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Theory of the Diffuse Scattering of X-Rays by Crystals in the Region of the K Critical Absorption Wave-Length

G. E. M. Jauncey
Wayman Crow Hall of Physics, Washington University, St. Louis, Missouri

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The scattering of x-rays according to the classical theory from a bound electron of natural frequency ν_q is first considered. Then Z electrons with various ν_q's are assembled into an atom and the scattering from the atom studied. The scattered rays are separated into coherent and incoherent parts by a study of the interference between the scattered rays from two similar atoms. From this S_{coh} and S_{incoh} are obtained for the atom. Kramers, Kallmann and Mark's idea of virtual oscillators is used so that S_{coh} and S_{incoh} are averaged for the distribution of oscillators. The λ^3 absorption law suggests either $2\nu_K{}^2\nu_q{}^{-3}d\nu_q$ or $4\lambda_K{}^{-4}\lambda_q{}^3d\lambda_q$ as the fraction of oscillators with frequencies between ν_q and $\nu_q+d\nu_q$ or with wave-lengths between λ_q and $\lambda_q+d\lambda_q$. In determining the averages it makes a difference which distribution is used. The theory gives $S_{\text{coh}}=(f-\Delta f)^2\times(1-e^{-2M})/Z$, where Δf is the atomic structure factor decrement and e^{-2M} the Debye-Waller temperature factor. Also the theory gives $S_{\text{incoh}}=1-(1/Z)\Sigma E_r{}^2+Y$, where Y is negligible for $\lambda>\lambda_K$ but is quite large for $\lambda<\lambda_K$. Its size when $\lambda<\lambda_K$ suggests that Y is the classical analog of the energy which goes into the K fluorescent rays. Since these rays are removed by absorption in aluminum in experiments on diffuse scattering, Y is omitted in S_{incoh}. Finally $S=S_{\text{coh}}+S_{\text{incoh}}/\{1+(h/mc)\text{ vers }\phi\}^3$. Hönl's theoretical value of $\Delta f=2.3$ is compared with McNatt's experimental value 2.5 for Cu $K\alpha$ x-rays scattered by zinc.

1. Introduction

UNTIL recently all of the experimental work on the diffuse scattering of x-rays by crystals has been done in this laboratory with wave-lengths much shorter than the K critical absorption wave-length of the crystal being examined. Recently, however, McNatt[1] has been investigating the diffuse scattering of Cu $K\alpha$ ($\lambda=1.54$A) and Zn $K\alpha$ ($\lambda=1.433$A) x-rays from single crystals of zinc ($\lambda_K=1.28$A). In these cases λ/λ_K is somewhat greater than unity and the theory of diffuse scattering must be extended to the region of anomalous dispersion.

The early papers by Debye,[2] Faxen,[3] and Laue[4] on the theory of diffuse scattering by single crystals took account only of what is now called the coherent part of the scattered rays. The early experiments of Jauncey[5] and Jauncey and May[6] immediately showed the inadequacy of the then existent theory to describe the experimental results. After the discovery of the Compton effect, Compton[7] suggested that the incoherent part of the scattered rays should be taken into account. Both theory and experiments on diffuse scattering then languished until 1931 when Jauncey,[8] Jauncey and Harvey,[9] and, independently, Woo[10] extended the theory so as to include the incoherently scattered rays. There was some discussion between Woo and Jauncey as to the correct separation of the coherent and incoherent rays, but finally in 1932 these two writers[11, 12] came to an agreement on the formulas

$$\begin{aligned} S&=S_{\text{coh}}+S_{\text{incoh}}/\{1+(h/mc)\text{ vers }\phi\}^3,\\ S_{\text{coh}}&=(f^2/Z)(1-e^{-2M}), \qquad (1)\\ S_{\text{incoh}}&=1-(1/Z)\sum E_r{}^2,\end{aligned}$$

where f is the true atomic structure factor, E_r is the electronic structure factor for the rth (K, L, etc.) type of electron, and e^{-M} is the Debye-Waller[2, 13] temperature factor. Further extension of the theory was made in 1933 by Harvey, Williams and Jauncey[14] to take account of the Pauli exclusion principle; but, since this leads to a small change in S_{incoh} which is negligible except in crystals consisting of light atoms (such as NaF)

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[1] E. M. McNatt, Phys. Rev. **56**, 406 (1939).

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

[3] H. Faxen, Ann. d. Physik **54**, 615 (1917).

[4] M. v. Laue, Ann. d. Physik **81**, 877 (1926).

[5] G. E. M. Jauncey, Phys. Rev. **20**, 405 (1922). Note: Figs. 2 and 6 in this article should be interchanged.

[6] G. E. M. Jauncey and H. L. May, Phys. Rev. **23**, 128 (1924).

[7] A. H. Compton, *X-Rays and Electrons* (Van Nostrand, New York, 1926), p. 170.

[8] G. E. M. Jauncey, Phys. Rev. **37**, 1193 (1931).

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

[10] Y. H. Woo, Phys. Rev. **38**, 6 (1931).

[11] Y. H. Woo, Phys. Rev. **41**, 21 (1932).

[12] G. E. M. Jauncey, Phys. Rev. **42**, 453 (1932).

[13] I. Waller, Zeits. f. Physik **17**, 398 (1923).

[14] G. G. Harvey, P. S. Williams and G. E. M. Jauncey, Phys. Rev. **46**, 365 (1934).

we shall not consider this further development in this paper.

2. Theory

We shall use the symbol CA to refer to Compton and Allison's[15] book on x-rays—thus CA (4.30) refers to Eq. (4.30) in this book.

(a) Scattering from a bound electron

The classical theory of the forced, damped oscillations of an electron is described according to CA (4.30) by the differential equation

$$\frac{d^2x}{dt^2}-(2e^2/3mc^3)\frac{d^3x}{dt^3}+\omega_q^2x=-E_0(e/m)\sin\omega t, \quad (2)$$

where x is the displacement of the electron from its "rest" position—that is, the position it would have occupied if no radiation were falling on the electron. The frequency of the incident rays is $\omega/2\pi$ and the natural frequency of the q-type of electron is $\omega_q/2\pi$. The impressed electric field is zero when $t=0$. The negative sign on the right of (2) is caused by the negative charge on the electron, since e represents the charge on the electron in magnitude only.

The steady-state solution of (2) is

$$x=A\sin(\omega t+\psi), \quad (3)$$

where

$$A^2=E_0^2(e^2/m^2)/\{(\omega^2-\omega_q^2)^2+4r_e^2\omega^6/9c^2\}, \quad (4)$$

$$\tan\psi=2r_e\omega^3/3c(\omega^2-\omega_q^2), \quad (5)$$

and $r_e=e^2/mc^2=2.82\times10^{-13}$ cm. The acceleration of the electron is

$$a=\frac{d^2x}{dt^2}=-A\omega^2\sin(\omega t+\psi). \quad (6)$$

According to CA (2.01) and (2.05), the field strength of the electric wave arriving at time t at a distance R from the accelerated electron and in a direction θ_E with the electric vector of the incident polarized rays is

$$E=E_{\theta E}\sin\{\omega(t-R/c)+\psi\}, \quad (7)$$

where

$$E_{\theta E}=Ae\omega^2\sin\theta_E/Rc^2. \quad (8)$$

Also, similar to CA (3.01), we have

$$\frac{I_{\theta E}}{I_0}=\frac{E_{\theta E}^2}{E_0^2}=\frac{e^4\sin^2\theta_E}{R^2m^2c^4}\cdot\frac{\omega^4}{(\omega^2-\omega_q^2)^2+4r_e^2\omega^6/9c^2}. \quad (9)$$

Finally, for unpolarized rays scattered across unit area in a direction ϕ with the primary beam we arrive at

$$I_\phi=B^2I_e, \quad (10)$$

where

$$B=\omega^2\{(\omega^2-\omega_q^2)^2+4r_e^2\omega^6/9c^2\}^{-\frac{1}{2}} \quad (11)$$

and

$$I_e=I_0(e^4/R^2m^2c^4)\cdot(1+\cos^2\phi)/2, \quad (12)$$

the Thomson formula for scattering from a single free electron.

For ordinary x-rays and for ω_q not exceedingly close to ω the term $4r_e^2\omega^6/9c^2$ under the braces in (11) is negligible with respect to $(\omega^2-\omega_q^2)^2$ and we may write

$$B=\omega^2/(\omega^2-\omega_q^2). \quad (13)$$

Unless ω is exceedingly close to ω_q, $\tan\psi$ is either a small negative or a small positive number. From (5) and (13), we may say that B retains the positive value

$$B=|\omega^2/(\omega^2-\omega_q^2)|=|\nu^2/(\nu^2-\nu_q^2)| \quad (14)$$

and that the phase changes suddenly by 180° as ω decreases through ω_q. For a "free" electron $\omega_q/\omega\rightarrow0$, so that $B=1$ and there is no change of phase on scattering.

(b) Scattering from a single atom

We shall proceed along the lines of Jauncey's paper of 1931. We introduce the reference line OZ which bisects the angle between the forward direction OB of the scattered rays and the backward direction OA of the primary rays. Perpendicular to this reference line, we draw the reference plane through the center, or nucleus, of the atom. Then at a given instant of time the rth electron of the electron cloud surrounding the nucleus is at P at a distance z_r from the plane. Draw a plane BD perpendicular to OB at a large distance R from O in Fig. 1. The phase of the scattered wave arriving at BD from a "free" electron on the reference plane is independent of the position of the electron in the reference plane and we shall assume for convenience that the phase of such a wave is zero. The phase of a

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[15] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (Van Nostrand, New York, 1935.)

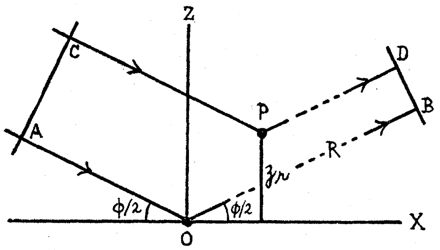

FIG. 1. Interference of x-rays scattered by a cloud of electrons.

scattered wave at BD from the rth electron at z_r is $kz_r+\psi_r$, where

$$k=(4\pi\sin\tfrac{1}{2}\phi)/\lambda \tag{15}$$

and ψ_r is the change of phase on scattering. The amplitudes of the waves scattered by all the Z electrons of the atom are added vectorially to obtain the resultant amplitude of the scattered waves arriving at the plane BD. Hence the scattered intensity per unit area on BD is

$$\begin{aligned}(I_\phi/I_e)_{\text{inst}}&=\{\sum_{r=1}^{Z}B_r\cos(kz_r+\psi_r)\}^2\\&\quad+\{\sum_{r=1}^{Z}B_r\sin(kz_r+\psi_r)\}^2\\&=\sum_{r=1}^{Z}B_r^2+\sum_{r=1}^{Z}{}'\sum_{s=1}^{Z}{}'B_rB_s\\&\quad\times\cos\{k(z_r-z_s)+\psi_r-\psi_s\},\end{aligned} \tag{16}$$

where B_r is the value of B as given by (11) or (14) for the rth electron and the symbol $\Sigma'\Sigma'$ indicates that in the double summation $r\neq s$. If for all electrons $\omega_r/\omega\rightarrow 0$, $B=1$ and $\psi_r-\psi_s=0$, so that (16) reduces to

$$I_\phi=I_e\{Z+\sum_{r=1}^{Z}{}'\sum_{s=1}^{Z}{}'\cos k(z_r-z_s)\}, \tag{17}$$

the formula given in Jauncey's paper[8] of 1931. We shall now simplify the problem by assuming that we are interested in the region $\lambda\approx\lambda_K$ and that therefore $B_r=B_K$ for the two K electrons and $B_r=1$ for the other electrons. Consequently, also $\psi_r-\psi_s=\pm\psi_K$ when r or s represents a K electron and $\psi_r-\psi_s=0$ when r and s represent either the two K electrons or two of the non-K electrons. Applying these assumptions to (16), we obtain

$$\begin{aligned}(I_\phi/I_e)_{\text{inst}}&=Z-2(1-B_K^2)\\&\quad+\sum_{r=3}^{Z}{}'\sum_{s=3}^{Z}{}'\cos k(z_r-z_s)+2B_K^2\cos k(z_1-z_2)\\&\quad+2B_K\sum_{r=3}^{Z}\sum_{s=1}^{2}\cos\{k(z_r-z_s)-\psi_K\},\end{aligned} \tag{18}$$

where the subscripts 1 and 2 refer to the K electrons and the subscripts 3, $4\cdots Z$ refer to the non-K electrons.

The intensity given by (18) is an instantaneous intensity resulting from an instantaneous configuration of the electrons in the atom. The probability of this intensity occurring is that of the configuration occurring. We shall represent this latter by $p(z_1, z_2, z_3, \cdots z_Z)dz_1dz_2\cdots dz_Z$. No further progress can be made unless further assumptions are made concerning this probability. These further assumptions are: (1) *the probability distribution function for the rth electron is independent of that of the sth electron,* so that we may write

$$p(z_1, z_2, \cdots z_Z)=p_1(z_1)\cdot p_2(z_2)\cdots p_Z(z_Z), \tag{19}$$

and (2) *the rth electron is just as likely to be above the reference plane as below it,* so that

$$p_r(z_r)=p_r(-z_r). \tag{20}$$

In other words $p_r(z_r)$ is an even function of z_r. The average scattered intensity is then given by

$$(I_\phi/I_e)_{\text{Av}}=\int_{-\infty}^{\infty}(I_\phi/I_e)_{\text{inst}}\prod_{r=1}^{Z}p_rdz_r, \tag{21}$$

where p_r is written for $p_r(z_r)$. Remembering that the integral of an odd function from $-\infty$ to $+\infty$ is zero and that the sine is an odd function and also that

$$\int_{-\infty}^{\infty}p_rdz_r=1, \tag{22}$$

since the rth electron must be somewhere, we obtain

$$\begin{aligned}(I_\phi/I_e)_{\text{Av}}&=Z-2+2B_K^2(1+E_K^2)\\&\quad+4B_KE_K\cos\psi_K\sum_{r=3}^{Z}E_r+\sum_{r=3}^{Z}{}'\sum_{s=3}^{Z}{}'E_rE_s,\end{aligned} \tag{23}$$

where

$$E_r=\int_{-\infty}^{\infty} p_r \cos kz_r dz_r, \tag{24}$$

the "electronic structure factor" for the rth electron. Now put

$$\sum_{r=1}^{Z} E_r=f,$$

so that

$$\sum_{r=3}^{Z} E_r=f-2E_K \tag{25}$$

and

$$\sum_{r=3}^{Z}{}' \sum_{s=3}^{Z}{}' E_rE_s=(f-2E_K)^2-(\sum_{r=1}^{Z} E_r^2-2E_K^2). \tag{26}$$

Eq. (23) now becomes

$$\begin{aligned}(I\phi/I_e)_{\text{Av}}=Z-\sum_1^Z E_r^2-2(1-B_K^2)\\ +2E_K^2\{1-B_K^2(2\cos^2\psi_K-1\}\\ +\{f-2E_K(1-B_K\cos\psi_K)\}^2. \qquad (27)\end{aligned}$$

When $\omega_K/\omega\rightarrow 0$, this reduces to

$$(I_\phi/I_e)_{\text{Av}}=Z-\sum_1^Z E_r^2+f^2, \tag{28}$$

which Raman[16] and Compton[17] have obtained for this case.

(c) Separation of the coherent rays

If a large number n of atoms which individually scatter according to (28) are assembled into a three-dimensional lattice or crystal, Jauncey, Harvey and Woo[8, 9, 11, 12] have shown that the intensity of the rays scattered by the lattice is given by

$$(I_\phi/I_e)=n(Z-\sum_1^Z E_r^2)+f^2(n+Xe^{-2M}), \tag{28a}$$

where X is a triple trigonometrical summation and e^{-2M} is introduced to take account of the thermal vibrations of the atoms in the lattice. The value of X is $-n$ excepting for the directions of the Laue-Bragg reflections when X takes on the value of $+n^2-n$. If the thermal vibrations are reduced to zero, then, except in the Laue-Bragg directions, the factor of f^2 in (28a) is $(n+X)=0$. This means that the destructive interference except in the Laue-Bragg directions is complete. Following the ideas of Raman[16] the part of (28) which is reduced to zero by multiplication by $(n+X)$ in (28a) is the coherent part of (28). Hence f^2 represents the coherent part of (28), while the remainder, $Z-\Sigma E_r^2$, represents the incoherent part. This second part exists whether or not the atoms are assembled into a lattice.

As a simplification of this method of separating out the coherent scattered rays, the n atoms need only be assembled into a line of equally spaced atoms. In this case

$$X=2\sum_{r=1}^{n-1}(n-r)\cos rka, \tag{28b}$$

where a is the projection of the separation of two adjacent atoms on the z axis or reference line of Fig. 1. A graph of X/n against ka is shown in Fig. 2 for $n=8$. It is seen that, even for a small number like 8, X/n is close to -1 or X to $-n$ except in directions near to those where $ka=2m\pi$, m being zero or an integer. These exceptional directions are those included in the cones shown in CA Fig. V-14 and they correspond to the Laue-Bragg directions in the case of a three-dimensional lattice.

For the purpose of separating the coherent rays we may reduce the linear lattice to two atoms. In this case we have two atoms at A and B, Fig. 3. In this case $(n+X)$ reduces to $2(1+\cos ka)$. Let the reference plane pass through the center of the atom at A, we then

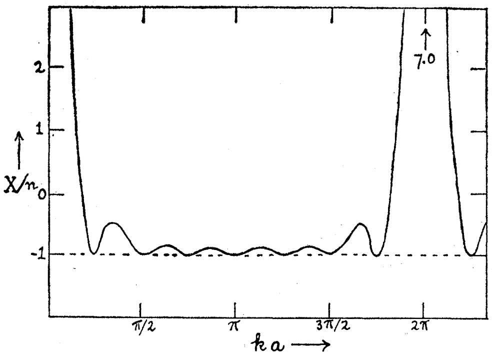

FIG. 2. Graph of X/n against ka for a line lattice.

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[16] C. V. Raman, Ind. J. Phys. **3**, 357 (1928).

[17] A. H. Compton, Phys. Rev. **35**, 925 (1930).

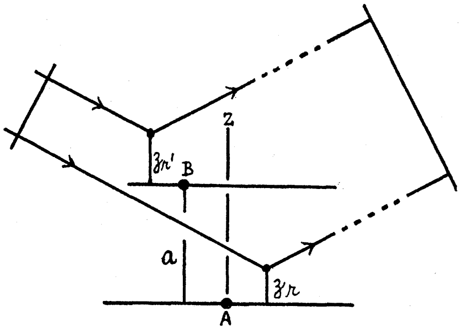

FIG. 3. Interference of x-rays scattered by the electrons in two atoms.

represent the z of an electron in atom A as z_r and the z of an electron in atom B as $z_{r'}+a$. The subscripts r and s refer to electrons in atom A and r' and s' to electrons in atom B. Eq. (16) now becomes

$$
\begin{aligned}
(I_\phi/I_e)_{\text{inst}} &= \sum_{r=1}^{Z} B_r^2 + \sum_{r'=1}^{Z} B_{r'}^2 \\
&+ \sum_{r=1}^{Z}{}' \sum_{s=1}^{Z}{}' B_r B_s \cos\{k(z_r - z_s) + \psi_r - \psi_s\} \\
&\quad \sum_{r'=1}^{Z}{}' \sum_{s'=1}^{Z}{}' B_{r'} B_{s'} \cos\{k(z_{r'} - z_{s'}) + \psi_{r'} - \psi_{s'}\} \\
&+ 2\sum_{r=1}^{Z} \sum_{s'=1}^{Z} B_r B_{s'} \cos\{k(z_r - z_{s'} + a) + \psi_r - \psi_{s'}\}. \qquad (29)
\end{aligned}
$$

Introducing the probability distribution functions, p_r, as before and assuming that the p_r for the rth electron in atom A (or B) is not affected by the presence of atom B (or A), we find after tedious computation that

$$
\begin{aligned}
(I_\phi/I_e)_{\text{Av}} &= 2(1+\cos ka) \\
&\quad \times [\{f - 2E_K(1 - B_K \cos\psi_K)\}^2 \\
&\quad + 4E_K^2 B_K^2 \sin^2\psi_K] \\
&\quad + 2[Z - \sum_{r=1}^{Z} E_r^2 - 2(1-B_K^2)(1-E_K^2)]. \qquad (30)
\end{aligned}
$$

The factor of $2(1+\cos ka)$ in (30) is the coherent part of (27). The remainder of the right side of (27) is the incoherent part.

We now introduce the symbol

$$S \equiv (1/nZ)\cdot(I_\phi/I_e)_{\text{Av}}, \qquad (31)$$

where n is the number of atoms participating in the production of the scattered intensity I_ϕ, n being small enough, however, so that no correction for absorption need be made. After introducing the effect of the Compton change of wave-length on the incoherent portion of (27), we write (27) in the form

$$S_{\text{atom}} = S_{\text{coh}} + S_{\text{incoh}}/\{1+(h/mc)\text{ vers }\phi\},^3 \qquad (32)$$

where

$$
\begin{aligned}
S_{\text{coh}} = \frac{1}{Z}[\{f - 2E_K(1 - B_K\cos\psi_K)\}^2 \\
+ 4E_K^2 B_K^2 \sin^2\psi_K], \qquad (33)
\end{aligned}
$$

$$S_{\text{incoh}} = 1 - \frac{1}{Z}\sum_{r=1}^{Z} E_r^2 + Y \qquad (34)$$

and

$$Y = -2(1-B_K^2)(1-E_K^2)/Z. \qquad (34\text{a})$$

(d) Frequency of the orbital motion of the electrons

In the previous subsections (*b*) and (*c*), it has been tacitly assumed that an electron did not on account of its orbital motion appreciably change its position in the atom during a complete cycle of the incident x-rays. In other words, it was assumed that

$$\frac{\text{orbital frequency}}{\text{x-ray frequency}} \ll 1. \qquad (35)$$

For the nth Bohr orbit of a hydrogenic atom this ratio is $(Z^2/2\pi n^3)\cdot(\lambda/137\ a_H)$ where a_H is the radius of the first Bohr orbit in hydrogen. For Cu $K\alpha$ rays scattered from the L electrons of zinc the effective Z is about 25 and the ratio is 0.266. Although this is not very small compared to unity we shall as an approximation assume that (35) is fulfilled for the L electrons. For the K electrons the effective Z is about 29.5 and the ratio is 2.94. For this case the condition of (35) is not fulfilled and E_K for the K electrons is not given by (24).

In McNatt's experiments[1] the largest value of $(\sin\frac{1}{2}\phi)/\lambda$ is 0.6, for which, according to James and Brindley's tables,[18] E_K for zinc is 0.990. This departure from unity is due to the probability

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[18] R. W. James and G. W. Brindley, Phil. Mag. 12, 81 (1931).

distribution function $p_K(z_K)$ in (24) being small but appreciable for values of z_K greater than zero. However, if during a cycle of the incident wave the electron makes something like three revolutions about the nucleus, then no matter what the value of z_K at the beginning of the cycle z_K passes through the value zero and cos kz_K passes through the value unity. It is plausible to expect that the average of cos kz_K is closer to unity than the value given by (24). Hence we may expect E_K to be closer to unity than 0.990. To be on the safe side we shall use James and Brindley's values of E_K. Then in (34) we have, from (14) and for Zn $K\alpha$ rays ($\lambda/\lambda_K=1.12$) scattered from zinc, $Y=0.02$. The value of Y for Cu $K\alpha$ rays ($\lambda/\lambda_K=1.20$) is 0.005 and its value for $\lambda/\lambda_K=1.06$ is 0.1. Since S values have not been measured under the best conditions with an error less than about 0.1, we are justified in neglecting the quantity Y in the region λ greater than but not too close to λ_K. In this region

$$S_{\text{incoh}}=1-\frac{1}{Z}\sum_{r=1}^{Z}E_r^2. \tag{36}$$

Also for Zn $K\alpha$ rays on zinc, the term

$$(4E_K^2B_K^2\sin^2\psi_K^2)/Z$$

in (33) is from (5) and (14) of the order 10^{-7} and is completely negligible and we replace (33) by

$$S_{\text{coh}}=\{f-2E_K(1-B_K\cos\psi_K)\}^2/Z. \tag{37}$$

(e) Atomic structure factor decrement

In the theory of refraction and absorption of x-rays, Kramers, Kallmann and Mark[19] introduced the idea of virtual oscillators. Instead of the K electrons of all atoms at all times having a natural frequency $\omega_K/2\pi$, they introduced virtual oscillators having natural frequencies $\nu_q=\omega_q/2\pi$ all the way from $\omega_K/2\pi$ to infinity. In an assembly of atoms let the probability of a K electron having a frequency ν_q in the range $d\nu_q$ be $P(\nu_q)d\nu_q$. Applying the method of Kramers, Kallmann and Mark, we then calculate an average S_{atom} for all the virtual oscillators. But now comes the question of the distribution or averaging fraction $P(\nu_q)d\nu_q$. Kramers, Kallmann and Mark obtain this from the experimental absorption law which states that the mass absorption coefficient varies as $1/\nu^3$ or as λ^3 so long as $\nu=c/\lambda>\nu_K$. If we think of the frequency aspect of the law, we are inclined to adopt

$$2\nu_K^2d\nu_q/\nu_q^3 \tag{38}$$

for the averaging fraction, while, if we think of the wave-length aspect, we are inclined to adopt

$$4\lambda_q^3d\lambda_q/\lambda_K^4 \tag{39}$$

for the averaging fraction. The averaging fraction (38) was used by Kramers, Kallmann and Mark. Either of these is suggested by the absorption law. It should be noted that (38) does not transform into (39) when we put $\nu=c/\lambda$ but into $2\lambda_qd\lambda_q/\lambda_K^2$ which implies a λ instead of λ^3 law of absorption! The averaging fraction is thus arbitrary even for a given absorption law.

Because of the distribution of oscillators from ν_K to ∞ (λ_K to 0), we can no longer neglect the quantities Y and $(4E_K^2B_K^2\sin^2\psi_q)/Z$ when $\lambda<\lambda_K$. We must therefore recognize two cases: $\lambda>\lambda_K$ and $\lambda<\lambda_K$.

Case I. $\lambda>\lambda_K$.—In this case it is only S_{coh} which according to (32), (36) and (37) is a function of ν_q/ν or λ_q/λ and hence we need only average this portion of S_{atom}. Since the coherent part of the radiation comes from the addition of amplitudes we find $(\langle S_{\text{coh}}^{\frac{1}{2}}\rangle_{\text{Av}})^2$. For this, from (37), we need $\langle B_q\cos\psi_q\rangle_{\text{Av}}$. Using the averaging fraction (38), we obtain[20] from (5) and (14)

$$\langle B_q\cos\psi_q\rangle_{\text{Av}}=-\{1+w_K^2\log(1-w_K^{-2})\}, \tag{40}$$

since $\cos\psi_q\approx-1$. We shall in this paper define Δf by

$$\Delta f=f-Z^{\frac{1}{2}}\langle S_{\text{coh}}^{\frac{1}{2}}\rangle_{\text{Av}}, \tag{41}$$

whence, in virtue of (37) and (40),

$$\Delta f=-2w_K^2\log(1-w_K^{-2}), \tag{42}$$

since $E_K\approx1$. Δf is called the atomic structure factor decrement. On the other hand, if we use the averaging fraction (39), we obtain

$$\langle B_q\cos\psi_q\rangle_{\text{Av}}=-\{1+2w_K^2+2w_K^4\log(1-w_K^{-2})\} \tag{43}$$

and

$$\Delta f=-4w_K^2\{1+w_K^2\log(1-w_K^{-2})\}. \tag{44}$$

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[19] H. Kallmann and H. Mark, Ann. d. Physik **82**, 585 (1927). See also CA, p. 292.

[20] B. O. Peirce, *A Short Table of Integrals*, pp. 10, 11 and 26.

We see therefore that the calculation of Δf is somewhat arbitrary. Others have encountered the same difficulty in working out the theoretical formula for the intensity of the Bragg reflection of x-rays from crystals. We shall not attempt any further in this paper to calculate Δf but shall use the theoretical value of Δf as found by others. So far the most satisfactory theoretical formula for Δf has been found independently by Hönl[21] and Williams.[22] Bruce[23] using Hönl's theory has obtained a simple formula for calculating Δf.

Case II. $\lambda < \lambda_K$.—It is now no longer possible to neglect the quantities we have previously mentioned, nor can we substitute (14) for (11)since in the range of integration ω_q (or ν_q) passes through the value ω (or ν) and B_q according to (14) goes to infinity. However, if we include the radiation damping term $4r_r^2\omega^6/9c^6$ which occurs in formula (11) for B_q, the integrand in the integral for determining $\langle B_q \cos \psi_q \rangle_{\text{Av}}$ no longer goes to infinity when ω_q passes through ω. It turns out that $\langle B_q \cos \psi_q \rangle_{\text{Av}}$, if the averaging fraction (38) is used, is given by the right side of (40) plus a term with $2r_e\omega/3c$ as a factor. The order of magnitude of this factor is 10^{-4} and so the added term may be neglected. However, in virtue of (33) and (34), $B_q \cos \psi_q$ does not determine Δf as it does when $\lambda > \lambda_K$. We leave the calculation of Δf to others.

The quantity Y is of interest because it occurs in the incoherent part of the scattered rays. We shall attempt to find the magnitude of Y. We first determine $\langle B_q^2 \rangle_{\text{Av}}$ rather than $(\langle B_q \rangle_{\text{Av}})^2$ since the incoherent part comes from the addition of intensities. Applying the averaging fraction (38) to the square of (11), we obtain[20]

$$\begin{aligned} B_q^2 = (1+D^2)^{-1} + w_K^2(1+D^2)^{-2} \\ \times \log\{(1-w_K^{-2})^2 + D^2 w_K^{-4}\} \\ + \{(1-D^2)/D(1+D^2)\} \\ \times \tan^{-1}\{D/(w_K^2-1)\}, \quad (45) \end{aligned}$$

where $D = 2r_e\omega/3c = 1.17 \times 10^{-4}/\lambda$ when λ is in angstroms. Since D is small (45) reduces to

$$\begin{aligned} \langle B_q^2 \rangle_{\text{Av}} = 1 + 2w_K^2 \log(1-w_K^{-2}) \\ + (w_K^2/D) \tan^{-1}\{D/(w_K^2-1)\}. \quad (46) \end{aligned}$$

In this $\tan^{-1}\{D/(w_K^2-1)\}$ approaches π or $D/(w_K^2-1)$ according as $\lambda <$ or $> \lambda_K$. In the latter case $\langle B_q^2 \rangle_{\text{Av}} \rightarrow 0$ when $w_K \gg 1$, while in the former case the term containing D becomes by far the most important term on the right of (46) and we write

$$\langle B_q^2 \rangle_{\text{Av}} = w_K^2 \pi / D, \quad (47)$$

when $\lambda < \lambda_K$.

Since the Schroedinger probability distribution function for a K electron of an element like zinc is very nearly that of an electron in a hydrogenic atom with a nuclear charge $+Ze$, we may write as an approximation

$$1 - E_K^2 = (Z^2\alpha^2\lambda_K^2/\lambda^2) \sin^2 \tfrac{1}{2}\phi, \quad (48)$$

where $\alpha = 2\pi e^2/hc = 1/137$. We now have

$$\langle Y \rangle_{\text{Av}} = (3Z\alpha^2/2r_e)\lambda \sin^2 \tfrac{1}{2}\phi, \quad (49)$$

since we may replace $1 - \langle B_q^2 \rangle_{\text{Av}}$ by $-\langle B_q^2 \rangle_{\text{Av}}$.

Instead of applying the averaging fraction (38), we might have applied (39). In this case, after making approximations, (47) is replaced by

$$\langle B_q^2 \rangle_{\text{Av}} = 2w_K^4 \pi / D \quad (50)$$

and (49) by

$$\langle Y \rangle_{\text{Av}} = (3Z\alpha^2/r_e) \cdot (\lambda^3/\lambda_K^2) \cdot \sin^2 \tfrac{1}{2}\phi. \quad (51)$$

The numerical values of $\langle Y \rangle_{\text{Av}}$ are 30 from (49) and 18.5 from (51) when zinc is irradiated by Mo $K\alpha$ rays ($\lambda = 0.71$A) and the secondary rays are measured at $\phi = 90°$. At this place we shall drop the average sign from Y and from now on use Y to represent its average. The greatest value of $S = S_{\text{coh}} + S_{\text{incoh}}$ for zinc measured in this laboratory is about 6 while the value of S_{incoh} is always less than unity when Y is neglected or omitted. So if Y is considered as a correction term it is much greater than the quantities which are being corrected.

It is known that when x-rays fall upon a substance both scattered rays and much more intense K fluorescent rays are produced provided that $\lambda < \lambda_K$. These fluorescent rays are incoherent with the primary rays. The magnitude of Y suggests that Y represents the classical analog of the energy which appears as fluorescent rays when a substance is irradiated by x-rays whose $\lambda < \lambda_K$. In experiments on diffuse scattering it is usual when $\lambda < \lambda_K$ to place absorbing material

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[21] H. Hönl, Zeits. f. Physik **84**, 1 (1933).
[22] E. J. Williams, Proc. Roy. Soc. **143**, 358 (1933).
[23] W. A. Bruce, Phys. Rev. **53**, 802 (1938).

such as aluminum in the scattered beam so as to cut out the more absorbable fluorescent component of the beam. Consequently the quantity Y does not enter into what is ordinarily called "diffuse scattering." This is a paper on diffuse scattering and the writer feels that further consideration of Y should be deferred to a later paper.

(f) Diffuse scattering from a crystal

Jauncey[12] and Woo[11] have shown that if atoms whose S values are known are assembled into a crystal lattice, the S values for the diffuse scattering from the crystal are obtained by subtracting e^{-2M} times the coherent part of S for the atom from the S_{atom} values. Thus, using (32), (36) and (41), we obtain the very good approximation

$$S_{\text{crystal}} = (f-\Delta f)^2(1-e^{-2M})/Z + \{1-(1/Z)\Sigma E_r^2\}/\{1+(h/mc)\text{ vers }\phi\}^3 \quad (52)$$

for the region $\lambda > \lambda_K$ and also for the region $\lambda < \lambda_K$ if in the latter case care is taken to remove or to correct for the fluorescent rays.

3. CONCLUSION

The formula for the diffuse scattering of x-rays from a crystal in the region λ/λ_K close but not exceedingly close to unity differs only from the formula previously worked out for the region $\lambda/\lambda_K \ll 1$ in that f in the formula for S is replaced by $f-\Delta f$.

TABLE I. *Values of Δf for zinc.*

λ/λ_K	McNATT (EXP.)	EQ. (42) (THEORY)	HÖNL (THEORY)
1.12	3.65	4.0	2.8
1.20	2.5	3.4	2.3

McNatt's experimental values of Δf for zinc are shown in Table I. These are the only experimental values of Δf so far obtained by diffuse scattering. Theoretical values are shown in the table. The agreement of experiment with Hönl's theory is little better than with (42) of this paper. However, on account of the relatively low intensity of the Zn $K\alpha$ rays in McNatt's experiments, the writer believes that McNatt's value for Δf is more reliable for the stronger Cu $K\alpha$ rays ($\lambda/\lambda_K = 1.20$). Here the agreement of McNatt's and Hönl's values is as good as can at present be expected. On account of the arbitrariness in averaging $B_q \cos \psi_q$ the writer holds no particular brief for the values shown in the third column of Table I.

Finally the writer wishes to point out that Δf as given by (42) or (44) for $\lambda > \lambda_K$ leads to the value 2 when $\lambda/\lambda_K \gg 1$. This implies that the K electrons are inoperative in the scattering process in this region. Similarly the L electrons become inoperative when $\lambda/\lambda_L \gg 1$. In the case of ordinary light irradiating a substance like zinc, the K, L and some or all of the M electrons are inoperative as far as scattering is concerned.