

function in the crystal almost vanishes in the shaded region in Fig. 2, and the wave which departs from the aperture  $S_a$  depends only on the wave function in the region  $a'b'b''a''$ .

### Diffraction by a polyhedral crystal

In the case of a polyhedral crystal, we divide the crystal as shown in Fig. 3; then we can calculate the wave functions for each division from (3) to (7). Their superposition satisfies approximately the boundary condition on the whole crystal surface by the above considerations and therefore represents the wave-field for a finite crystal of polyhedral shape according to the

dynamical theory. Further calculation of (8) and comparison with the kinematical theory will be given in the next note.

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## Dynamical Theory of Electron Diffraction for a Finite Polyhedral Crystal. II. Comparison with the Results of Kinematical Theory

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In the previous note (Kato & Uyeda, 1951), we have shown that Bethe's dynamical theory of electron diffraction (Bethe, 1928) can be extended to the case of a finite crystal. In the present note, we shall develop the theory further and compare its results with those derived from the kinematical theory.

### Dynamical and kinematical formula for a polyhedral crystal

The equation (7) of the previous note, which gives the diffracted wave due to one of the divisions of a crystal shown in Fig. 3 there, can be approximated by a more practical formula, provided the conditions described in the previous note are satisfied. The final formula for the diffracted amplitude at large distance,  $\mathbf{R}$ , from the crystal turns out to be

$$\begin{aligned} \Phi_{\mathbf{g}}^d(\mathbf{R}) = & \frac{1}{2iR} \frac{|V_{21}|}{\sqrt{(u^2 + w^2)}} \exp 2\pi i KR \\ & \times \left[ \exp 2\pi i \{(\mathbf{d}'_e, \mathbf{R}_e) + (\mathbf{d}'_a, \mathbf{R}_a)\} \int_{\Sigma} \exp 2\pi i(\Delta'_d, \mathbf{s}) d\mathbf{s} \right. \\ & \left. - \exp 2\pi i \{(\mathbf{d}''_e, \mathbf{R}_e) + (\mathbf{d}''_a, \mathbf{R}_a)\} \int_{\Sigma} \exp 2\pi i(\Delta''_d, \mathbf{s}) d\mathbf{s} \right]; \end{aligned} \quad (1)$$

here  $V_{21}$  is Bethe's dynamical structure factor which is approximately equal to the Fourier coefficient  $v_{\mathbf{g}}$  of the crystal potential, and  $w$  stands for

$$(|V_{21}|/K) \sqrt{(\mathbf{k}_{\mathbf{g}}, \mathbf{n}_e) / (\mathbf{k}_0, \mathbf{n}_e)}.$$

The notations used are explained in the legends of Figs. 1 and 3 of the preceding note.

On the other hand, the kinematical theory gives the expression of the amplitude diffracted by a finite crystal as follows:

$$\Phi_{\mathbf{g}}(\mathbf{R}) = \frac{\pi}{R} v_{\mathbf{g}} \int_C \exp 2\pi i(\mathbf{K}_e + \mathbf{g} - \mathbf{K}_{\mathbf{g}}, \mathbf{r}) d\mathbf{r}, \quad (2)$$

where the integral covers the whole volume of the crystal,  $C$ . If we consider the wave due to one of the divisions as above, the integration is limited to this division, and we can rewrite (2) as follows:

$$\begin{aligned} \Phi_{\mathbf{g}}^k(\mathbf{R}) = & \frac{1}{2iR} \frac{v_{\mathbf{g}}}{u_0} \exp 2\pi i KR \\ & \times \left[ \exp 2\pi i(\mathbf{d}_e, \mathbf{R}_e) \int_{\Sigma} \exp 2\pi i(\Delta_{\mathbf{g}}^e, \mathbf{s}) d\mathbf{s} \right. \\ & \left. - \exp 2\pi i(\mathbf{d}_a, \mathbf{R}_a) \int_{\Sigma} \exp 2\pi i(\Delta_{\mathbf{g}}^a, \mathbf{s}) d\mathbf{s} \right], \end{aligned} \quad (3)$$

where the notations are given in Fig. 1 of this note, and the other notations are the same as those in the previous note.

### Discussion by means of *Intensitätsbereich*

The interpretation of the kinematical formula (3) can be given most clearly by making use of the conception of Laue's *Intensitätsbereich* (Laue, 1936) in Ewald's construction of the wave vector. This construction can be obtained in Fig. 1 if we transfer the vector  $\mathbf{K}_{\mathbf{g}} = \overrightarrow{AG}$  by parallel displacement so that the initial point  $A$  coincides with the point  $E$ . Then, the end-point  $G$  is displaced to a new point, say  $Q$ , and  $\overrightarrow{GQ} = \overrightarrow{AE}$ , which

is expressed by  $-(\mathbf{d}_e + \Delta_k^e) = -(\mathbf{d}_a + \Delta_k^a)$ . The point  $Q$  and a part of the Ewald sphere near the lattice point  $G$  are illustrated in a new diagram, Fig. 2 (a). When we consider the case where the projected aperture  $\Sigma$  extends infinitely, the diffraction function  $\int \exp 2\pi i(\Delta, \mathbf{s}) ds$  becomes a  $\delta$ -type function and the *Intensitätsbereich* is contracted to the normals of the crystal,  $\mathbf{n}_e$  and  $\mathbf{n}_a$ , passing through the point  $G$ , and the two diffracted spots appear corresponding to  $Q_k^e$  and  $Q_k^a$ .

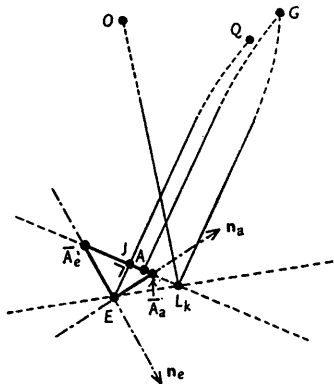


Fig. 1. Schematic diagram illustrating wave points projected on  $OEG$  plane.

$\overrightarrow{EJ} = u_0$  (corresponding to  $u$  in Fig. 1 of the previous note).

$\overrightarrow{EA}_e = \mathbf{d}_e$ ,  $\overrightarrow{EA}_a = \mathbf{d}_a$ ;  $\overrightarrow{A_e A} = \Delta_k^e$ ,  $\overrightarrow{A_a A} = \Delta_k^a$ .

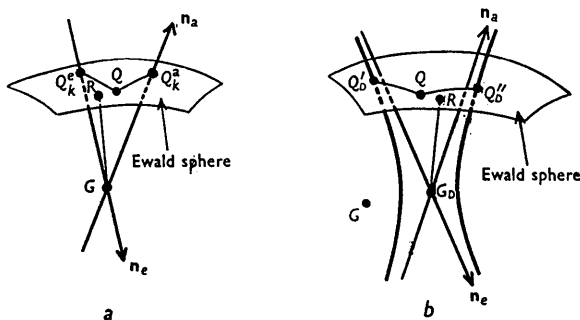


Fig. 2. Diagrams illustrating the geometrical interpretation of equations (1) and (3).

$G$ : reciprocal lattice point.

$Q$ : end point of the vector  $\mathbf{K}_g = \overrightarrow{EQ}$ .

$\overrightarrow{GR}$  or  $\overrightarrow{G_a R}$  is perpendicular to Ewald sphere.

(a) Kinematical:  $\overrightarrow{GQ_k^e} = -\mathbf{d}_e$ ,  $\overrightarrow{GQ_k^a} = -\mathbf{d}_a$ ;  
 $\overrightarrow{Q_k^e Q} = -\Delta_k^e$ ,  $\overrightarrow{Q_k^a Q} = -\Delta_k^a$ ,  $\overrightarrow{GR} = u_0$ .

(b) Dynamical:  $\overrightarrow{GQ'_a} = -(\mathbf{d}'_e + \mathbf{d}'_a)$ ,  $\overrightarrow{GQ''_a} = -(\mathbf{d}''_e + \mathbf{d}''_a)$ ;  
 $\overrightarrow{Q'_a Q} = -\Delta'_a$ ,  $\overrightarrow{Q''_a Q} = -\Delta''_a$ ;  $\overrightarrow{G_a R} = u$ .

When the crystal is finite, the diffraction function does not vanish at all points  $Q$  in the neighbourhood of the point  $G$ , and the diffracted beams become diffuse. If the two terms in (3) are independent of each other, the intensity on the normals varies according to

$(v_e/u_0)^2$ , but their interference produces maxima and minima.

Although the dynamical formula (1) is rather complicated, it can be interpreted along the same lines. Fig. 2 (b) shows the dynamical diagram which corresponds to Fig. 2 (a). When the crystal has an infinite lateral extension the *Intensitätsbereich* is contracted to the hyperbola whose asymptotes are the normals  $\mathbf{n}_e$  and  $\mathbf{n}_a$  passing through a point  $G_a$  ( $\overrightarrow{GG_a} = \overrightarrow{A_e E_L}$ ), and the diffracted spots appear corresponding to  $Q'_a$  and  $Q''_a$ . The splitting of the diffracted spots occurs, in this case, even when the Ewald sphere passes through the point  $G_a$ . When the crystal is finite the wave functions designated with single and double primes become diffuse around the wave vectors  $\overrightarrow{EQ'_a}$  and  $\overrightarrow{EQ''_a}$  according to the diffraction function of the projected aperture,  $\Sigma$ , which has the same form as in the case of the kinematical theory.

When the effective mean inner potential is neglected, the points  $G$  and  $G_a$  coincide. Moreover, the dynamical formula (1) can be reduced approximately to an expression identical with the kinematical formula (3) by a short calculation, provided one of the following conditions (1) or (2) is satisfied, i.e. if extinction is small:

(1) The product of the maximum thickness of the crystal,  $\rho_{\max}$ , and the reflecting power,  $w$ , of the net plane is very small, i.e.  $\rho_{\max} w \ll 1$ .

(2) The direction of the incident beam differs considerably from the direction which satisfies exactly the Bragg condition, i.e.  $w \ll u$ .

In the above consideration, we have applied the conception of *Intensitätsbereich* to the dynamical theory and obtained a clear interpretation of the result. It must, however, be mentioned here that in the case of the kinematical theory the *Intensitätsbereich* is fixed in the reciprocal lattice, but, in the case of the dynamical theory, it is deformed according to the azimuth of the primary beam around  $\mathbf{g}$ .

### Numerical example

We have performed a numerical calculation for the (100) reflexion on a cubic crystal of cubic shape. We adopted a set of numerical values nearly equal to those obtained by Sturkey (1948) for MgO:

$$v_0 - V_{11} > 14 \text{ eV.}, \quad v_0 - V_{22} \sim 14 \text{ eV.}, \quad |V_{21}| \sim 7 \text{ eV.}$$

and the energy of incident electrons  $E = 35 \text{ keV}$ . We assumed the incident beam to be parallel to the face diagonal and to satisfy the Bragg condition strictly, i.e.  $u = 0$ . We divided the crystal into two parts following the procedure mentioned in the previous note and superposed the diffracted waves due to both. When the crystal is very small,  $c. 30 \text{ \AA}$ ., no difference appears between the results of the two theories; when the crystal becomes larger than  $c. 50 \text{ \AA}$ ., the difference becomes discernible, but the doubly refracted spots are

not distinguishable as long as the crystal is smaller than *c.* 270 Å.

Although the present theory disregards the effects of inelastic scattering, it may be useful to interpret the fine structure and anomalous intensity observed in the electron-diffraction patterns, and it may serve also for a better understanding of results observed in electron micrographs and diffraction patterns of convergent electron beams (e.g. Heidenreich, 1942).

We hope soon to give elsewhere a more detailed derivation of the formulae, together with the interpretation of the results and some numerical examples.

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## Crystal Chemical Studies of the 5*f*-Series of Elements. XIV. Oxyfluorides, XOF

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The hydrolysis of LaF<sub>3</sub> and YF<sub>3</sub> has been studied, and isolated preparations of AcOF and PuOF have been examined. LaOF and YOF have been prepared in two forms, one being rhombohedral and the other tetragonal. The crystal structures of both forms have been determined and are shown to be superstructures based upon the fluorite type.

PuOF is shown to have the tetragonal structure. The single investigated sample of AcOF appears to be truly cubic with the fluorite structure.

This paper gives the results of a structural study of oxyfluorides XOF, where *X* represents a 5*f*-element, a 4*f*-element or yttrium. The specific compounds which have been investigated are AcOF, PuOF, LaOF and YOF. Yttrium was used as a crystal chemical stand-in for elements at the end of the 4*f*-series. Since LaOF and YOF have been found to be isostructural, it may be safely assumed that oxyfluorides XOF of all 4*f*-elements will be structurally analogous. The fact that AcOF and YOF are isostructural, actinium being the largest of the trivalent 5*f*-elements, makes it possible to predict with assurance that oxyfluorides XOF of all 5*f*-elements will belong to the same isostructural series of compounds.

### The preparations of PuOF and AcOF

#### *PuOF*

In early 1944 J. Karle tried to prepare plutonium metal by atomic hydrogen reduction of plutonium tetrafluoride. The reduction was carried out on the 20 μg. scale. The reaction product was submitted to me for identification and X-ray diffraction study.

The diffraction pattern showed the preparation to contain about 10% of PuF<sub>3</sub>. The bulk of the sample was found to consist of a cubic face-centered phase with  $a = 5.70 \pm 0.01$  Å. A few very weak diffraction lines corresponded neither to PuF<sub>3</sub> nor to the cubic phase. It was at the time assumed that these diffraction lines were due to a small amount of impurity.

On the basis of the method of preparation the cubic phase would have to be plutonium metal, a plutonium fluoride, an oxyfluoride or an oxide. (In preparations on the microgram scale the possible presence of oxygen must always be considered.) At the time X-ray diffraction investigations had led to conclusive identification of plutonium metal and of the following oxides and fluorides: PuO<sub>2</sub>, Pu<sub>4</sub>O<sub>7</sub>, PuO, PuF<sub>4</sub> and PuF<sub>3</sub>. The cubic face-centered phase found in Karle's preparation corresponded to none of the previously identified compounds.

On the basis of extensive experimental data I had shown that the volume required by an oxygen or a fluorine atom in compounds of the heavy elements is about 19 Å.<sup>3</sup>, and that the volume requirement of the heavy cation could be neglected in the first approximation. Since the unit-cell volume of the cubic phase is 185 Å.<sup>3</sup>, eight oxygen plus fluorine atoms per unit cell were strongly indicated. The observed intensities required four plutonium atoms in the unit cell and a fluorite type of structure.

Thus the two possible chemical formulas for the unknown cubic phase were found to be PuF<sub>2</sub> or PuOF. The cation-anion distance of 2.47 Å. favored the formula PuOF. However, too little was known about the chemistry and crystal chemistry of plutonium at that time to justify a reliable decision between the two formulas on the basis of interionic distances.