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TEMPERATURE AND DIFFUSE SCATTERING OF X-RAYS FROM CRYSTALS

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Abstract

Since the discovery of the Compton effect it has been evident that the old calculation by Debye of the diffuse scattering of x-rays by a crystal should be amended to take account of the modified radiation, which is generally presumed to be incoherent. Extending the idea suggested by the writer in his theory of x-ray scattering by gases, it is postulated that, in considering the scattering of x-rays by a crystal, only the coherent radiation from the different lattice units will interfere with each other, whereas the incoherent radiation will be simply added up. An expression for the intensity of the diffuse scattering is thence developed which consists of two parts, one taking care of the coherent scattering as originally worked out by Debye and the other accounting for the incoherent scattering. The mathematical formulation is based on the theoretical investigation by Raman and A. H. Compton on the scattering of x-rays by a dynamic atom. The theory is compared with the absolute measurements of the scattering from rocksalt reported by Jauncey and May and the agreement seems to be very close if the temperature factor is taken to be e^{-2M} as calculated by Debye and Waller. The comparison also seems to suggest the presence of the zero-point energy. These are in accord with the conclusions recently drawn by James, Waller and others from a study of the temperature effect on the intensity of the x-rays regularly reflected. The theory therefore seems to account for the so-called excess scattering, for the small scattering in the region of 0° scattering angle, for the position of the maximum scattering as well as the shift of this position with the wave-length of the primary x-rays, for the occurrence of the minimum scattering at about 100° instead of at 90° and finally for the general departure of the scattering curve from that predicted by Thomson's theory. A comparison is also made with Jauncey's experiment on the variation of the scattering by rocksalt with temperature and the result indicates that, owing to the presence of the incoherent term, measurements of this type will not test the present theory. It is pointed out that, being developed for a single crystal in which the atoms are supposed to be arranged with perfect regularity, the theory will not hold for the scattering of x-rays by the so-called amorphous substances. In these substances, the arrangement of atoms evidently introduces a type of irregularity which results in diffusely scattered rays in addition to those due to the thermal agitation. Thus, under certain conditions, only a negligible portion of the coherent intensity of the x-rays diffusely scattered by an amorphous substance is influenced by the temperature. This explains the experimental fact recently reported by Jauncey and Bauer that there is no effect of temperature on the ratio of modified to unmodified rays in the Compton effect. Theoretical predictions for the crystal sylvine are given and absolute measurements performed with homogeneous x-rays should easily test these results.

I. Introduction

THE influence of temperature on the intensity of scattering of x-rays by a crystal was first investigated theoretically by Debye,[1] who based his

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[1] P. Debye, Ann. d. Physik 14, 65 (1914).

work on the dynamical theory of crystal lattices due to Born and Kármán by considering the heat-motions as a series of elastic waves in the crystal. The theory as worked out by Debye requires (1) that the intensity of the interference maximum, i.e. x-rays regularly reflected, should be multiplied by a factor e^{-M}, and (2) that the regular reflection should be accompanied in all directions by diffuse scattering, whose intensity is proportional to $(1-e^{-M})$, where

$$M = \frac{3h^2}{\mu k\Theta},\frac{\phi(x)}{x}\cdot\frac{1-\cos\theta}{\lambda^2}\cdot \tag{1}$$

In this expression, which refers only to a simple cubic lattice composed of atoms of one kind, λ is the wave-length of the incident x-rays, θ is the scattering angle, μ is the mass of an atom, h is Planck's constant, Θ is the characteristic temperature of the crystal, which occurs in the theory of specific heats, $x=\Theta/T$, where T is the absolute temperature, $\phi(x)$ is a certain function of x, which Debye evaluates in his paper. The formula for M given here supposes that there is no zero-point energy. If such energy be assumed, $\phi(x)/x$ should be replaced by $(\phi(x)/x)+\frac{1}{4}$.

The calculation of Debye has been later examined by Faxén[2] and Waller,[3] each of whom finds for the intensity of diffuse scattering a different expression, which is much more complicated than that obtained by Debye. This, of course, just represents the result of another possible method of attacking the problem and has nothing to do with the validity of Debye's theory.[4] The work of Waller also indicates that for a simple lattice the temperature should be e^{-2M} instead of e^{-M}. This comes out from the fact that the treatment of Waller differs from that of Debye in the method of obtaining the "normal coordinates" in terms of which the energy of the lattice is expressed. As we shall see later, this modification really forms a correction which should be applied to Debye's work.

In the case of regular reflection the theory of Debye as amended by Waller seems to be supported quantitatively for temperatures from that of liquid air up to about 500°K by the recent experiments of James and Firth[5] and others.[6] The diffuse scattering of x-rays by crystals has been studied by Jauncey,[7] who concludes, on the basis of his experiments, that the intensity determined experimentally is considerably greater than the value demanded by Debye's formula and that the intensity varies much more slowly with the temperature than theoretically predicted.

Now since the discovery of the Compton effect it has been evident that a certain fraction of the diffusely scattered x-rays is the modified radiation, which is generally presumed to be incoherent. Owing to the existence of this

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[2] H. Faxen, Ann. d. Physik **54,** 615 (1918); Zeits. f. Physik **17,** 266, (1923).

[3] I. Waller, Zeits. f. Physik **17,** 389 (1923); "Upsala Dissertation," 1925.

[4] Cf. P. Debye, Ann. d. Physik **14,** 69, footnote (1914).

[5] James and Firth, Proc. Roy. Soc. **A117,** 62 (1927).

[6] James, Brindley and Wood, Proc. Roy. Soc. **A125,** 401 (1929); James and Brindley, Proc. Roy. Soc. **A121,** 155 (1928).

[7] G. E. M. Jauncey, Phys. Rev. **20,** 405 and 421 (1922).

incoherent radiation it appears that the old calculation of Debye should be modified. The present investigation was therefore undertaken.

II. Intensity of X-rays Diffusely Scattered by Crystals

In two recent papers[8] the writer has developed a general theory of the intensity of total scattering of x-rays by gases on the assumption that, in considering the scattering of x-rays by a polyatomic molecule, only the coherent radiation from the different atoms will produce interference effect, while the incoherent radiation will be simply added up. The theory has been compared with Barrett's experiments[9] on the scattering of x-rays by different gases and the agreement seems to be satisfactory. It appears that the idea just stated is of quite general character and can be applied to the scattering of x-rays by a crystal as well. We shall accordingly postulate that, in considering the scattering of x-rays by a crystal, only the coherent radiation scattered from the different lattice units will interfere with each other according to the classical wave theory, whereas the incoherent radiation will be simply added up. On this view, the intensity of the incoherent radiation scattered from a crystal should be independent of the temperature and therefore Jauncey's conclusion is to be theoretically expected.

In the writer's theory of scattering of x-rays by gases, the mathematical formulation is based on the fundamental investigation according to classical electrodynamics by Raman[10] and A. H. Compton[11] on the scattering of x-rays by an atom in which the electrons are regarded to be arranged with random orientation and with arbitrary radial distribution. The intensity of the x-rays of wave-length λ scattered at an angle θ to a distance R is found to be

$$I_\theta = I_1 + I_2[1 + \gamma(1 - \cos\theta)]^{-3}. \tag{2}$$

In this equation, $\gamma = h/mc\lambda$,

$$I_1 = \frac{Ie^4(1 + \cos^2\theta)}{2R^2m^2c^4}F^2 \text{ and } I_2 = \frac{Ie^4(1 + \cos^2\theta)}{2R^2m^2c^4}\left(Z - \frac{F^2}{Z}\right) \tag{3}$$

where I is the intensity of the primary beam, Z is the atomic number, h is Planck's constant, e and m are the charge and mass of the electron, and c is the velocity of light. The factor F is the atomic structure factor for the scattering atom and for the purpose of the present paper may be defined by the integral

$$F = \int_0^\infty U(r)\frac{\sin kr}{kr}\,dr,$$

where $k = (4\pi/\lambda)\sin\frac{1}{2}\theta$ and $U(r)dr$ is the amount of charge in electrons lying between r and $r+dr$ from the center of the atom. F is a function of $(\sin\frac{1}{2}\theta)/\lambda$ and approaches a value equal to the total number of electrons in the scatter-

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[8] Y. H. Woo, Proc. Nat. Acad. Sci. **17**, (1931).

[9] C. S. Barrett, Proc. Nat. Acad. Sci. **14**, 20 (1928); Phys. Rev. **32**, 22 (1928).

[10] C. V. Raman, Indian J. Physics **3**, 357 (1928).

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

ing atom for small values of θ. The factor $[1+\gamma(1-\cos\theta)]^{-3}$ in Eq. (2) is introduced by Compton[11] to correct for the change of wave-length in the Compton effect in accordance with the theoretical investigation by Breit[12], Dirac[13] and others. From classical considerations Raman[10] has called attention to the incoherent or "fluctuating" character of the part represented by I_2 and emphasized the fundamental difference in physical nature between I_2 and I_1 which is a perfectly determinate and invariable part representing the diffraction pattern of the atom. Compton has come to the same conclusion by comparing Eq. (2) with Wentzel's quantum theory of x-ray scattering.[14]

Since Debye's calculation for the diffuse scattering is supposed to take account only of the coherent radiation, we have therefore, according to the point of view put forward here, for the scattered intensity from a crystal

$$I_\theta = \frac{NIe^4(1+\cos^2\theta)}{2m^2R^2c^4}\left\{(1-e^{-B})F^2 + \frac{Z - F^2/Z}{[1+\gamma(1-\cos\theta)]^3}\right\} \tag{4}$$

where N is the number of atoms per unit volume of the crystal, B is equal to M according to Debye's theory and is equal to $2M$ if the modification suggested by Waller is introduced, and the other notations have the same meaning as those employed in Eq. (2) It will be noticed that the first term on the right-hand side of Eq. (4) is the original expression derived by Debye multiplied by the factor F^2 as suggested by Eq. (2), while the second term takes care of the incoherent part of the diffusely scattered intensity, which was of course entirely neglected in Debye's work.

Eq. (4) may be subjected to experimental test. In sylvine crystal, KCl, the two kinds of atom have very nearly the same size and mass, so that the lattice can be treated as if it were a simple cubic one, to which the expression (1) for M properly applies. Unfortunately no experimental data in this case are available for this test. In the next section a comparison of Eq. (4) with experiments described by Jauncey[15] and Jauncey and May[16] on the scattering of x-rays by rocksalt crystal will be made.

III. Comparison with Experiments

Jauncey and May[16] have recently reported experiments on the absolute measurements of the intensity of the x-rays diffusely scattered from a single rocksalt crystal. Owing to experimental difficulties, filtered x-rays of wave-lengths ranging from 0.3A to 0.9A were employed. According to these authors the spectrum of the x-rays scattered from the crystal shows two very distinct maxima at 0.40A and 0.71A and therefore the average wave-length of the primary x-rays can be roughly taken as 0.545A. The units adopted in this absolute measurement are as follows. According to Thomson's theory, the linear scattering coefficient s per unit solid angle in the direction of the scattering angle θ should be given by

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[12] Breit, Phys. Rev. **27,** 242 (1926).

[13] P. A. M. Dirac, Proc. Roy. Soc. **A111,** 405 (1926).

[14] G. Wentzel, Zeits. f. Physik **43,** 1 and 779 (1927).

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

[16] Jauncey and May, Phys. Rev. **23,** 128 (1924); Also Jauncey, Phys. Rev. **20,** 405 (1922).

$$s = \frac{NZe^4}{2m^2c^4}(1 + \cos^2 \theta). \tag{5}$$

The value of s obtained from (5) when $\theta = 90°$ is taken as the unit of scattered intensity. The experimental results for s in these units determined by Jauncey and May are plotted against θ as curve I in Fig. 1. It is seen that the experimental curve has two maxima, one at 30° and the other at 15°. These are ascribed by Jauncey and May to be corresponding to the two maxima in the scattered spectrum just mentioned.

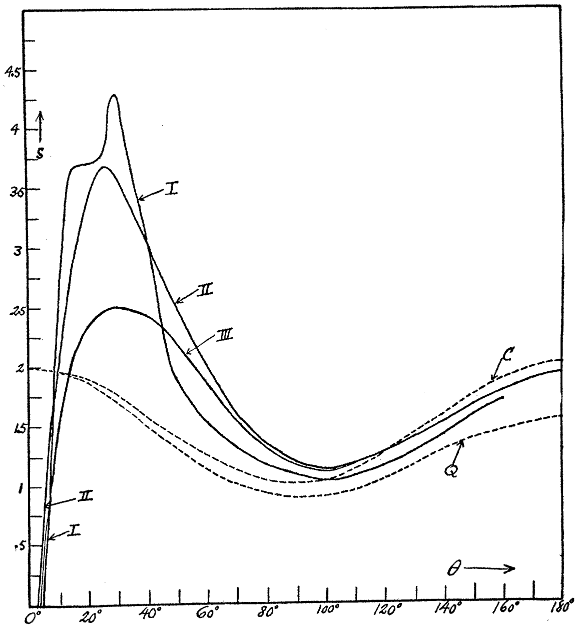

Fig. 1.

Strictly speaking, Eq. (4) is not applicable to the case of rocksalt crystal, for the expression of M is calculated for a simple cubic lattice composed of atoms of one kind, whereas the rocksalt contains atoms of Na and Cl. Each kind of atom should have its own values of F as well as its own value of B. To a first approximation, however, we may treat the crystal rock-salt as simple cubic, composed of atoms whose mass is the mean of those of sodium and chlorine and whose atomic number is equal to 14. Keeping this in view, a calculation is made of the intensity of the scattering of x-rays by a rock-salt crystal according to Eq. (4) for a wave-length equal to 0.545A. Taking the characteristic temperature of rock-salt as 281°, we get from Debye's formula

$$B = M = 0.69 \frac{\phi(x)}{x} \frac{1 - \cos \theta}{\lambda^2},$$

so that according to Waller the exponent should be

$$B = 2M = 1.38 \frac{\phi(x)}{x} \frac{1 - \cos\theta}{\lambda^2},$$

where the wave-length is in angstrom units. The value of T for the experiments of Jauncey and May is assumed to be 290°K. The values of F^2 are taken as $(F_1^2+F_2^2)/2$ and those of F^2/Z as $(F_1^2/Z_1+F_2^2/Z_2)/2$ where the indices 1 and 2 refer to Na and Cl respectively. In each case the F curve was estimated from the atomic field of Thomas and Fermi. The results of this calculation in the units adopted by Jauncey and May are plotted as curves II and III in Fig. 1. While the curve II shows the results calculated for $B=2M$, the curve III represents those for $B=M$. In both cases, zero-point energy is assumed to exist. If such energy is not assumed, the peak corresponding to the maximum scattering will be slightly depressed. Considering the approximate nature of the calculation as well as the uncertainties regarding the wave-length and the intensity distribution of the primary rays, the agreement between the theoretical curve II and the experimental curve I should be regarded satisfactory. Better agreement could be obtained if the average or effective wave-length be assumed to be shorter than 0.545A. This is certainly not inconsistent with the conditions of Jauncey and May's experiments, but it seems unnecessary to do it here. Thus we may conclude that, on the whole, the experiments of Jauncey and May support Eq. (4) for the case $B=2M$ as calculated by Debye and Waller. This is in accord with the experimental results recently reported by James and Firth[5] and others.[6] Since the peak in curve II will be depressed by assuming no zero-point energy, this comparison seems to suggest the existence of such energy. This is in agreement with the conclusion recently drawn by Waller, James and Hartree.[17] This, however, can not be considered certain, as the comparison made here is of an approximate nature. In order that definite conclusion could be obtained, it is desirable that data be secured on the scattering of homogeneous x-rays.

It is interesting to note that the theory agrees closely with experiment in predicting the positions of the maximum and the minimum in the intensity curve. It is also satisfactory that the theory and experiment agree about the change of the position of the maximum scattering with the wave-length of the primary beam.

In an early paper by Jauncey,[18] the variation of the scattering of x-rays ($\lambda=0.28$A) by rocksalt with temperature has been studied. The results obtained by Jauncey are summarized in Table I. The theoretical values given in the third and fourth columns were calculated by Jauncey from Debye's formula. The average atomic weight of NaCl was taken as 29 and Θ as 260°K. Taking $\Theta=281°$ a calculation is made of the scattering from rocksalt according to Eq. (4) and the results are compared with Jauncey's experi-

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[17] Waller and James, Proc. Roy. Soc. **A117,** 214 (1927). James, Waller and Hartree, Proc. Roy. Soc. **A118,** 334 (1928).

[18] G. E. M. Jauncey, Phys. Rev. **20,** 421 (1922). In the same paper Jauncey has also described experiments for a calcite crystal. As calcite is not even approximately simple cubic, we shall not discuss it here.

mental data in Table II. Though the numerical agreement between theory and experiment seems to be very much improved, this comparison rather indicates that, owing to the presence of the incoherent term, experiments of this type will not give data for a test of the present theory.

TABLE I

$$\frac{\text{Scattered Intensity at 568°K.}}{\text{Scattered Intensity at 290°K.}}$$

Scattering angle θ	Experimental value	Theoretical value	
		No zero-point energy	Zero-point energy
15°	1.33	1.87	1.65
30°	1.18	1.37	1.26

TABLE II

$$\frac{\text{Scattered Intensity at 568°K.}}{\text{Scattered Intensity at 290°K.}}$$

θ	Experimental value	Theoretical value			
		$B=M$		$B=2M$	
		No 0-pt. energy	0-pt. energy	No 0-pt. energy	0-pt. energy
15°	1.33	1.69	1.31	1.36	1.28
30°	1.18	1.15	1.11	1.14	1.06

IV. DIFFUSE SCATTERING FROM SYLVINE

The close agreement between theory and experiment in the case of rocksalt is extremely interesting, but, in order to place the quantitative treatment of the x-ray scattering on an entirely satisfactory basis, it appears to be of some importance to see whether a similar agreement can be obtained with other crystals. As pointed out above, the sylvine crystal, KCl, can be regarded as if the lattice were simple cubic with a single value of M and the formula (1) properly applies. It seems therefore not out of place here to give briefly a theoretical prediction for this case. Taking $T=290°\text{K}$, $\lambda=0.71\text{A}$, $\Theta=230°\text{K}$, $\mu=6.15\cdot 10^{-23}\text{g}$, a calculation is made of the intensity of diffuse scattering from KCl according to Eq. (4). M is found to be $1.72(1-\cos\theta)$ for the existence of zero-point energy and is $1.39(1-\cos\theta)$ for the absence of zero-point energy. Since KCl is generally regarded as ionic lattice, the F curve is calculated as if the atom had an atomic number equal to 18. The results of this calculation are shown in Fig. 2, where the linear scattering coefficient per unit solid angle in the units adopted in section 3 is plotted against the scattering angle θ. The curves I and I′ represent the results calculated for $B=M$ and the curves II and II′ represent those for $B=2M$. In each case the prime curve refers to the theoretical data calculated without zero-point energy. The broken curves marked C and Q are plotted according to the theories of Thomson and Breit-Dirac respectively. It will be noticed that absolute measurements performed with homogeneous x-rays should easily test these predictions. These measurements may perhaps also offer direct information regarding to the zero-point energy, since the differences between the intensities calculated with and without it are considerable, as is shown in Fig. 2.

In this connection it may be mentioned that experiments performed with a single crystal of a metallic element such as Al should also furnish valuable data for testing the present theory.

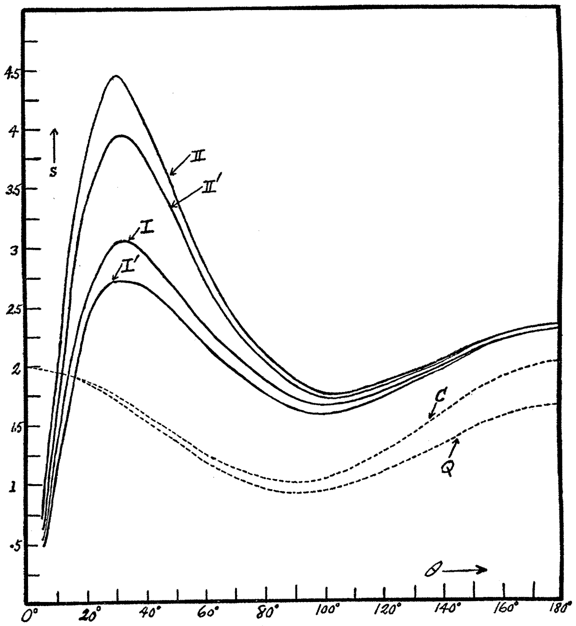

Fig. 2.

V. Discussion

A formula for the intensity of diffuse scattering of x-rays from a crystal has been obtained, which agrees fairly well with the experimental results for rocksalt. That is, the theory seems to account for the so-called excess scattering, for the small scattering in the region of 0° scattering angle, for the position of the maximum scattering as well as the shift of this position with the wave-length of the incident x-rays, for the occurrence of the minimum scattering at about 100° instead of at 90°, and finally for the general departure of the scattering curve from that predicted by Thomson's theory. It should be noted, however, that, according to Eq. (4), the coherent part of the diffuse scattering disappears when the temperature approaches absolute zero. This means that, the coherent rays at any angle other than that nearly satisfying Bragg's law should be completely extinguished by interference, if the atoms in the crystal have no thermal agitation. This is to be expected, because the present theory is developed for a single crystal in which the atoms are supposed to be arranged with perfect regularity. It is clear that the present theory will not be applicable to the scattering of x-rays by the so-called amorphous substances such as graphite, in which minute crystals are present. In these substances, the arrangement of the atoms evidently introduces a type of irregularity which must make the interference incomplete even though the heat-motions are absent. On this account diffuse scattering will occur which is probably proportional to

$$\left[1 - \frac{\Omega}{V} f(u)\right]$$

as suggested by the recent work of Debye.[19] In this expression Ω is the total volume of the action spheres of all the atoms (or molecules) effective in scattering, V is the volume of the scattering substance and $f(u) = (3/u^3)$ $(\sin u - u \cos u)$, where $u = (8\pi a/\lambda) \sin \theta/2$, a is the radius of the scattering atom (or molecule), λ and θ have their usual significance. The function $f(u)$ has a value 1 when $u = 0$. For solids and liquids Ω/V may be taken as unity. Thus the total coherent intensity of the x-rays diffusely scattered by an amorphous substance should be proportional to

$$[(1 - e^{-\beta}) + (1 - f(u))]F^2. \tag{6}$$

This explains the experimental fact recently reported by Jauncey and Bauer[20] that there is no effect of temperature on the ratio of modified to unmodified rays in the Compton effect. For, under the conditions of Jauncey and Bauer's experiments, only a negligible portion of the coherent intensity will be influenced by temperature as indicated by the expression (6), while the incoherent part is independent of temperature as already remarked. These considerations seem to play a very important role in accounting for the intensity of the x-rays scattered by an amorphous substance as well as for the energy distribution between the modified and the unmodified rays in the Compton effect. A detailed discussion will be reserved for another paper.

As mentioned in the introduction, the effect of temperature on the diffuse scattering has also been investigated by Faxen[2] and Waller.[3] Since, however, the predictions of the theories of these authors seem not to fit with experimental facts which have come to light, we shall not enter into a discussion here.

In conclusion the writer wishes to express his appreciation of the inspiration of his former teacher, Professor A. H. Compton of University of Chicago, U. S. A.

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[19] P. Debye, Jour. of Math. and Phys., M.I.T. **4,** 133 (1925) and in German Phys. Zeits. **28,** 135 (1927).

[20] Jauncey and Bauer, Phys. Rev. **34,** 387 (1929).