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Theory of the Effect of Temperature on the Reflection of X-Rays by Crystals
I. Isotropic Crystals

CLARENCE ZENER AND G. E. M. JAUNCEY,* *Wayman Crow Hall of Physics, Washington University, St. Louis*

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A short derivation of the Debye-Waller temperature factor in the reflection of x-rays from isotropic crystals is given. This short derivation clearly brings out the assumptions involved and paves the way for the extension of the theory to the more complex case of anisotropic crystals. One of the authors will give this extension in a subsequent paper.

1. INTRODUCTION

IN the reflection of x-rays from crystals and in the scattering of x-rays from gases, we meet two forms of the atomic structure factor. If we represent the structure factor relative to a lattice point in a crystal by F and that relative to the center of the atom by f, the relation between F and f is

$$F=fH, \tag{1}$$

where H is the temperature factor. This is given by

$$H=\int_{-\infty}^{\infty} p(z) \cos\left(\frac{4\pi z \sin\theta}{\lambda}\right)dz, \tag{2}$$

where $p(z)$ is the layer distribution function relative to a crystal plane of the atoms associated with that plane (the plane of x and y), the axis of z bisects the angle between the forward direction of the reflected rays and the backward direction of the primary rays, and θ is the glancing angle of incidence of the x-rays on the reflecting plane. The temperature factor is usually written in the form

$$H=e^{-M}. \tag{3}$$

The function M has been derived for isotropic solids by Debye.[1] Later, Waller[2] showed that Debye's formula for M should be multiplied by a factor of two. In this paper a new derivation is given. The authors believe that this third derivation is justified on two grounds. Firstly, the two previous derivations have been so lengthy, and the approximations so obscure, that it is difficult to see just what physical assumptions have been made. Secondly, one of the authors is communicating a paper in which the method of the present paper is extended to the derivation of M for anisotropic crystals. It is desirable to separate the case of isotropy from the more complex case of anisotropy.

2. THE LAYER DISTRIBUTION FUNCTION

We assume the displacements of the atoms from their equilibrium positions to be so small that the potential energy of the lattice is a quadratic function of the coordinates of the atoms. The actual displacement of a given atom from its lattice point is then given by the vector sum of the displacements arising from the various normal modes of vibration of the crystal. In particular, the component of the displacement of an atom along any axis, say along the z axis, is equal to the algebraic sum of the components of the displacements due to the vibrational modes. Since the probability of a displacement between z and $z+dz$ due to one vibrational mode is the same whether z is positive or negative, and since the displacements due to any two vibrational modes are independent, the calculation of the probability function $p(z)$ is identical with the calculation of the probability function for a net error which is due to a large number of independent errors,[3] or for the diffusion of Brownian particles from a plane.[4] The result is well known:

$$p(z)=\frac{1}{(2\pi\mu)^{\frac{1}{2}}}\cdot e^{-z^2/2\mu}, \tag{4}$$

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

[2] I. Waller, Zeits. f. Physik **51**, 213 (1923). A comprehensive list of references is given by Compton and Allison in *X-rays in Theory and in Experiment*, 435–436 (1935).

[3] See J. Rice, *Statistical Mechanics*, p. 10.

[4] A. Einstein, Ann. d. Physik **17**, 556 (1905).

where

$$\mu = \Sigma_s \mu_s. \tag{5}$$

Here μ_s is the mean square of the z component of the displacement due to the sth vibrational mode, and the summation is over all the vibrational modes of the crystal. Substitution of (4) into (2) gives

$$M = (8\pi^2 \mu \sin^2 \theta)/\lambda^2. \tag{6}$$

3. The Mean Square Displacement

In order to calculate μ, we must assume a definite model for the solid. We shall take that model introduced by Debye[5] in his theory of the specific heats of solids. The normal coordinates are taken to be the amplitudes of the vibrational modes which would be present if the solid were a continuous medium with the same gross elastic properties as the actual discontinuous solid. Since the number of normal coordinates must be $3n$, where n is the number of atoms in the solid under consideration, Debye found it necessary to exclude vibrational modes of a frequency greater than a certain maximum frequency, ν_m. It should be noted, however, that this method of obtaining the correct number of normal coordinates is not unique. In this paper we shall follow the procedure of Debye's theory of specific heats in excluding those vibrational modes with a frequency greater than ν_m.

The mean square μ is to be identified with the average square of the z component of the displacement vector $\mathbf{D}(\mathbf{r}, t)$ of the fictitious continuous medium. If we expand $\mathbf{D}$ into a Fourier series,

$$\mathbf{D}(\mathbf{r}, t) = 2^{\frac{1}{2}} \sum \mathbf{a}_{j,\,\mathbf{k}}(t) \cos(\mathbf{k}\cdot\mathbf{r} + \delta_j),$$

and let $\gamma_{j,\,\mathbf{k}}$ be the cosine of the angle which $\mathbf{a}_{j,\,\mathbf{k}}$ makes with the z axis, then, in virtue of (5),

$$\mu = \sum \gamma^2_{j,\,\mathbf{k}} \cdot \overline{\mathbf{a}^2_{j,\,\mathbf{k}}}. \tag{7}$$

In the classical mechanics $\mathbf{a}_{j,\,\mathbf{k}}$ is a periodic function of time

$$\mathbf{a}_{j,\,\mathbf{k}}(t) = c_{j,\,\mathbf{k}} \cos(2\pi\nu t + \phi_{j,\,\mathbf{k}}),$$

the phases $\phi_{j,\,\mathbf{k}}$ being independent. In the quantum mechanics the $\mathbf{a}_{j,\,\mathbf{k}}$'s are independent dynamical variables. In both mechanics the average energy associated with $\mathbf{a}_{j,\,\mathbf{k}}$ is

$$\epsilon_{j,\,\mathbf{k}} = 4\pi^2\nu^2 M_0 \overline{\mathbf{a}^2_{j,\,\mathbf{k}}}, \tag{8}$$

where ν is the classical frequency of $\mathbf{a}_{j,\,\mathbf{k}}$ and M_0 is the total mass of the solid. From the classical viewpoint this relation is obtained most readily by equating $\epsilon_{j,\,\mathbf{k}}$ to the kinetic energy $\frac{1}{2}M_0\dot{\mathbf{a}}^2_{j,\,\mathbf{k}}$ associated with $\mathbf{a}_{j,\,\mathbf{k}}$ at the instant when $\mathbf{a}_{j,\,\mathbf{k}}$ is zero. From the quantum viewpoint this relation is obtained via the virial theorem. By means of (8) and of the quantum formula

$$\epsilon_{j,\,\mathbf{k}} = \frac{h\nu}{\exp(h\nu/kT) - 1} + h\nu/2 \tag{9}$$

($h\nu/2$ being the zero-point energy), we now transform (7) into

$$\mu = \frac{h}{4\pi^2 M_0} \sum \gamma^2_{j,\,\mathbf{k}} \left\{ \frac{1/\nu}{\exp(h\nu/kT) - 1} + \frac{1}{2\nu} \right\}. \tag{10}$$

Eq. (10) is not restricted to isotropic crystals; it will in fact be used in a following paper on anisotropic crystals. Assuming isotropy, $\gamma^2_{j,\,\mathbf{k}}$ is replaced by its spatial average $\frac{1}{3}$, while, as in specific heat theory, the number of vibrational modes with frequencies between ν and $\nu + d\nu$ is $9n\nu_m^{-3}\nu^2 d\nu$. Hence (10) may be replaced by an integral between the limits $\nu = 0$ and $\nu = \nu_m$. Introducing the quantity $\xi = h\nu/kT$ and the characteristic temperature $\Theta = h\nu_m/k$, we obtain an expression for μ which when inserted in (6) gives the Waller formula

$$M = \frac{6h^2}{m_a k \Theta} \cdot \left\{ \frac{\phi(\Theta/T)}{\Theta/T} + \frac{1}{4} \right\} \frac{\sin^2\theta}{\lambda^2}, \tag{11}$$

where $m_a = M_0/n$ is the mass of a crystal atom and

$$\phi(x) = \frac{1}{x} \int_0^x \frac{\xi}{e^{\xi} - 1} d\xi, \tag{12}$$

the well-known Debye function.

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[5] P. Debye, Ann. d. Physik **39**, 789 (1912).