THEORY OF THE EFFECT OF THERMAL AGITATION ON THE REFLECTION OF X-RAYS BY CRYSTALS

By S. Y. Szr (施士元)

Department of Physics, National Central University, Nanking.

(*Received Nov. 14, 1936*)

ABSTRACT

A simplified wave-mechanical method of deriving the temperature factor in the reflection of X-rays from crystals is given(1). The general expression for the function M is the same as calculated by Zener and Jauncey. Hence the discrepency between Zener's theory for hexagonal crystals and the experiments may be due to the special model used in his calculation.

ZENER(2) has calculated the Debye-Waller function M for hexagonal crystals. His theoretical value does not agree very well with the experimental values of Brindley(3) and Jauncey and Bruce(4) for Zn. As he has assumed(5) that the layer distribution function $P(z)$ is identical with the probability function for a net error due to a large number of independant errors, it is desirable to see whether it will be necessary to modify his general expression M for isotropic as well as for anisotropic crystals, if this function is calculated by other means.

Let us consider a crystal composed of N similar atoms, and suppose that its temperature is not too high so that the amplitude of vibrations of the atoms is small and the potential energy is quadratic in the displacements of all the atoms. Then the problem can be considered by introducing the normal coordinates, which are $3N$ in number for the N particles.

(1) A paper read before the physics seminar in National Central University Nov. 5, 1936.

(2) C. Zener, Phys. Rev. **49**, 122, 1936

(3) G. W. Brindley and F. W. Spier, Phil. Mag. **20**, 865, 1935.
G. W. Brindley, Phil. Mag. **21**, 790, 1936.

(4) Jauncey and Bruce, Phys. Rev. **50**, 408, 1936.

(5) C. Zener and Jauncey, Phys. Rev. **49**, 17, 1936

With these normal coordinates, Schrödinger's equation is separable. Each of the $3N$ equations corresponding to the $3N$ corrdinates is just like that of a linear oscillator, namely

$$\frac{d^2\psi_i}{dr_i^2} + (\lambda_i - \alpha_i^2\ r_i^2)\psi_i = 0, \qquad i = 1,\ 2,\ \cdots\cdots\ 3N$$

where

$$\lambda_i = \frac{8\pi^2 m W_i}{h^2}, \qquad \alpha_i = \frac{4\pi^2 m \nu_i}{h},$$

r_i is the displacement along the ith coordinate, ν_i is the proper frequency of the vibration along this coordinate, and m is the mass of the crystal.

For the state of lowest energy

$$\psi_{i0}(r_i) = \left(\frac{\alpha_i}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha_i}{2} r_i^2}$$

and the probability of finding the displacement r_i between r_i and $r_i + dr_i$ is

$$\psi_{i0}^2(r_i)\, dr_i.$$

Assuming that the direction of the ith coordinate makes an angle φ_i with the z axis which bisects the angle between the foreward direction of the reflected rays and the backward direction of the incident rays, and writing $\cos\varphi_i = \gamma_i$, then the projection of r_i on the z axis is $z = \gamma_i r_i$. And the probability of finding the projection within the range of z and $z + dz$ is

$$P_i(z) = \left(\frac{\alpha_i}{\pi\gamma_i^2}\right)^{\frac{1}{2}} e^{-\frac{\alpha_i}{\gamma_i^2} z^2}\, dz.$$

The contribution of this vibration to the temperature factor is

$$H_i = \int_{-\infty}^{+\infty} P_i(z)\ \cos\left(\frac{4\pi z \sin\theta}{\lambda}\right) dz$$

where λ is the wave length of the incident X-rays, and θ is the glancing angle of incidence of the X-rays on the reflecting plane. We have

$$H_i = \int_{-\infty}^{+\infty} \left(\frac{\alpha_i}{\pi\gamma_i^2}\right)^{\frac{1}{2}} e^{-\frac{\alpha_i}{\gamma_i^2}z^2} \cos\left(\frac{4\pi z \sin\theta}{\lambda}\right) dz$$

$$= e^{-\frac{4\pi^2\gamma_i^2 \sin^2\theta}{\lambda^2 \alpha_i}}$$

$$= e^{-M_i}$$

where

$$M_i = \frac{2\gamma_i^2 \sin^2\theta}{\lambda^2 m \nu_i^2} \cdot \frac{h\nu_i}{2}$$

is the contribution of the ith normal vibration to the Debye-Waller function. In this expression we notice that the factor $\frac{h\nu_i}{2}$ represents the energy of the linear oscillator in its lowest state. In the theory of specific heat the intrinsic energy of the crystal at a temperature T is

$$E = \sum_{i=1}^{i=3N} \left(\tfrac{1}{2} h\nu_i + \frac{h\nu_i}{e^{\frac{h\nu_i}{kT}} - 1} \right).$$

This means that each normal vibration contributes an energy of

$$\tfrac{1}{2} h\nu_i + \frac{h\nu_i}{e^{\frac{h\nu_i}{kT}} - 1}.$$

Therefore at any temperature T, M_i should be written as

$$M_i = \frac{2\gamma_i^2 \sin^2\theta}{\lambda^2 m \nu_i^2} \left(\tfrac{1}{2} h\nu_i + \frac{h\nu_i}{e^{\frac{h\nu_i}{kT}} - 1} \right).$$

For all the $3N$ normal vibrations, the temperature factor is

$$H = \prod_{i=1}^{i=3N} H_i = e^{-\sum_{i=1}^{i=3N} M_i}.$$

Therefore the M function is

$$M = \sum_{i=1}^{i=3N} M_i = \frac{2\sin^2\theta}{m\lambda^2} \sum_{i=1}^{i=3N} \frac{\gamma_i^2}{\nu_i^2} \left(\tfrac{1}{2} h\nu_i + \frac{h\nu_i}{e^{\frac{h\nu_i}{kT}} - 1} \right).$$

This expression is valid for isotropic as well as for anisotropic crystals and it is exactly the same as that obtained by Zener and Jauncey's method[5].

In view of this result we conclude that the general expression for the function M needs no modification, but that the particular model used in calculating the value M for hexagonal crystals may need some modifications.

The writer will give a modified method of calculation in a subsequent paper.