

On the Total Scattering of X-Rays from Crystals

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A general formula is derived for the total intensity of x-radiation scattered by a general crystal in any direction. In those directions satisfying the Laue equations the formula gives the usual result, while in other directions there is obtained a formula for the total intensity of the diffuse scattering. The derivation is based on classical electromagnetic theory. The form of the result is independent of any assumptions as to spherical symmetry of the scattering atoms or isotropy of thermal vibrations, these factors merely affecting the numerical values of scattering factors and temperature factors and their dependence on angle. Absorption, and the effects of the interaction of incident and scattered radiation are neglected.

THE problem of the scattering of x-rays by crystals has been treated by numerous writers from many points of view. Debye^{1, 2} in his original papers on the subject was concerned with the problem of the effect of temperature on the intensity of the reflected radiation. He showed¹ that a crystal consisting of atoms vibrating about lattice points would give rise to two kinds of scattering: first, the regularly reflected rays in certain directions satisfying the Laue equations, due to the periodic arrangement of the scattering centers; and second, a diffusely scattered radiation in all directions, due to the thermal vibrations of the atoms. Since a crystal does not consist of atoms bound by elastic forces to lattice points about which they vibrate, but rather of atoms bound to each other and forming a vibrating system, it is satisfactory to find that essentially the same result² was obtained on taking account of the normal vibrations of the lattice. In fact, von Laue has shown the equivalence of the two methods in a comprehensive paper.³ Other treatments of the same problem have been given by Darwin,⁴ Waller,⁵ Faxén,⁶ and v. Laue^{3, 7} the results in all cases being essentially the same. Most of these papers have been rather formidable. Their main object has been

an investigation of the effect of temperature on the intensity of the reflected radiation and they have been concerned with the problem of calculating the temperature factor in terms of known atomic constants and crystalline properties. The diffusely scattered radiation has usually been an incidental feature; in none of these cases has a quantitative formula been given for the intensity of the diffuse scattering in a form which can be directly compared with experiment. The scattering elements have usually been taken as atoms, considered as points. This defect can be partially remedied by introducing a scattering factor for each atom^{3, 7} but such a procedure necessarily omits the incoherent portion of the scattering from each atom, since point atoms do not give rise to such scattering. The usual procedure has been to add on the Compton scattering.⁸ Although this can be justified it seems rather artificial. From the point of view of one interested in the diffuse scattering the Compton radiation is just as much a part of the process as is the radiation scattered as a result of the thermal vibrations.

On the other hand, when considering the theory of diffuse scattering it has been usual to avoid reflected radiation.⁸⁻¹⁰ This has been done by assuming throughout the calculation that the direction of scattering is well away from a direction of reflection.

If one is not concerned with a detailed calcu-

¹ P. Debye, *Verh. d. Deutsch. Phys. Ges.* **15**, 678, 738 and 857 (1913).

² P. Debye, *Ann. d. Physik* **43**, 49 (1914).

³ M. v. Laue, *Ann. d. Physik* **81**, 877 (1926).

⁴ C. G. Darwin, *Phil. Mag.* **27**, 315 (1914).

⁵ I. Waller, *Zeits. f. Physik* **17**, 398 (1923); *Ann. d. Physik* **79**, 261 (1926); **83**, 154 (1927); *Zeits. f. Physik* **51**, 213 (1928); *Diss. Upsala* (1925).

⁶ H. Faxén, *Ann. d. Physik* **54**, 615 (1917); *Zeits. f. Physik* **17**, 266 (1923).

⁷ M. v. Laue, *Ann. d. Physik* **42**, 1561 (1913).

⁸ E.g., Y. H. Woo, *Phys. Rev.* **38**, 6 (1931), and other papers.

⁹ G. E. M. Jauncey and G. G. Harvey, *Phys. Rev.* **37**, 1193 and 1203 (1931).

¹⁰ G. E. M. Jauncey, *Phys. Rev.* **42**, 453 (1932).

lation of the temperature factor in terms of known constants but merely with its existence, then it is an easy matter to derive a formula for the total intensity of the radiation scattered in any direction by a general crystal.¹¹ It is the purpose of the present note to do this from the point of view of classical electromagnetic theory. It is well known that such a procedure leads to the same results as a quantum-mechanical calculation except for effects of electron exchange and relativity. Strictly speaking, a rigorous calculation of the scattering from a crystal is a problem in dispersion theory and has been treated very fully from this point of view, especially by Waller.⁵ We shall here be concerned with those cases in which dispersion may be neglected.

THEORY

Consider a general triclinic crystal having n atoms, of any number of kinds, in a unit cell determined by the three translation vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 . Let \mathbf{r}_j be a vector from the origin of any unit cell to the equilibrium position of the center of the j th atom in that cell. Let the direction of an incident beam of x-rays be specified by a unit vector \mathbf{s}_0 in the direction of the beam; it is desired to compute the intensity of the radiation scattered in a direction determined by a unit vector \mathbf{s} . We may consider an incident beam of plane-polarized radiation with its electron vector \mathcal{E} perpendicular to the plane of scattering determined by \mathbf{s} and \mathbf{s}_0 . Then the electric intensity of the incident beam at any point will be given by

$$\mathcal{E} = \Re \mathcal{E}_0 \exp [2\pi\nu i(t - \mathbf{s}_0 \cdot \mathbf{r}/c)], \quad (1)$$

where ν is the frequency of the incident radiation, \mathbf{r} a vector from any convenient origin O to the point in question and $t=0$ is chosen so that \mathcal{E}_0 is real. \Re denotes the real part of the expression following it. Then at a distance R from the crystal, large compared with the crystal dimen-

sions, the instantaneous wave scattered by a fixed configuration of the N electrons contained in the crystal will be given by $\Re A$ where

$$A = \frac{e^2}{mc^2 R} \sum_{\alpha=1}^N \mathcal{E}_\alpha \quad (2)$$

and

$$\begin{aligned} \mathcal{E}_\alpha &= \mathcal{E}_0 \exp [2\pi\nu i\{t - R/c + \mathbf{R}_\alpha \cdot (\mathbf{s} - \mathbf{s}_0)/c\}] \\ &= \mathcal{E}_0 \exp [(2\pi i/\lambda)(ct - R)] \\ &\quad \times \exp [(2\pi i/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{R}_\alpha]. \end{aligned} \quad (3)$$

\mathbf{R}_α is a vector from O to the α th electron in the crystal. The square of the amplitude of this wave is

$$|A|^2 = AA^* = \frac{e^4}{R^2 m^2 c^4} \sum_{\alpha=1}^N \sum_{\beta=1}^N \mathcal{E}_\alpha \mathcal{E}_\beta^*, \quad (4)$$

where X^* is the complex conjugate of X . The solution to the problem now consists in evaluating Eq. (4) and then obtaining an average value of the intensity.

With this end in view we express the vector \mathbf{R}_α in more explicit form. Using \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 and \mathbf{r}_j as previously defined we introduce a vector $\boldsymbol{\zeta}_j$ measured from the end of \mathbf{r}_j to the instantaneous position of the center of the j th atom in any unit cell (this displacement being due to thermal motion) and a vector $\boldsymbol{\rho}_{jk}$ from the instantaneous center of atom j to the k th electron in that atom. Without any loss of generality we may take the crystal to be a parallelepiped $M_1 - 1$ units along \mathbf{a}_1 , $M_2 - 1$ units along \mathbf{a}_2 and $M_3 - 1$ units along \mathbf{a}_3 . We may conveniently take the origin O to be at the origin of the crystal. Then the vector \mathbf{R} from O to the k th electron in the j th atom in the unit cell m_1, m_2, m_3 units along $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, respectively, will be given by

$$\mathbf{R}_{m, jk} = m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2 + m_3 \mathbf{a}_3 + \mathbf{r}_j + \boldsymbol{\zeta}_j + \boldsymbol{\rho}_{jk}. \quad (5)$$

For abbreviation we shall write

$$\mathbf{A}_m = m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2 + m_3 \mathbf{a}_3 \quad (6)$$

and by a subscript m shall always mean three quantities m_1, m_2, m_3 . Eq. (5) then becomes

$$\mathbf{R}_{m, jk} = \mathbf{A}_m + \mathbf{r}_j + \boldsymbol{\zeta}_j + \boldsymbol{\rho}_{jk}. \quad (7)$$

¹¹ Ewald (*Handbuch der Physik*, Vol. 23, Pt. 2 (1933)) has given a simple derivation for crystals of one kind of atom, obtaining essentially Debye's result (reference 2), but he, too, uses atoms rather than electrons as scattering units. He states also that the diffuse scattering increases monotonically with scattering angle, whereas this is actually not the case on taking account of the electron distribution in the atom.

Substituting this value for \mathbf{R} in Eqs. (3) and (4) gives

$$AA^* = \frac{e^4 \mathcal{E}_0^2}{R^2 m^2 c^4} \sum_{m, i, k} \exp \left[\frac{2\pi i}{\lambda} (ct - R) \right] \\ \times \exp \left[\frac{2\pi i}{\lambda} (\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{R}_{m, i, k} \right] \\ \times \sum_{m', i', k'} \exp \left[\frac{-2\pi i}{\lambda} (ct - R) \right] \\ \times \exp \left[\frac{-2\pi i}{\lambda} (\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{R}_{m', i', k'} \right], \quad (8)$$

where the summations are taken so as to include all possible pairs of electrons in the crystal. If for abbreviation we write

$$\boldsymbol{\kappa} = \frac{2\pi}{\lambda} (\mathbf{s} - \mathbf{s}_0) \quad (9)$$

and use Eq. (7), expressing the summations more explicitly, Eq. (8) becomes

$$AA^* = \frac{e^4 \mathcal{E}_0^2}{R^2 m^2 c^4} \sum_{m, m'} \exp [i\boldsymbol{\kappa} \cdot (\mathbf{A}_m - \mathbf{A}_{m'})] \\ \times \sum_{i, i'} \{ \exp [i\boldsymbol{\kappa} \cdot (\mathbf{r}_j + \boldsymbol{\zeta}_j - \mathbf{r}_{j'} - \boldsymbol{\zeta}_{j'})] \\ \times \sum_{k, k'} \exp [i\boldsymbol{\kappa} \cdot (\boldsymbol{\rho}_{jk} - \boldsymbol{\rho}_{j'k'})] \}. \quad (10)$$

The expression given by Eq. (10) is proportional to the intensity scattered by a given configuration of electrons instantaneously at rest, the quantities $\boldsymbol{\zeta}$ and $\boldsymbol{\rho}$ depending on the time. The observed intensity will be obtained by averaging over all values of $\boldsymbol{\zeta}$ and $\boldsymbol{\rho}$. $\boldsymbol{\zeta}$ varies due to thermal vibrations of the atoms while $\boldsymbol{\rho}$ varies due to the "orbital" motion of the electrons. The greatest frequency of thermal vibration will be of the order of magnitude of ν_m where $h\nu_m/k = \Theta$, the characteristic temperature of the crystal. The "frequency" of the orbital motion will be of the order of magnitude of the orbital frequency in an hydrogenic Bohr atom:

$$\omega = 2RcZ^2/n^3 \quad (11)$$

in the n th quantum state, R being the Rydberg constant. $\omega \sim 10^{15} Z^2/n^3$ while all $\nu_m \sim 10^{12}$ sec.⁻¹;

for radiation of wave-length $\lambda \sim 1A$, $\nu \sim 10^{18}$ sec.⁻¹. Hence for not too high atomic numbers and not too long a wave-length of incident radiation we may assume that the electrons remain essentially at rest while the electric vector of the incident wave goes through a complete cycle. For this reason we may disregard the phase of the radiation given by Eq. (10). In the same way we may assume the atomic centers to be essentially at rest while the electrons perform several complete excursions about their respective nuclei.¹²

To take account of the orbital motion of the electrons let $p_{jk}(\boldsymbol{\rho})dv_{jk}$ be the probability that electron k in atom j is in a volume element dv_{jk} at a vector distance $\boldsymbol{\rho}$ from the instantaneous center of atom j . Eq. (10) is to be multiplied by $p_{jk}(\boldsymbol{\rho})p_{j'k'}(\boldsymbol{\rho}')dv_{jk}dv_{j'k'}$ and integrated over all space. By definition

$$\int p_{jk}(\boldsymbol{\rho})dv_{jk} = 1, \quad (12)$$

since it is certain that each electron must be somewhere. Thus, for those terms in Eq. (10) for which $m=m'$, $j=j'$ and $k=k'$ we shall get a contribution

$$M_1 M_2 M_3 \sum_{j=1}^n Z_j, \quad (13)$$

where Z_j is the atomic number of the j th atom and n the number of atoms in the unit cell. Those terms in Eq. (10) for which $m=m'$, $j=j'$ but $k \neq k'$ refer to two different electrons in the same atom. These terms will contribute

$$M_1 M_2 M_3 \sum_{j=1}^n \int \int_{k, k'=1}^{Z_j} \sum' \exp [i\boldsymbol{\kappa} \cdot (\boldsymbol{\rho}_{jk} - \boldsymbol{\rho}_{j'k'})] \\ \times p_{jk}(\boldsymbol{\rho})p_{j'k'}(\boldsymbol{\rho}')dv_{jk}dv_{j'k'}, \quad (14)$$

the accent denoting the omission of those terms for which $k=k'$. For the purposes of the present discussion we are not interested in the form of $p_{jk}(\boldsymbol{\rho})$ but merely recall that

$$\int \exp [i\boldsymbol{\kappa} \cdot \boldsymbol{\rho}_{jk}] p_{jk}(\boldsymbol{\rho})dv_{jk} = f_{(kk)j}, \quad (15)$$

where $f_{(kk)j}$ is the amplitude scattered coherently

¹² We shall neglect the Doppler effect due to these motions. See v. Laue (reference 3).

by an electron of type k in an atom of type j . Now

$$\sum_{k, k'} f_{(kk)} i f_{(k'k')}^* = \sum_{k, k'} f_{(kk)} i f_{(k'k')}^* - \sum_k f_{(kk)} i f_{(kk)}^* \quad (16)$$

$$\text{and} \quad \sum_{k, k'} f_{(kk)} i f_{(k'k')}^* = f_j f_j^*, \quad (17)$$

$$\text{where} \quad f_j = \sum_k f_{(kk)} \quad (18)$$

and $|f_j|$ is the usual atomic scattering factor for an atom of type j . Hence expression (14) becomes

$$M_1 M_2 M_3 \sum_{j=1}^n \{ f_j f_j^* - \sum_{k=1}^{Z_j} f_{(kk)} i f_{(kk)}^* \}. \quad (19)$$

Next consider the terms for which $m = m'$ but $j \neq j'$. For such terms the ρ_{jk} are completely independent of each other so that as far as summation with respect to k is concerned we shall merely have $f_j f_j^*$ and shall be left with

$$M_1 M_2 M_3 \sum_{j, j'} f_j f_j^* \exp [i\mathbf{k} \cdot (\mathbf{r}_j + \boldsymbol{\zeta}_j - \mathbf{r}_{j'} - \boldsymbol{\zeta}_{j'})] \quad (20)$$

and this expression is to be averaged over all values of $\boldsymbol{\zeta}$. Suppose the probability that the center of atom j is in dv_j at a vector distance $\boldsymbol{\zeta}_j$ from its equilibrium position to be $q_j(\boldsymbol{\zeta}) dv_j$; then the expression (20) is to be multiplied by $q_{j'}(\boldsymbol{\zeta}') dv_{j'}$ and integrated over all configurations, i.e., we require the value of

$$M_1 M_2 M_3 \sum_{j, j'} f_j f_j^* \exp [i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_{j'})] \times \int \int \exp [i\mathbf{k} \cdot (\boldsymbol{\zeta}_j - \boldsymbol{\zeta}_{j'})] q_j(\boldsymbol{\zeta}) q_{j'}(\boldsymbol{\zeta}') dv_j dv_{j'} \quad (21)$$

with the requirement

$$\int q_j(\boldsymbol{\zeta}) dv_j = 1.$$

Again, we are not concerned with the form of the probability functions $q_j(\boldsymbol{\zeta})$ but merely remark that the expression

$$\left| \int \exp [i\mathbf{k} \cdot \boldsymbol{\zeta}_j] q_j(\boldsymbol{\zeta}) dv_j \right| \equiv \exp [-M_j] \quad (22)$$

is the temperature factor for an atom of type j in the crystal in question; it is convenient to denote this in the usual Debye-Waller form $\exp [-M_j]$ where M_j is defined by Eq. (22). If we denote the atomic scattering factor for an atom in the crystal at temperature T by f_j^T then

$$f_j^T = f_j \exp [-M_j] \quad (23)$$

and expression (21) becomes

$$M_1 M_2 M_3 \sum_{j, j'} f_j^T f_{j'}^{T*} \exp [i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_{j'})]. \quad (24)$$

$$\text{Now} \quad \sum_j f_j^T \exp [i\mathbf{k} \cdot \mathbf{r}_j] = F, \quad (25)$$

where F is the structure factor of the unit cell. Thus the summation in (24) can be written

$$\sum_{j, j'} f_j^T f_{j'}^{T*} \exp [i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_{j'})] = FF^* - \sum_j f_j^T f_j^{T*}. \quad (26)$$

Finally, those terms for which $m \neq m'$ contribute

$$\begin{aligned} & \sum_{m, m'} \exp [i\mathbf{k} \cdot (\mathbf{A}_m - \mathbf{A}_{m'})] \\ & \times \sum_{j, j'} \exp [i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_{j'})] f_j^T f_{j'}^{T*} \\ & = FF^* \sum_{m, m'} \exp [i\mathbf{k} \cdot (\mathbf{A}_m - \mathbf{A}_{m'})] \\ & = FF^* \{ \sum_{m, m'} \exp [i\mathbf{k} \cdot (\mathbf{A}_m - \mathbf{A}_{m'})] \\ & \quad - M_1 M_2 M_3 \}. \quad (27) \end{aligned}$$

$$\text{But} \quad \sum_{m, m'} \exp [i\mathbf{k} \cdot (\mathbf{A}_m - \mathbf{A}_{m'})]$$

is the usual interference function for a parallelepipedal lattice and may easily be shown¹³ to have the value

$$\prod_{l=1}^3 \frac{\sin^2 \frac{1}{2} M_l \mathbf{k} \cdot \mathbf{a}_l}{\sin^2 \frac{1}{2} \mathbf{k} \cdot \mathbf{a}_l}. \quad (28)$$

Thus the average value of Eq. (10), obtained by

$$\begin{aligned} & \text{E.g.} \quad \sum_{m=0}^{M-1} e^{imx} \sum_{m'=0}^{M-1} e^{-im'x} \\ & = [1 + e^{ix} + e^{2ix} + \dots + e^{i(M-1)x}] \\ & \quad \times [1 + e^{-ix} + e^{-2ix} + \dots + e^{-i(M-1)x}] \\ & = \frac{e^{iMx} - 1}{e^{ix} - 1} \times \frac{e^{-iMx} - 1}{e^{-ix} - 1} \\ & = \frac{(e^{\frac{1}{2}ix} - e^{-\frac{1}{2}ix})^2}{(e^{\frac{1}{4}ix} - e^{-\frac{1}{4}ix})^2} = \frac{\sin^2 \frac{1}{2} Mx}{\sin^2 \frac{1}{2} x}, \text{ etc.} \end{aligned}$$

combining the terms in expressions (13), (19), (26), (27) and (28), is given by

$$\overline{AA^*} = \frac{e^4 \mathcal{E}_0^2}{R^2 m^2 c^4} \left\{ FF^* \prod_{l=1}^3 \frac{\sin^2 \frac{1}{2} M_l \boldsymbol{\kappa} \cdot \mathbf{a}_l}{\sin^2 \frac{1}{2} \boldsymbol{\kappa} \cdot \mathbf{a}_l} + M_1 M_2 M_3 \sum_{j=1}^n [Z_j - \sum_{k=1}^{Z_j} f_{(kk)j} f_{(kk)j}^* + f_j f_j^* - f_j^T f_j^{T*}] \right\}. \quad (29)$$

Eq. (29) gives the average square of the electric vector of the radiation scattered from an incident beam polarized with its electric vector \mathcal{E}_0 perpendicular to the plane of scattering. If the incident beam is unpolarized then we shall obtain the actual scattered intensity by replacing the expression $e^4 \mathcal{E}_0^2 / R^2 m^2 c^4$ in Eq. (29) by I_e , the Thomson scattering from a single electron for unpolarized radiation

$$I_e = I_0 \frac{e^4}{R^2 m^2 c^4} \left(\frac{1 + \cos^2 2\theta}{2} \right), \quad (30)$$

where I_0 is the intensity of the incident beam and 2θ is the angle of scattering. The scattered intensity is thus

$$I = I_e F^2 \prod_{l=1}^3 \frac{\sin^2 \frac{1}{2} M_l \boldsymbol{\kappa} \cdot \mathbf{a}_l}{\sin^2 \frac{1}{2} \boldsymbol{\kappa} \cdot \mathbf{a}_l} + I_e M_1 M_2 M_3 \sum_{j=1}^n [Z_j - \sum_{k=1}^{Z_j} f_{(kk)j}^2 + f_j^2 - f_j^{T2}], \quad (30)$$

where we have replaced ff^* by f^2 and understand by f the usual tabulated scattering factor, i.e. $|f|$, and have done the same for f_{kk} and F . Eq. (30) is the solution to the problem and gives the total intensity of the scattered radiation in any direction. However, for those directions for which the Laue equations

$$\boldsymbol{\kappa} \cdot \mathbf{a}_l = 2\pi h_l \quad (h_l = 0, 1, 2, \dots) \quad (31)$$

or in their more usual form

$$\begin{aligned} (\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_1 &= h\lambda, \\ (\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_2 &= k\lambda, \quad (h, k, l = 0, 1, 2, \dots) \\ (\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_3 &= l\lambda, \end{aligned} \quad (32)$$

are satisfied, the first term of Eq. (30) becomes

$$I_1 = I_e M_1^2 M_2^2 M_3^2 F^2 \quad (33)$$

and is thus the only one of importance since each of the M 's is a very large number except for exceedingly fine particles. Eq. (33) is the usual expression for the intensity of reflection from a crystal. On the other hand, since the maxima of $\sin^2 nx / \sin^2 x$ are extremely sharp for large n (having widths at half-maximum $\sim 1/n$) we may completely disregard this first term if we stay sufficiently far away from the directions of reflection.¹⁴

Thus the intensity of the diffuse scattering, which must always be measured in regions in which no regular reflection is present, will be given by

$$I_2 = M_1 M_2 M_3 I_e \sum_{j=1}^n \{ Z_j - \sum_{k=1}^{Z_j} f_{(kk)j}^2 + f_j^2 - f_j^{T2} \}. \quad (34)$$

The first two terms of Eq. (34) are obtained by adding intensities and correspond to incoherent Compton scattering; if the atoms were points instead of having finite size the sum of these terms would vanish. The last two terms correspond to radiation scattered as a consequence of the thermal vibrations of the atoms in the crystal lattice. If the atoms were at rest the sum of these terms would vanish. It is to be noticed that no assumption was made as to the isotropy of such vibrations. If the vibrations are not isotropic then the temperature factor Eq. (22) will depend not only on $(\sin \theta) / \lambda$ but also on the orientation of the crystal with respect to the x-ray beam.¹⁵ Eq. (34), however, remains formally the same. The same is true in regard to the electronic distributions in the atoms. Whether or not they are spherically symmetrical does not affect the form of the result but only the values of the f 's.¹⁶

Equation (34) is as far as classical theory can take us under the assumptions made. But recog-

¹⁴ Just what is meant by "sufficiently far" is a question into which we do not enter here.

¹⁵ In this connection see, for example, C. Zener, Phys. Rev. **49**, 122 (1936); G. W. Brindley, Phil. Mag. **21**, 790 (1936). Also G. E. M. Jauncey and W. A. Bruce, Phys. Rev. **50**, 408 and 413 (1936); E. O. Wollan and G. G. Harvey, Phys. Rev. **51**, 1054 (1937).

¹⁶ A formula similar to Eq. (34) has been given by Jauncey (reference 10) for the diffuse part of the scattering from a complex crystal. In his derivation, however, Jauncey made the (unnecessary) assumption that the thermal vibrations and electronic distributions had spherical symmetry.

nizing that the first two terms of this equation are due to Compton scattering we may see what modifications would be brought about in a quantum-mechanical treatment of the problem. First, the Pauli exclusion principle would restrict the number of possible transitions giving rise to incoherent scattering. This means that an amount

$$\sum_{k \neq l} f^2_{(kl)j}, \quad (35)$$

the summation being taken over all pairs of electrons with the same spin and $k \neq l$, is to be subtracted from the expression in { } in Eq. (34).¹⁷ The quantities f_{kl} are defined by

$$f_{kl} = \int \psi_k \exp [i\mathbf{k} \cdot \mathbf{r}] \psi_l^* dv \quad (36)$$

and for $k=l$ reduce to the expressions in Eq. (15) since $|\psi|^2 dv = p(\mathbf{r}) dv$. The expression (35) repre-

¹⁷ I. Waller and D. R. Hartree, Proc. Roy. Soc. **119**, 124 (1929).

sents a small correction term.¹⁸ In addition, all those terms corresponding to Compton scattering must be divided by $(1 + \alpha \text{ vers } 2\theta)^3$, where $\alpha = h/mc\lambda$, in order to take account of the fact that the scattered quanta have lost some of their energy in the scattering process. Thus the intensity of the diffuse scattering is given by

$$I_{\text{e.u.}} = \frac{1}{N_o} \sum_{j=1}^n \left\{ \frac{Z_j - \sum_{k=1}^{Z_j} f^2_{(kk)j} - \sum_{k \neq l} f^2_{(kl)j}}{(1 + \alpha \text{ vers } 2\theta)^3} + f_j^2 - f_j^2 \right\}, \quad (37)$$

where the intensity is now expressed in *electron units* per molecule of scattering substance; N_o is the number of molecules per unit cell of the crystal.

¹⁸ For the relative importance of this term in the diffuse scattering from crystals see G. G. Harvey, P. S. Williams and G. E. M. Jauncey, Phys. Rev. **46**, 365 (1934).

On Alleged Discontinuities in the Diffuse Scattering of X-Rays from Crystals at Small Angles

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It is pointed out that the positions of discontinuities in the diffuse scattering from crystals, reported by Laval, all occur at places corresponding to reflections of radiation of one-half, one-third, etc. the wave-length of the main beam. For the case of aluminum, microphotometer traces of films exposed in such a way as to accentuate the expected effect, are reproduced. They show no discontinuities of the kind reported by Laval, but do show peaks corresponding to the reflection of radiation of half the primary wave-length. It is concluded that the effect reported by Laval most probably does not exist.

IN a short note Laval¹ claims to have found that the diffuse scattering from a large number of crystals varies in a discontinuous manner at small angles of scattering. Taking the case of Cu $K\alpha$ radiation diffracted by powdered aluminum, he reports a total of nine discontinuities, six of which occur at values of $(\sin \theta)/\lambda$ less than that corresponding to the first Debye-Scherrer-

¹ J. Laval, Comptes rendus **201**, 889 (1935).

Hull line (111) for this wave-length. He states that the diffuse scattering increases smoothly with increasing scattering angle until a discontinuity is reached; the scattered intensity then suddenly drops to a smaller value and then increases again until the next edge is reached, and so on. A decrease of 40 percent in intensity is reported for one edge at $(\sin \theta)/\lambda = 0.072$. The magnitude of the discontinuity is not given