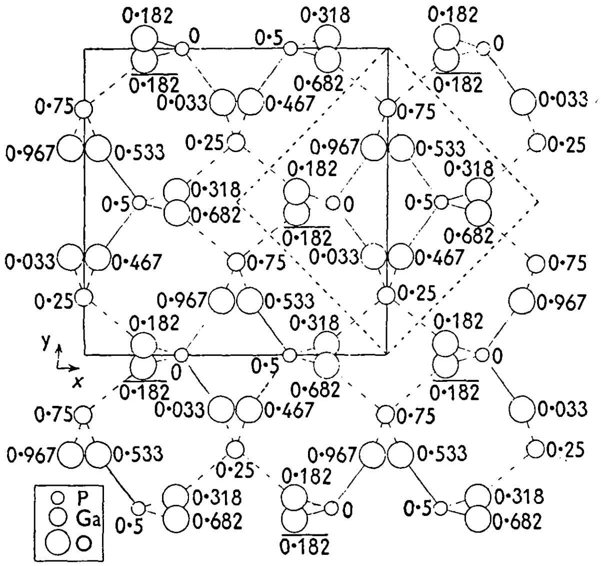

Fig. 1. Gallium phosphate, low-cristobalite type; [001] projection of the crystal structure. The true base-centered cell is indicated by full lines, and the pseudo-cell, comparable to that of low-cristobalite silica, by heavy broken lines.

In low-cristobalite SiO_2 the angle Si–O–Si is 150°. The analogous angle is smaller in the two phosphates, and decreases with the heavier metal: it is 145° for Al–O–P, and 135° for Ga–O–P. This difference in the orientation of the oxygen tetrahedra accounts for the facts that the $AlPO_4$ cell is not quite as large compared to that of SiO_2 as might be expected from spatial considerations; and that the structural unit of $GaPO_4$ can be accommodated in a smaller cell volume than that of $AlPO_4$ or even SiO_2, despite its larger M–O separation.

No preliminary assumptions were made concerning the magnitude of the M–O distances in the MPO$_4$ structures; a wide range of values were tested with various phosphate group positions. In the case of low-cristobalite $AlPO_4$, the distance Al–O was found to be 1·70 Å. This value has also been reported for four-coordinated Al–O in the crystal of $AlAsO_4$ (Machatski, 1935), which is structurally analogous to low-quartz. It is considerably smaller than would be deduced from the assumption of ionic radii. For instance, in Al_2O_3 (corundum) the average O–Al distance in six-coordination is 1·91 Å (three at 1·89, three at 1·93 Å). Correction of this distance to four coordination gives about 1·79 Å.

The value of 1·78 Å was found for the Ga–O distance in low-cristobalite $GaPO_4$. There are no available experimental data with which to compare it. For ionic radii, the distance for four coordination would be in the neighborhood of 1·85 Å.

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A Note on the Debye–Waller Theory

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The effect of temperature on the Bragg reflexion from crystals is examined theoretically for a general crystal. It is shown that measurements of this effect can be used to obtain information about the vibrational spectrum of a crystal. A comparison is made of the existing data and the theoretical predictions.

1

The effect of temperature on the reflexion of X-rays from crystals was first investigated by Debye (1914), and in the form due to Waller (1925) is part of standard X-ray theory. The theory shows that the intensity of X-rays reflected by a particular set of Bragg planes varies with temperature in the form $\exp(-2M)$, where

$$M = 8\pi^2 \overline{u_z^2} \sin^2 \theta / \lambda^2 , \qquad (1)$$

θ being the Bragg angle, λ the wavelength of the X-rays and $\overline{u_z^2}$ an averaged mean square displacement in the direction z perpendicular to the planes. The exponent M has the properties of a second-order tensor (Zener, 1936) and can be expressed as

$$M_s = M_1 l_1^2 + M_2 l_2^2 + M_3 l_3^2 , \tag{2}$$

where M_1, M_2, M_3 are the values of M along principal axes and l_1, l_2, l_3 are the direction cosines of a vector in the direction S with respect to these axes. An expression of this form has been used by Zener in discussing close-packed hexagonal metals. (Though there are here two particles per cell, their arrangement is such that it can be concluded that the M values are the same for each particle.)

The Debye–Waller theory, as normally used, employs a Debye vibrational spectrum in the evaluation of (1) for cubic crystals, and a set of Debye θ_D values in the more general case. An exact evaluation has been given by Waller in the case of simple cubic crystals; here M is independent of the direction of z and it is possible to express $\overline{u_z^2}$ in terms of an integral involving the vibrational spectrum. An analysis of the effects to be expected from various vibrational spectra has been given by Blackman (1937) in such cases.

Experimental investigations of a more detailed character than those so far available are necessary before the theory can be employed to supplement usefully the information on the vibrational spectrum derived from other sources. It does, however, appear likely that recent improvements in technique of measurement could provide accurate data.

It seems worth while to point out that the theory can be extended to the case of a general crystal, yielding an expression involving the vibrational spectrum in a direct manner. In the case of complex crystals where specific-heat data alone do not provide anything like unique information on the vibrational spectrum, measurements on the temperature-dependence of X-rays can provide very useful additional evidence.

2

The scattering of X-rays by a lattice is treated here in the same way as for a large molecule in the form given by Born (1942). The particles are numbered successively by the index p ($p = 1, 2, \ldots, n$), the masses being m_p and the displacements u_p. The intensity of X-rays scattered from an assembly of particles is proportional to $|F|^2$, where

$$F = \sum_p f_p \exp[i(\mathbf{Q}.\mathbf{r}_p)] \exp[i(\mathbf{Q}.\mathbf{u}_p)] . \tag{3}$$

Here $\mathbf{Q} = 2\pi(\mathbf{S}-\mathbf{S}_0)/\lambda$, where $\mathbf{S}_0$ and $\mathbf{S}$ are unit vectors in the direction of the incident and the scattered radiation respectively. The vector $\mathbf{r}_p$ is drawn from an arbitrary origin to the particle p when in its undisturbed condition. The term f_p is the atomic scattering factor of the particle p.

The displacements are represented in terms of normal coordinates ξ_j ($j = 1, 2, \ldots, 3n$) by the linear transformation

$$m_p^{\frac{1}{2}} \mathbf{u}_p = \sum_j \mathbf{e}_p^j \xi_j . \tag{4}$$

The vectors $\mathbf{e}_p^j$ form an orthonormal set in $3n$-dimensional space, $e_{p,\alpha}^j$ ($\alpha = x, y, z$) being generalized direction cosines in this space. It follows that

$$\sum_p \mathbf{e}_p^j . \mathbf{e}_p^{j'} = \delta_{jj'} . \tag{5}$$

The intensity function FF^* can then be written as

$$FF^* = \sum_{pp'} I_p I_{p'}^* \exp[i(\sum_j \mu_{pp'}^j \xi_j)] , \tag{6}$$

where

$$I_p = f_p \exp[i(\mathbf{Q}.\mathbf{r}_p)] , \tag{7a}$$

$$\mu_{pp'}^j = \mathbf{Q}.(\mathbf{e}_p^j m_p^{-\frac{1}{2}} - \mathbf{e}_{p'}^{j'} m_{p'}^{-\frac{1}{2}}) . \tag{7b}$$

The statistical averaging of the intensity function, which is a somewhat doubtful point in the earlier work, has been investigated thoroughly by several authors (Ott, 1935; Born, 1942), the result being

$$\overline{FF^*} = \sum_{pp'} I_p I_{p'}^* \prod_j \exp[-\tfrac{1}{2}(\mu_{pp'}^j)^2 \bar{\varepsilon}_j \omega_j^{-2}] , \tag{8}$$

$\bar{\varepsilon}_j$ being the mean energy of a linear harmonic oscillator of frequency $\omega_j/2\pi$.

The important quantity $(\mu_{pp'}^j)^2$ takes the form

$$(\mu_{pp'}^j)^2 = Q^2 \left(\frac{(e_{pq}^j)^2}{m_p} + \frac{(e_{p'q}^{j'})^2}{m_{p'}} - \frac{2 e_{pq}^j e_{p'q}^{j'}}{m_p^{\frac{1}{2}} m_{p'}^{\frac{1}{2}}} \right) , \tag{9}$$

e_{pq}^j being the component of $\mathbf{e}_p^j$ along the direction of Q.

Of the three terms in (9) only the first two are important in considering the effects in the immediate neighbourhood of a Bragg reflexion. The third term leads to the 'thermal spots' observed in directions where the Bragg condition is not satisfied. Hence, in considering the variation with temperature of a Bragg reflexion, it is sufficient to investigate the intensity function

$$I = \sum_{pp'} I_p I_{p'}^* \exp[-M_{pq}] \exp[-M_{p'q}] , \tag{10}$$

where

$$M_{pq} = \tfrac{1}{2} Q^2 \sum_j \frac{\bar{\varepsilon}_j}{m_p \omega_j^2} (e_{pq}^j)^2 . \tag{11}$$

It follows from (11) that

$$\sum_p m_p M_{pq} = \tfrac{1}{2} Q^2 \sum_j \frac{\bar{\varepsilon}_j}{\omega_j^2} \sum_p (e_{pq}^j)^2 . \tag{12}$$

We now consider three directions for the vector $\mathbf{Q}(\mathbf{Q}_\alpha, \alpha = 1, 2, 3)$ which are perpendicular to each other, these being labelled as the x, y, z axes. Adding the three terms of type (12), we find

$$\sum_p 2m_p\left(\frac{M_{px}}{Q_x^2}+\frac{M_{py}}{Q_y^2}+\frac{M_{pz}}{Q_z^2}\right)$$
$$=\sum_j \frac{\bar{\varepsilon}_j}{\omega_j^2}\sum_p\left[(e^j_{px})^2+(e^j_{py})^2+(e^j_{pz})^2\right]=\sum_j\frac{\bar{\varepsilon}_j}{\omega_j^2}\,. \qquad (13)$$

We can now specialize the result for the case of a lattice containing N cells with g particles in each cell. The symbol p is replaced by two indices (l, k), where l numbers the cells and k the particles in each cell. Then, because of the periodic nature of the lattice,

$$M_{l,k,q}=M_{l+l',k,q}\,, \qquad (14)$$

i.e. it is independent of l. (A rather more formal proof can be obtained by using the explicit form for $\mathbf{e}^j_p$ given by Born (1923) for a lattice, using periodic boundary conditions.) We can therefore omit the suffix l, and write (13) in the form

$$N\sum_k 2m_k\left(\frac{M_{kx}}{Q_x^2}+\frac{M_{ky}}{Q_y^2}+\frac{M_{kz}}{Q_z^2}\right)=\sum_j\frac{\bar{\varepsilon}_j}{\omega_j^2}\,, \qquad (15)$$

in which the vibrational spectrum enters directly, and which is directly related to M values that can be obtained experimentally. This expression can be put into a rather more familiar form by writing

$$M_{kx}=\tfrac{1}{2}Q_x^2\overline{u^2_{kx}}=\frac{8\pi^2}{\lambda^2}\sin^2\theta\,\overline{u^2_{kx}}\,.$$

Then (15) becomes

$$\sum_k m_k(\overline{u^2_{kx}}+\overline{u^2_{ky}}+\overline{u^2_{kz}})=\frac{1}{N}\sum_j\frac{\bar{\varepsilon}_j}{\omega_j^2}=\frac{3g}{4\pi^2}\frac{\int\varrho(\nu)\bar{\varepsilon}\nu^{-2}d\nu}{\int\varrho(\nu)d\nu}\,, \qquad (16)$$

where the integrals are taken over the whole vibrational spectrum, $\varrho(\nu)$ is the distribution function for the frequencies and

$$\int\varrho(\nu)d\nu=3gN\,.$$

Equations (15) and (16) represent, then, the generalization of the form found in the case of cubic crystals containing one particle per cell. A discussion of particular cases and a comparison with experimental results will be given below.

3

If we consider the general form of M_{pq} given in (11) for a particular particle p in the lattice and a given direction q, it can be seen that this has the properties of a second-order tensor. It we take a set of cartesian axes then

$$e^j_{pq}=e^j_{px}l_1+e^j_{py}l_2+e^j_{pz}l_3\,, \qquad (17)$$

where l_1, l_2, l_3 are the direction cosines of $\mathbf{Q}$ with respect to these axes. Hence M_{pq} will be a general quadratic form in l_1, l_2, l_3 which can be transformed into a sum of squares of the l_α if the axes are suitably chosen. This result holds for all the M_{pq} values for the particles in a lattice cell. The principal axes do not in the general case need to be the same for all particles, but this will be so for crystals with a high degree of symmetry where the principal axes will coincide with the crystal axes.

For hexagonal crystals it will follow, for instance, that

$$M_{kq}=M_{kz}\cos\theta_1^2+M_{ks}\sin^2\theta_1\,, \qquad (18)$$

where θ_1 is the angle made by $\mathbf{Q}$ with the hexagonal (z) axis and s denotes a direction perpendicular to this axis. The hexagonal metals contain two particles ($k = 1, 2$) per cell of equal mass, each surrounded by particles which are such that one set can be transformed into the other, for example by a rotation through 180° about the hexagonal axis. It follows that the equations of motion of one of the particles can be arranged to have the same form as that of the other by a reversal of the coordinate axes and a change in the numbering of the cells. The magnitude of $\overline{u^2_{1q}}$ should therefore be the same as $\overline{u^2_{2q}}$.

A general point can be made concerning the value of $\overline{u^2_{pq}}$ at high temperatures, which has the form

$$\overline{u^2_{pq}}=\frac{kT}{m_p}\sum_j\frac{(e^j_{pq})^2}{\omega_j^2}\,. \qquad (19)$$

It has been pointed out by Waller (1925) in the case of alkali halides that the sum over the normal vibrations will be proportional to the mass of the particle, i.e. $\overline{u^2_{kq}}$ is independent of the mass of the particle but depends only on the forces between particles. This follows from a formal evaluation of the sum, using the equations of motion and the properties of the eigenvectors. The result, however, is of general validity, as can be seen from the work of Waller, or by examining the expression for the sum in (19) given by Born (1942).

For crystals with cubic symmetry M_{kq} will be independent of the direction of $\mathbf{Q}$, and $\overline{u^2_{kz}}$ independent of z, though in the latter case the suffix is retained. From (16) it follows that

$$\sum_k m_k\overline{u^2_{kz}}=\frac{g}{4\pi^2}\frac{\int\varrho(\nu)\bar{\varepsilon}\nu^{-2}d\nu}{\int\varrho(\nu)d\nu}\,. \qquad (20)$$

In the case of one particle per cell (e.g. in the case of f.c.c. or b.c.c. metals), this leads to the general form of the Debye–Waller theory obtained in earlier work. When there are two particles per cell, as for the alkali halides, we have

$$\tfrac{1}{2}(m_1\overline{u^2_{1z}}+m_2\overline{u^2_{2z}})=\frac{1}{4\pi^2}\int\varrho(\nu)\bar{\varepsilon}\nu^{-2}d\nu\Big/\int\varrho(\nu)d\nu\,. \qquad (21)$$

This type of averaging has been employed by Waller & James (1927) in comparing experimental measurement on rocksalt with theory. Unfortunately, a rather approximate theoretical formula was used. We can now use the exact form, as the vibrational spectrum of rocksalt has been evaluated (Kellermann, 1940). As the experimental values are concerned with moderately high temperatures, we use (21) in the limiting form where $\bar{\varepsilon} = kT$. We define a limiting θ(X-R.) value in terms of a frequency ν(X-R.) defined as

$$\frac{3}{\nu(\text{X-R.})^2} = \frac{\int \varrho(\nu)\nu^{-2}d\nu}{\int \varrho(\nu)d\nu} . \qquad (22)$$

If a Debye vibrational spectrum were used, ν(X-R.) would be equal to the Debye frequency ν_D. It is theoretically unlikely that the ν(X-R.) value as calculated from (22) will differ from that evaluated in the more general averaging, using (21) at moderately high temperatures. In using (22) it is convenient to work out the ratio $\nu(\text{X-R.})/\nu_D$ (or $\theta(\text{X-R.})/\theta_D$) where the ν_D value is obtained from the elastic constants at room temperature. In the case of rocksalt this ratio is found to be 0·925. As the θ_D (elastic) value is 300° K., θ(X-R.) is 278° K. The value obtained from the experimental work of James is 281° K. The agreement would appear to be perfect. It is rather disturbing, therefore, to find that the recent measurements of Renninger (1952) give a different θ value, namely 320° K., which is much higher than can be accounted for. The relation $\theta(\text{X-R.})/\theta_D(\text{elastic}) < 1$ is of a very general nature and is due to the existence of peaks in the vibrational spectrum at low frequencies. The elastic constants of rocksalt have been measured by a number of investigators and the agreement is reasonably good. The vibrational spectrum calculated theoretically gives good agreement with specific-heat data. It is therefore difficult to see any reason for the discrepancy.

It should however be pointed out that there does also appear to be a discrepancy in the case of sylvine. The experimental θ(X-R.) value is given as 240° K. (James, 1948), the θ_D(elastic) value calculated from elastic data at room temperature is 230° K., and the theoretical θ(X-R.) value which we obtain using the vibrational spectrum (Iona, 1941) is 220° K.

Apart from the alkali halides, little appears to have been done experimentally, but measurements have been reported on the hexagonal metals (see Lonsdale, 1942). It has been usual to assume, in interpreting these measurements, that the variation with temperature of $\overline{u_q^2}$ along and perpendicular to the hexagonal axis can be represented by a Debye–Waller formula with different θ values for these directions. While it is possible to produce arguments for this procedure when a continuum approach is used, it is by no means clear that this is justified when the lattice character of the crystal is taken into account. Calculations which have been carried out so far have used the continuum approach. Zener (1936) worked out the values of $\overline{u_q^2}$ at moderately high temperatures for zinc and cadmium, but the agreement with experiment, though qualitatively correct, was poor in magnitude. Kohler (1939) concentrated on the low-temperature aspect and calculated the ratio $(\overline{u_z^2}/\overline{u_s^2})^*$ (cf. (18)) in which the contribution of the zero-point energy was excluded. This investigation, which made use of the elastic constants only, is certainly theoretically well founded provided the temperature is sufficiently low. The value calculated is remarkably close to the ratio given by experiment; since however the experiments were carried out at temperatures well above those for which the theory should apply, one can only conclude that the ratio must be rather insensitive to temperature.

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