by diffraction. This resolution, like all the extraordinary effects, is better for pure metals than for alloys, even if the ordinary diffraction for the two materials is equally sharp indicating crystals of similar size and regularity. The extraordinary spots are more absorbable than the ordinary spots, and are relatively more reduced in intensity by filters designed to improve contrast in the ordinary pattern. This prediction of the theory has been checked experimentally by omitting the filters and thereby reducing the exposure necessary to obtain marked extraordinary effects. The most striking peculiarity of the extraordinary spots is, however, that they can be found closer to the center of the pattern than can the ordinary spots. This closeness in itself enhances the intensity of the photographic effect by superposing the spots from various crystals within a more limited area, so that the first extraordinary ring of the combined pattern may even exceed in intensity the first ordinary ring. That this is not a spurious effect due to imperfect screening is conclusively shown by its complete absence under identical experimental conditions when the crystals contain no atoms of low enough atomic number to yield characteristic *K*-radiations when exposed to the molybdenum *K*-radiations available. No extraordinary diffractions of the molybdenum



radiations have been observed with silver, palladium, or gold, while they are always present to some extent with iron, nickel, and copper.

If the proposed explanation be accepted as sound, it appears probable that all the entities causing characteristic secondary emission are exactly alike, and that such secondary emission only occurs when these entities meet the atoms under a very limited range of conditions. The evidence that extraordinary diffraction takes place is then in favor of the existence of spatially limited energy quanta in the incident beam, and also in favor of cyclic motions within the atom which cause occasional recurrences of configurations unstable when coincident in time with the presence of a passing quantum of sufficient energy. A quantitative study of the new phenomena may be expected to give valuable information regarding its possible dependence upon the direction of incidence, the nature of inter-atomic bonding and other factors of interest to students of atomic structure and the nature of luminous radiations of all wave-lengths.

I desire in conclusion to express my appreciation of the interest and helpful suggestions of my colleague, Dr. K. K. Darrow, in the analysis here presented.

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