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THEORY OF THE DIFFUSE SCATTERING OF X-RAYS BY SOLIDS

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ABSTRACT

The classical theory of x-ray scattering has been applied to the scattering of x-rays by the electrons in the atoms of a solid. The case in which the solid consists of atoms of one kind has been considered. The interactions of the waves scattered by each electron with those scattered by every other electron in the solid has been considered. The analysis is simplified by the fact that the orbital periods of the electrons in the atoms are very much shorter than the vibrational periods of the atoms due to thermal agitations. The final formula obtained is

$$S = 1 + (Z - 1)\frac{f'^2}{Z^2} + \frac{F^2}{ZN}X$$

where S is the scattered intensity per electron relative to the scattered intensity from a single isolated electron, Z is the atomic number, F the atomic structure factor including the effect of thermal agitation, f' is related to f the true atomic structure factor (without thermal agitation), N is the total number of atoms, and X is a certain double summation. The value of X has not been obtained for an amorphous substance but it has been evaluated for the case of a simple cubic crystal by Jauncey and Harvey in the following paper in this issue of the Physical Review.

I. INTRODUCTION

IN 1922, Jauncey[1] found that x-rays are diffusely scattered by crystals in a way which is similar to the scattering by amorphous solids. In particular, the spatial distribution of the scattered rays was found to be about the same for the crystals of rocksalt and calcite as for the amorphous substance glass. These experimental results were in distinct contrast to the results predicted by Debye's theory[2] of the intensity of x-rays regularly reflected by crystals. Debye's theory requires that diffuse scattering from crystals must occur, but that the spatial distribution and intensity of the rays scattered by crystals should be very different from the distribution and intensity of the rays scattered by amorphous substances. Furthermore, Debye's theory predicts that a rise of temperature will cause an increase in the intensity of the rays scattered

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

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

by crystals. Accordingly, Jauncey[3] investigated the effect of temperature by measuring the intensities of the rays scattered by rocksalt and calcite at 568°K and at 290°K. It was found that neither rocksalt nor calcite showed as great an increase of temperature as was demanded by the theory. In 1924, Jauncey and May[4] again investigated the scattering of x-rays by rocksalt and determined absolute values of the scattered intensity. The results agreed with the results previously found by Jauncey.[1]

In 1917, A. H. Compton[5] carried out a theoretical investigation of the effect of atomic structure on the intensity of x-rays regularly reflected by crystals. The unit in the diffraction or scattering of x-rays by matter is the electron. The intensity of the x-rays scattered per unit solid angle by a single isolated electron in a direction ϕ with the primary x-rays has been shown by J. J. Thomson[6] to be

$$I = I_0(e^4/2m^2c^4)(1+\cos^2\phi) \tag{1}$$

where I_0 is the intensity of the primary x-rays. If Z electrons are closely packed together so that the charge of the aggregation is Ze and its mass is Zm, it is seen from Eq. (1) that the intensity of the rays scattered by the aggregation is Z^2 times the intensity scattered by a single isolated electron, or that the scattered intensity per electron in the aggregation is $Z^2/Z=Z$ times the intensity scattered by a single isolated electron. Hence, an atom which contains Z electrons closely packed at the center will give rise to scattered x-rays in a direction ϕ which have an intensity per electron of Z times the intensity scattered by a single isolated electron. If, however, the electrons are not massed close to the center of the atom, but are at distances from the center comparable with the wave-length of the x-rays, both constructive and destructive interference takes place between the x-rays scattered by the various electrons in the atom, with the result that the intensity per electron of the scattered rays is less than Z times the intensity scattered by a single isolated electron. The intensity of the x-rays scattered by a number of atoms depends upon the configuration of the electrons within each atom and upon the configuration of the atoms themselves. If the atoms are arranged in a crystal lattice, there are certain special directions in which the x-rays are scattered with great intensity, and thus we obtain Laue spots. However, if a Laue photograph is examined, it is found that in between the black spots on the developed photographic film there is general but less intense blackening. Part of this general blackening is due to the diffuse scattering found by Jauncey.[1] There are thus two effects in the scattering of x-rays by crystals, namely, special scattering, which produces Laue spots and which is caused by regular reflection from planes of atoms according to Bragg's law, and diffuse scattering.

The problem of the intensity of the special scattering by crystals has been

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[3] G. E. M. Jauncey, Phys. Rev. **20,** 421 (1922).

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

[5] A. H. Compton, Phys. Rev. **9,** 49 (1917).

[6] J. J. Thomson, "Conduction of Electricity through Gases," 2nd Edition, p. 325.

discussed at length by Compton.[7] The configuration of the electrons in an atom is both rapidly and continually changing, and it becomes necessary to obtain a time average of the intensity of the x-rays scattered (the term "scatter" includes the ideas of both special and diffuse scattering) by the atoms of a crystal. However, the kind of average depends upon the particular effect in which we are interested. If we are studying the special scattering (i.e. Bragg reflection), we take one kind of average, whereas, if we are studying diffuse scattering, we take another kind of average. The first kind of average leads to the atomic structure factor as discussed by Compton.[7] Recently Compton[8] has developed the theory of diffuse scattering from the atoms of a monatomic gas. The scattering per electron in a direction ϕ with respect to the primary rays is determined only by the average configuration of the electrons within each atom, and not by the configuration of the atoms themselves. The atoms are so far apart that they can be treated as isolated systems of electrons. In the case of a gas there are no directions in which special scattering takes place.

The amplitude of the waves scattered in a direction ϕ by a single isolated electron is proportional to the square root of the right side of Eq. (1). For convenience, this amplitude is represented by unity. In the case of special scattering by a crystal (Bragg reflection), the intensity is proportional to the square of the time average of the amplitude per electron. In the case of diffuse scattering, the intensity of the scattered rays is proportional to the time average of the square of the amplitude per electron.

As example of the two kinds of average, let us consider the case of an atom with two electrons, both at a distance $r=a$ from the center, but with random orientations. If a crystal consists of atoms of this kind and if the center of each atom (the nucleus) is exactly at a lattice point and there is no thermal agitation, Compton[7] has shown that the square of the average amplitude per electron is E^2, where

$$E = (\sin ka)/ka \tag{2}$$

and

$$k = (4\pi \sin\theta)/\lambda. \tag{3}$$

In Eqs. (2) and (3), θ is the glancing angle of incidence when the crystal is set for the regular reflection of the wave-length λ. If, however, a monatomic gas consists of atoms of this kind, Compton[8] has shown that the average square of the amplitude per electron is

$$S = 1 + (\sin^2 ka)/k^2a^2 \tag{4}$$

where k is given by Eq. (3) and θ is half the angle of scattering.

When E, the average amplitude per electron in a crystal, is multiplied by Z, the atomic structure factor F is obtained. In 1921, Bragg, James and Bosanquet[9] showed how experimental values of the atomic structure factor,

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[7] A. H. Compton, "X-Rays and Electrons," Chap. V.

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

[9] Bragg, James and Bosanquet, Phil. Mag. **41,** 309 (1921); **42,** 1 (1921).

or F values as they are called, can be obtained from the experimental values of the intensity of x-rays reflected in different orders from the different sets of planes in a crystal. In an actual crystal, however, the atomic nuclei are subject to thermal agitation and the atomic structure factor F which is obtained from crystal reflection is not referred to the center of the atom but to a lattice point about which the center of the atom vibrates. We shall call the atomic structure factor which is referred to the center of the atom or nucleus the true atomic factor, and we shall represent this by f.

For several years it has seemed to the writer that in order to unravel the structure of atoms by means of x-rays it would not only be necessary to make observations on the x-rays regularly reflected, but also on the x-rays diffusely scattered by crystals. The one effect must in some way be complementary to the other. It is the purpose of this and the following paper to show how the two effects are interrelated.

II. General Theory

We shall first consider the intensity of the x-rays scattered by a large number, n, of electrons. Take a point O as shown in Fig. 1. Let AO represent the direction of the primary x-rays and OB the direction of the scattered rays. The plane containing AO and OB is then the plane of scattering. Let OV bisect the angle AOB. Now draw a plane perpendicular to the line OV, and let OU be the line where this plane cuts the plane of scattering. We shall call the plane whose trace is OU the reference plane. The waves which are scattered by all electrons in the reference plane are in phase with each other. We shall assume the phase angle of all such waves to be zero. Consider an electron at P. The path retardation of the rays scattered by the electron at P relative to the rays scattered by an electron in the plane OU is $CP+PD$. This retardation can be shown to be $2z \sin \theta$, where z is the length of PE and PE is perpendicular to the plane OU. The angle θ is one-half the scattering angle ϕ. The retardation depends only upon the distance of P from the reference plane and is not affected by moving P in any direction parallel to the ref-

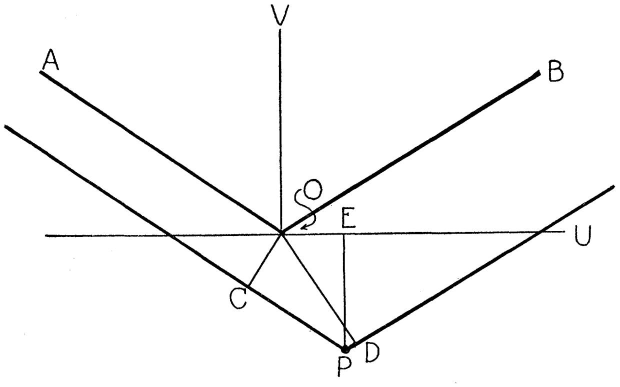

Fig. 1.

erence plane. The phase angle of the waves scattered by an electron at P is then

$$(2\pi/\lambda)2z\sin\theta = (4\pi z\sin\theta)/\lambda \tag{5}$$

For brevity we shall call this phase angle kz where k is given by Eq. (3) and θ of that equation is $\phi/2$.

Let the rth electron be at a distance z_r from the reference plane, so that the phase angle associated with this electron is kz_r. The amplitude of the waves scattered by a single isolated electron is unity, so that the resultant amplitude of the waves scattered by n electrons is the vector sum of the amplitudes associated with each electron. The resultant intensity I is the square of this vector sum, so that

$$I = \left(\sum_{r=1}^{r=n}\cos kz_r\right)^2 + \left(\sum_{r=1}^{r=n}\sin kz_r\right)^2. \tag{6}$$

Since $\cos^2 kz_r + \sin^2 kz_r = 1$, this reduces to

$$I = n + \sum_{r=1}^{r=n}{}' \sum_{s=1}^{s=n}{}' \cos k(z_r - z_s). \tag{7}$$

The symbol $\sum'\sum'$ implies that in the double summation r is never taken equal to s. The value of I given by Eq. (7) is that due to a particular configuration of the n electrons. If the electrons are moving about, we must consider the probability of the configuration which gives rise to the intensity I. Let the probability that the rth electron is between z_r and z_r+dz_r be $p_r(z_r)dz_r$. For brevity we shall write this $p_r dz_r$. The probability of a given configuration is then $\Pi_{r=1}^{r=n} p_r dz_r$. The average intensity is therefore given by the n-tuple integral

$$I_{\text{ave}} = \int \cdots n \cdots \int \left\{ n + \sum{}' \sum{}' \cos k(z_r - z_s) \right\} \prod_{r=1}^{r=n} p_r dz_r. \tag{8}$$

It should be remembered that n is the total number of electrons in, say, a 0.1 mm cube of a substance, and is therefore a number perhaps of the order 10^{17}. The limits of each integral are such that each

$$\int p_r dz_r = 1 \tag{9}$$

In consequence of Eq. (9),

$$\int \cdots n \cdots \int n \prod_{r=1}^{r=n} p_r dz_r = n \tag{10}$$

immediately. To evaluate the integral of the double summation, let us fix our attention on one of the terms of the summation, say, $\cos k(z_u - z_v)$, which refers to the two particular electrons, the uth and the vth electrons. In carrying out the n-tuple integration, each integral with respect to z_r will equal unity unless $r=u$ or v. Hence we can perform $(n-2)$ integrations, so that

$$\int \cdots n \cdots \int \cos k(z_u - z_v) \prod_{r=1}^{r=n} p_r dz_r$$

$$= \int\int p_u p_v \cos k(z_u - z_v) dz_u dz_v \quad (11)$$

Hence

$$I_{\text{ave}} = n + \sum{}' \sum{}' \int\int p_r p_s \cos k(z_r - z_s) dz_r dz_s. \quad (12)$$

Dividing Eq. (12) by n, we obtain the scattered intensity per electron, thus

$$S = 1 + (1/n) \sum{}' \sum{}' \int\int p_r p_s \cos k(z_r - z_s) dz_r dz_s. \quad (13)$$

III. Scattering from a Solid

Actually, of course, electrons are aggregated into atoms. We shall now consider the scattering of x-rays by the electrons in the atoms in a solid consisting of one kind of atom each of which contains Z electrons. We shall assume that the motions of the electrons within an atom are very much more rapid than the heat motion of the atom. This enables us to obtain a time average of the configuration of the electrons within an atom over a time interval which is long compared to the orbital period of an electron within the atom, but which is still so short that the configuration of the atoms themselves has practically remained unchanged during the interval.

The rth and sth electrons of Eq. (13) may or may not be in the same atom. Let us consider the case where they are in the same atom. In this case we may take the reference plane of Fig. 1 through the nucleus of the atom. If we assume that the probability function for each electron is symmetrical about the reference plane through the nucleus, then each

$$\int p_r \sin kz_r dz_r = 0 \quad (14)$$

so that

$$\int\int p_r p_s \cos k(z_r - z_s) dz_r dz_s$$

$$= \left(\int p_r \cos kz_r dz_r \right) \times \left(\int p_s \cos kz_s dz_s \right) \quad (15)$$

By referring to Compton,[7] it will be seen that

$$\int p_r \cos kz_r dz_r = E_r \quad (16)$$

where E_r is the average amplitude associated with the rth electron. Hence

$$\iint p_r p_s \cos k(z_r - z_s) dz_r dz_s = E_r E_s. \tag{17}$$

In each atom there are $Z(Z-1)/2$ pairs of electrons and this is the number of the products $2E_rE_s$ for each atom. Let us now introduce an average quantity E', defined by

$$Z(Z - 1)E'^2 = \sum_{r=1}^{r=z}{}' \sum_{s=1}^{s=z}{}' E_r E_s \tag{18}$$

where in the summation r is not taken equal to s. Also let us introduce a quantity f' defined by

$$f' = ZE' \tag{19}$$

In the theory of crystal reflection,[7] the true atomic structure factor f is defined by

$$f = \sum_{r=1}^{r=z} E_r \tag{20}$$

The double summation for each atom is therefore $Z(Z-1)f'^2/Z^2$, and, since there are n/Z atoms, we obtain on summing for all the atoms

$$(n/Z) \times Z(Z - 1)f'^2/Z^2 = n(Z - 1)f'^2/Z^2. \tag{21}$$

Multiplying by $1/n$, Eq. (13) reduces to

$$S = 1 + (Z - 1)f'^2/Z^2 + (1/n) \sum{}'' \sum{}'' \iint p_r p_s \cos k(z_r - z_s) dz_r dz_s \tag{22}$$

where the symbol $\sum''\sum''$ denotes summation when the rth and sth electrons are always in different atoms.

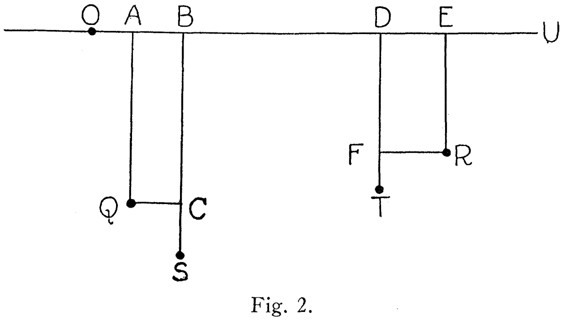

Fig. 2.

IV. Orbital Motions of the Electrons in the Atoms

In Fig. 2, let OU be the reference plane and let the center of the tth atom be at Q and let the vth electron which is in the tth atom be at S. Let $AQ = x_t$

and $CS = y_{tv}$, so that the distance of the electron at S from the reference plane is

$$z_{tv} = x_t + y_{tv}. \tag{23}$$

Similarly, let the center of the uth atom be at R, and the wth electron in this atom be T. Let $ER = x_u$ and $FT = y_{uw}$, so that

$$z_{uw} = x_u + y_{uw}. \tag{24}$$

Taking two particular atoms, together with a particular electron in the first atom and a particular electron in the second, we may average for the positions of the two electrons by taking an interval of time which is long compared with the orbital period of the electrons, but so short that the centers of the atoms have practically remained stationary during this interval. Hence we can treat the x's as constant when we integrate and dz may be replaced by dy. In this case

$$\begin{aligned}
&\iint p_r p_s \cos k(z_r - z_s) dz_r dz_s \\
&= \iint p_1 p_2 \cos k(x_t - x_u + y_1 - y_2) dy_1 dy_2 \\
&= \cos k(x_t - x_u) \iint p_1 p_2 \cos k(y_1 - y_2) dy_1 dy_2 \\
&\quad - \sin k(x_t - x_u) \iint p_1 p_2 \sin k(y_1 - y_2) dy_1 dy_2
\end{aligned} \tag{25}$$

where the subscripts 1 and 2 have been written for the subscripts *tv* and *uw*. The p's are now probability functions referred to the center of each respective atom. If the atom is symmetrical the integral containing $\sin k(y_1 - y_2)$ vanishes and we are left with the integral containing $\cos k(y_1 - y_2)$. The term containing this integral then reduces to

$$\begin{aligned}
&\left(\int p_1 \cos k y_1 dy_1\right) \times \left(\int p_2 \cos k y_2 dy_2\right) \cos k(x_t - x_u) \\
&= E_1 E_2 \cos k(x_t - x_u)
\end{aligned} \tag{26}$$

where the E's are given by Eq. (16). If the atoms are of the same kind and we sum for the Z electrons in each of the two particular atoms, we obtain

$$\left(\sum_{r=1}^{r=Z} E_r\right)^2 \cos k(x_t - x_u).$$

Then, summing for all the atoms, we obtain

$$\sum_r{}'' \sum_s{}'' \iint p_r p_s \cos k(z_r - z_s) dz_r dz_s = f^2 \sum_t{}' \sum_u{}' \cos k(x_t - x_u) \tag{27}$$

V. HEAT MOTIONS OF THE ATOM

We now remember that although the electrons in the atoms are moving much more rapidly than the centers of the atoms, yet the atoms are themselves moving with their thermal velocities. If we are dealing with a solid, the centers of the atoms are vibrating about their mean positions. We therefore introduce a probability function P for the center of the atom. Taking an average over a time long compared with the period of thermal oscillation of the atoms but short compared with the time during which scattering measurements are made, we see that Eq. (22) becomes

$$S = 1 + (Z-1)f'^2/Z^2 + (f^2/ZN)\sum_{t=1}^{t=N}{}' \sum_{u=1}^{u=N}{}' \iint P_t P_u \cos k(x_t - x_u)dx_t dx_u \quad (28)$$

where $N = n/Z$, the number of atoms involved.

Let us replace the x's in Eq. (28) by z's, and let z_r now refer to the distance of the center of the rth atom from the reference plane. Next, let the rth atom oscillate about a mean position whose distance from the reference plane is x_r. Also let the displacement of the center of the atom from its mean position be y_r, so that $z_r = x_r + y_r$. The problem thus becomes similar to that in section IV of this paper and the analysis is similar, excepting that in the case of an amorphous solid it does not seem reasonable to assume that the probability function for the displacement of the center of the atom from its mean position is symmetrical about the mean position. However, if we do make this assumption in order to simplify the analysis, the double integral of Eq. (28) becomes

$$\iint P_t P_u \cos k(z_t - z_u)dz_t dz_u = H_r H_s \cos k(x_r - x_s) \quad (29)$$

where

$$H_r = \int P_r \cos k y_r dy_r \quad (30)$$

H_r may be called the temperature factor for the rth atom. If, in addition, we make a second simplifying assumption that H is the same for all the atoms of the solid, and if we write F for fH,

$$S = 1 + (Z-1)f'^2/Z^2 + (F^2/ZN)\sum_{r=1}^{r=N}{}' \sum_{s=1}^{s=N}{}' \cos k(x_r - x_s) \quad (31)$$

where x_r is now the fixed mean position about which the center of the atom oscillates. The quantity F is the atomic structure factor which includes the effect due to thermal agitation, while f' in virtue of Eqs. (18), (19) and (20) is related to the true atomic structure factor f according to

$$f'^2 = f^2 + \left(f^2 - Z\sum_{r=1}^{r=z} E_r^2\right)/(Z-1). \quad (32)$$

Hence except when the probability function E_r is the same for each electron in the atom $f' < f$. It is unlikely that the probability function for a K electron is the same as that for an L electron and therefore f' should be greater than the true atomic structure factor.

The double summation in Eq. (31) has not been determined for an amorphous solid, but can be evaluated for a simple cubic crystal consisting of atoms of one kind. This evaluation has been effected by Jauncey and Harvey in the following paper in this issue of the Physical Review.