DEBYE TEMPERATURE OF SOME CUBIC ELEMENTS AND ALKALI HALIDES

by

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I would rather discover one cause

than gain the kingdom of Persia.

- - - Democritus

ABSTRACT

The Debye characteristic temperatures of 24 cubic elements and 18 alkali halides have been calculated from their elastic constants by the Hopf-Lechner method, which has been extended to a tenth degree polynomial approximation, the Houston-Bhatia-Tauber method, and the Fedorov method, to various degrees of approximation. The calculated values have been compared with the experimental ones and the relative merits of the three methods discussed.

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CHAPTER I

INTRODUCTION

The well known Debye T^3 law for the specific heat (C_v) of solids at low temperatures leads to a well defined value of the Debye temperature at 0°K (Θ_o^c). This temperature can also be calculated from the elastic stiffness constants (Θ_o^{el}) (Born and von Karman 1913, Born 1923). The equality

$$\Theta_o^{el} = \Theta_o^c$$

provides a useful check on the consistency and accuracy of elastic constant and specific heat data. During the last six decades, a number of methods have been proposed to calculate Θ_o^{el} to varying degrees of accuracy.

The present thesis concerns itself with three of these which were expected to provide accurate values:

(a) Hopf-Lechner (1914) method. We have extended this method by employing a tenth degree polynomial.

(b) Houston (1948) - Bhatia and Tauber (1954) method. 3-, 6-, 9- and 15-direction approximations, and

(c) a recent method due to Fedorov (1968).

Employing the best available elastic constant data for 24 cubic elements and 18 alkali halides, we have calculated the Debye temperatures for these substances using the above three methods. The calculated values have been compared with the experimental ones and the relative merits of these methods have been discussed.

CHAPTER II

REVIEW OF THE DEBYE THEORY

An Outline

Einstein (1907) was the first to apply quantum rules to specific heats and thus he was able to explain the low temperature deviations from the Dulong-Petit law of specific heats. He assumed that each atom of the solid was an oscillator and that all the oscillators had the same frequency ν_E, which was characteristic for the solid. This rather simple model gave suprisingly good agreement with experiment, especially for those times, but at low temperatures the theoretical values fell below the observed ones. Subsequently, as an improvement, Nernst and Lindemann (1911) modified the Einstein assumption by introducing a new characteristic temperature $\nu_E / 2$ in addition to ν_E. This gave a better agreement between theory and experiment at low temperatures, but there was no fundamental justification for its introduction. So it became apparent that the introduction of some more frequencies could still be justified, as Einstein himself, realizing the limitations of his assumption, suggested (1911). If one considers the Fourier analysis of the motion of the atoms then one sees that the motion will be characterized by many frequencies. This was the starting point of Debye's

theory of specific heats, only he did not use Fourier analysis, the calculations being very laborious, but he used a method analogous to Jeans' proof for the Rayleigh radiation formula.

Debye (1912) assumed that a monoatomic lattice may be treated as an elastic isotropic continuum with no dispersion of wave propagation. For an actual solid such an assumption is justified only for low frequencies, long wavelengths, but for high frequencies, at which the wavelength is comparable to the distance between two atoms, it is only approximately correct. The atomic nature of the lattice was taken into account only by the fact that the total number of the allowed modes of vibration was equal to the total number of degrees of freedom available to the lattice of discreet atoms. So on this model is then imposed the condition that there is a unique maximum frequency ν_D for the modes of vibration. This then leads to a characteristic temperature Θ_D, where $\Theta_D = h \nu_D / k$.

Born (1915) proposed that instead of a single cut off frequency ν_D there should be a single cutoff wavelength, since such a condition would be imposed by the atomic distance. Such an assumption, Brillouin (1946) has shown, leads to equipartition in the modes, and to three characteristic temperatures. These are often close to Θ_D. However, this theory gives a worse agreement with experiment, than the Debye theory (Bijl 1957).

Subsequent developments in this field (Blackman 1955) have shown that the Debye model is a very simplified model and the resulting expressions for the specific heat, C_v, is inadequate for representing the specific heats of real substances over a wide temperature range. However, for very low frequencies the Debye spectrum is indeed correct (Blackman 1955) and the Debye temperature at $0^\circ K$ has a definite theoretical significance.

Debye's Model

Assuming an isotropic non-dispersive medium, a plane wave propagating in such a medium with velocity v must satisfy the wave equation

$$\nabla^2 u = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where ∇^2 is the Laplacian, and u is a small displacement of the volume element at the point (x, y, z). In order to find the solution we can assume that the solid is a cube of side L, and that the boundary condition is either the "Born cyclic condition", which has a propagating wave type of solution, or that at the faces of the cube the amplitude is zero, which has a standing wave type of solution.

Assuming the "Born cyclic condition" and the origin of the

coordinate axes to lie at the centre of the cube the solution for the displacement u is

$$u = Ae^{i\left(\frac{2\pi n_x}{L}x + \frac{2\pi n_y}{L}y + \frac{2\pi n_z}{L} - \omega t\right)}$$

or

$$u = Ae^{i(k_x x + k_y y + k_z z - \omega t)} \qquad \ldots\ldots\ldots \quad (2)$$

where n_x, n_y and $n_z = 0 \pm 1, \pm 2, \ldots\ldots,$

and

$$k_x = \frac{2\pi n_x}{L}, \qquad k_y = \frac{2\pi n_y}{L}, \qquad k_z = \frac{2\pi n_z}{L}$$

are the components of the wave vector k in the direction of propagation of the wave. Thus substituting Eq. (2) into Eq. (1) we get

$$k_x^2 + k_y^2 + k_z^2 = \frac{1}{v^2}\omega^2$$

or

$$n_x^2 + n_y^2 + n_z^2 = n^2 = \frac{L^2}{v^2}\nu^2 \qquad \ldots\ldots\ldots \quad (3)$$

or

$$n = \pm \frac{L}{v}\nu \qquad \ldots\ldots\ldots \quad (4)$$

For any set of integers n_x, n_y and n_z there is a wave number and hence a frequency specified by Eq. (3). In fact to each set there are three normal modes of vibration, one longitudinal, and two independent transverse modes. Thus the same frequency can be obtained for several

combinations of integers. The number of identical frequencies, (or modes) can be calculated by noting that Eq. (3) is the equation of a sphere in the "quantum number space", if n_x, n_y and n_z could assume continuous values, but this is not the case, since they specify only certain points on the surface of a sphere. However, for large quantum numbers they will appear as continuous, resulting in a continuously varying frequency. Therefore the number of modes $g(\nu)\ d\nu$ within a range ν and $\nu + d\nu$ is

$$g(\nu)\ d\nu = 4\pi n^2\ d\nu$$

which is the volume of a spherical shell of radius n in n-space. Thus using Eq. (4) we get

$$g(\nu)\ d\nu = \frac{4\pi V \nu^2}{v^3}\ d\nu \qquad \ldots\ldots\ (5)$$

where $V = L^3$ is the volume of the solid. Considering the three modes of vibration for each wave vector, and an isotropic medium Eq. (5) becomes

$$g(\nu)\ d\nu = 4\pi V\ (v_L^{-3} + 2v_T^{-3})\ \nu^2\ d\nu \qquad \ldots\ldots\ (6)$$

Since there are only $3N$ degrees of freedom available to the N discrete atoms, there must be a limit to the frequency range of the solid specified by a maximum cutoff frequency ν_D, such that

$$\int_0^{\nu_D} g(\nu)\ d\nu \equiv 3N \qquad \ldots\ldots\ (7)$$

and therefore we get for ν_D

$$\nu_D = \left(\frac{9N}{4\pi V}\right)^{1/3} \left(v_L^{-3} + 2v_T^{-3}\right)^{-1/3} \quad \ldots\ldots\ldots \quad (8)$$

In general, in a real solid the three modes of vibration have different velocities in different crystallographic directions, so that removing the assumption of isotropy, we must consider the velocity of each type of wave averaged over all directions. We can define a mean velocity v_m as follows

$$F = \frac{3}{v_m^3} = \int \sum_{i=1}^{3} v_i^{-3} \frac{d\Omega}{4\pi} \quad \ldots\ldots\ldots \quad (9)$$

where $d\Omega$ is the element of solid angle, v_1 is the velocity of the longitudinal mode, and v_2 and v_3 are the velocities of the two transverse modes. So the expression for ν_D becomes

$$\nu_D = \left(\frac{3N}{4\pi V}\right)^{1/3} \cdot v_m$$

$$= \left(\frac{3N}{4\pi V}\right)^{1/3} \left[1/3 \int \sum_{i=1}^{3} v_i^{-3} \frac{d\Omega}{4\pi} \right]^{-1/3} \ldots\ldots \quad (10)$$

In discussing specific heats and other physical properties, it is better to use a parameter related to the temperature rather than to the frequency. Thus the characteristic Debye temperature, called Θ_o at $0^\circ K$, is defined to be

$$\Theta_o = \frac{h}{k} \nu_D \qquad \ldots\ldots\ldots \quad (11)$$

or

$$\Theta_o = \frac{h}{k} \left(\frac{3N}{4\pi V} \right)^{1/3} v_m \qquad \ldots\ldots\ldots \quad (11a)$$

or

$$\Theta_o = \frac{h}{k} \left(\frac{1}{4\pi} \frac{n}{v_c} \right)^{1/3} v_m \qquad \ldots\ldots\ldots \quad (11b)$$

where h is the Planck constant, k the Boltzmann constant, n is the number of degrees of freedom per cell, and v_c is the volume per cell. For a gram-atom of a monoatomic solid Θ_o takes the form

$$\Theta_o = \frac{h}{k} \left(\frac{3N}{4\pi} \frac{\rho}{M} \right)^{1/3} v_m \qquad \ldots\ldots\ldots \quad (12)$$

where N is Avogadro's number, $\frac{M}{\rho} = V$, M being the atomic weight and ρ the density at $0^\circ K$.

In the above relations it is seen that Θ_o depends on the average velocity v_m, Eq. (9), which in turn depends on the elastic constants of the solid (see next chapter). Real solids show dispersion which is due to their lattice nature, in contrast to a continuum, which the Debye theory assumes. Born and von Karman (1912) considered the atomic nature of the solid and a generalized spring force model holding together the atoms. Such a model gives dispersion. Since in

the limit of low frequencies, long wavelengths, which correspond to temperatures of the solid tending to $0^{\circ}K$, the velocity becomes independent of frequency, the Θ_o determined from calorimetric measurements (Debye theory) is the same with that determined from sound velocities, called Θ_o^{el}. At other temperatures they are usually different, Alers (1965).

The distribution function for the frequencies may be found by combining Eq. (5), (7), (9) and (10)

$$\left.\begin{aligned} g(\nu) &= \frac{9N}{\nu_D^3}\,\nu^2 \qquad \text{for } \nu \le \nu_D \\ &= 0 \qquad\qquad\quad \text{for } \nu > \nu_D \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (13)$$

Debye Specific Heat

The average energy $\bar{u}$ of a harmonic oscillator of frequency ν in thermal equilibrium at temperature T, as derived by the use of quantum mechanics is given by

$$\bar{u} = \frac{1}{2}\,h\nu + \frac{h\nu}{e^{h\nu/kT} - 1} \qquad \ldots\ldots\ldots \quad (14)$$

Hence the molar internal energy of a solid will be

$$E = \int_0^{\nu\,max} \bar{u}\, g(\nu)\, d\nu \qquad \ldots\ldots\ldots \quad (15)$$

According to the Debye theory $\nu_{max} = \nu_D$ and by Eq. (14)

Eq. (15) becomes:

$$E = \frac{9Nk}{8}\,\Theta_D + 9NkT\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{t^3}{e^t-1}\,dt \quad \ldots\ldots (16)$$

where $t = \frac{h\nu}{kT}$. Thus the molar specific heat, if $x = \Theta_D/T$, is

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v$$

$$= 9R\left[4\,\frac{1}{x^3}\int_0^x \frac{t^3}{e^t-1}\,dt - \frac{x}{e^x-1}\right] \quad \ldots\ldots\ldots \quad (17)$$

Functions of the type $\frac{n}{x^n}\int_0^x \frac{t^n}{e^t-1}\,dt$ are called Debye functions, the integral part of which has a series expansion as follows, provided $x > 0$ and $n \geq 1$:

$$\int_0^x \frac{t^n}{e^t-1}\,dt = n!\,\zeta(n+1) - \sum_{k=1}^{\infty} e^{-kx}\left[\frac{x^n}{k} + \frac{nx^{n-1}}{k^2} + \frac{n(n-1)x^{n-2}}{k^3} \cdots \frac{n!}{k^{n+1}}\right]$$

where $\zeta(z)$ is the Riemann zeta function. Thus Eq. (17) becomes:

$$C_v = 3R\left[\frac{4\pi^4}{5}\cdot\frac{1}{x^3} - \frac{3x}{e^x-1} - 12x\sum_{k=1}^{\infty} e^{-kx}\left(\frac{1}{kx} + \frac{3}{k^2x^2} + \frac{6}{k^3x^3} + \frac{6}{k^4x^4}\right)\right] \ldots (18)$$

High Temperature Limit

At high temperatures $\Theta_D/T = x$ tends to zero and C_v as expressed by Eq. (17) tends to the classical limit of the Dulong-Petit law, ie.

$$C_{v\infty} = 3R \qquad \ldots\ldots\ldots \quad (19)$$

Low Temperature Limit

At low temperatures $x \rightarrow \infty$ so that

$$C_v = 9R\left[\frac{4}{x^3}\int_0^{\infty}\frac{t^3}{e^t-1}\,dt - \left(\frac{x}{e^x-1}\right)_{x=\infty}\right]$$

$$= 9R\,\frac{4}{x^3}\,3!\,\zeta(3+1)$$

or

$$C_v = 3R\,\frac{4}{5}\,\pi^4\left(\frac{T}{\Theta_D}\right)^3 \qquad \ldots\ldots\ldots \quad (20)$$

This is the celebrated T^3 law for specific heats at very low temperatures. This law holds for $T < \Theta_D/50$ (Blackman 1941). Thus experimentally Θ_D can be determined from calorimetric measurements using either Eq. (20) for very low temperatures, or Eq. (18) for higher temperatures.

CHAPTER III

VELOCITY OF SOUND AND THE DEBYE TEMPERATURE

The characteristic temperature Θ_o^{el} of a solid is related to the mean velocity of sound, Eq. (9). In this section we will see how the sound velocity is related to the elastic constants of the solid.

The basic assumption is that the solid is considered as an elastic continuum obeying Hooke's law. Therefore this theory is good only for low frequencies. Hooke's law provides a relation between the stress and strain tensors. The coefficients of the strain components are related to the elastic constants. From the dynamical equation of motion of a small displacement, (Musgrave 1954), a set of three simultaneous differential equations arise. To solve the equations the relations for a plane wave propagating in the direction defined by the direction cosines p, q, and r are substituted It then follows that the three sound velocities are the three real roots of the Christoffel secular equation:

$$\begin{vmatrix} A_{11} - \rho v^2 & A_{12} & A_{13} \\ A_{12} & A_{22} - \rho v^2 & A_{23} \\ A_{13} & A_{23} & A_{33} - \rho v^2 \end{vmatrix} = 0 \quad \ldots \quad (21)$$

where ρ is the average density of the solid, and the elements A_{ij} are related to the elastic stiffness constants c_{ij} and to the direction cosines p, q, r as follows:

$$A_{11} = p^2 c_{11} + q^2 c_{66} + r^2 c_{55} + 2qr\, c_{56} + 2rp\, c_{15} + 2pq\, c_{16} ,$$

$$A_{22} = p^2 c_{66} + q^2 c_{22} + r^2 c_{44} + 2qr c_{24} + 2rp c_{46} + 2pq c_{26} ,$$

$$A_{33} = p^2 c_{55} + q^2 c_{44} + r^2 c_{33} + 2qr c_{34} + 2rp c_{35} + 2pq c_{45} ,$$

$$A_{12} = p^2 c_{16} + q^2 c_{26} + r^2 c_{45} + qr(c_{46} + c_{25}) + rp(c_{14} + c_{56}) + pq(c_{12} + c_{66}) ,$$

$$A_{13} = p^2 c_{15} + q^2 c_{46} + r^2 c_{35} + qr(c_{45} + c_{36}) + rp(c_{13} + c_{55}) + pq(c_{14} + c_{56}) ,$$

$$A_{23} = p^2 c_{56} + q^2 c_{24} + r^2 c_{34} + qr(c_{44} + c_{23}) + rp(c_{36} + c_{45}) + pq(c_{25} + c_{46}) .$$

For various lattices with particular symmetries the above relations simplify considerably, because many of the elastic moduli are equal to zero. From the above secular equation the velocity of sound can now be found in any direction. Only in the case of the hexagonal lattice it is possible to factorize Eq.(21), but for others it is possible to do so,

only in some preferred directions. After this, the integral for the mean velocity, Eq. (9), has to be evaluated. This is not always possible analytically, so a number of approximate methods have been developed.

Methods of Calculating Θ_o^{el}

In this section we first summarize some of the general methods for obtaining the mean velocity v_m and then give a few explicit approximate expressions for crystals of cubic symmetry. Discussion of three of the important methods, viz. those due to Hopf-Lechner (1914), Houston (1948) - Bhatia-Tauber (1954), and Fedorov (1968) is deferred to the next chapter.

Direct Numerical Integration

The evaluation of the integral for the mean velocity v_m, Eq. (9), can be approximated by a direct numerical integration. In order to do this a minimum section of the unit sphere is considered. The size of this section, which must be large enough to represent the solid in all directions in the unit sphere, will depend on the symmetry of the particular lattice, for example, it is 1/48 of the unit sphere for cubic lattices, 1/16 for tetragonal lattices and larger for lattices of lower symmetry. Then the area A of the surface subtended by this section is further subdivided into $\tilde{N}$ smaller equal areas a_j, and the direction

cosines corresponding to the centre of each small geometrical area are determined. These are substituted into the secular equation, Eq. (21), and the corresponding three real roots are found. Then the integration sign of equation (9) is replaced by the summation one, and the sum of the reciprocal of the cube of the velocities multiplied by the associated small area a_j divided by the total area A is found.. This then is equal to $\frac{3}{v_m^3}$, and Θ_o^{el} becomes:

$$\Theta_o^{el} = \frac{h}{k}\left(\frac{3N}{4\pi V}\right)^{1/3}\left[1/3\sum_{j=1}^{\tilde{N}}\sum_{i=1}^{3} v_{ij}^{-3}\ \frac{a_j}{A}\right]^{-1/3} \quad \ldots\ldots\ (22)$$

The accuracy of this method will depend on the anisotropy of the solid, and on the number N of the directions considered, that is the larger the N the greater the accuracy. This method is capable of very high accuracy.

Harmonic Series Expansion

Another method for cubic, and non cubic lattices with a principal axis of symmetry, is the expansion of the integrand of equation (9) in terms of harmonic polynomials having the same symmetry as that of the corresponding Christoffel equations of elasticity. This is an extension of Houston's method for integrating approximately functions of complete cubic symmetry. Betts el al. (1956) have worked out the formulae for hexagonal, tetragonal and trigonal crystals, and Joshi (1961)

for orthorhombic crystals. For the cubic case this method will be considered in detail in a subsequent chapter.

From Young's and Shear Moduli

For an isotropic medium the integration called for by equation (9) for the mean velocity v_m reduces to

$$\frac{3}{v_m^3} = \frac{1}{v_L^3} + \frac{2}{v_T^3}$$

where v_L and v_T are the longitudinal and transverse velocities respectively. The condition for isotropy, for any material of any lattice symmetry, is realized, to a certain extent, by the randomness of the grains for the polycrystalline state of the material. Thus the Young's modulus E and the shear modulus G, which describe the polycrystalline solid and are related to the single crystal moduli (for cubic solids see Voigt 1910, and Reuss 1929) are related also to v_L and v_T by the following equations

$$v_L = \left[\frac{G}{\rho}\left(\frac{4G - E}{3G - E}\right)\right]^{1/2}$$

and

$$v_T = \left(\frac{G}{\rho}\right)^{1/2}$$

For polycrystalline solids this method gives quite reasonable values.

Cubic Symmetry

In the case of cubic crystals the secular equation (14) reduces to

$$\begin{vmatrix} -\rho v^2+c_{11}p^2+c_{44}(q^2+r^2) & (c_{12}+c_{44})pq & (c_{12}+c_{44})pr \\ (c_{12}+c_{44})qp & -\rho v^2+c_{11}q^2+c_{44}(r^2+p^2) & (c_{12}+c_{44})qr \\ (c_{12}+c_{44})rp & (c_{12}+c_{44})rq & -\rho v^2+c_{11}r^2+c_{44}(p^2+q^2) \end{vmatrix} = 0 \quad .. \quad (23)$$

For a nearly isotropic medium Born and von Karman (1913) have given the following equation for v_m

$$\frac{3}{v_m^3} = \rho^{3/2}\left[\frac{2}{c_{44}^{3/2}} + \frac{1}{c_{11}^{3/2}} + \frac{3}{5}(c_{12}-c_{11}+2c_{44})\left(\frac{1}{c_{44}^{5/2}} - \frac{1}{c_{11}^{5/2}}\right)\right] \quad .. \quad (24)$$

provided

$$\delta = (c_{12}-c_{11}+2c_{44}) / (c_{11}-c_{44})$$

is small compared to unity.

When the ratios c_{12}/c_{11}, c_{44}/c_{11} are small, an approximate expression was given by Blackman (1935a, 1935b):

$$v_m = \left(\frac{c_{11}\, c_{44}^2}{\rho^3} \right)^{1/6} \qquad \ldots\ldots\ldots \qquad (25)$$

It was found, (Varshni 1964), that this equation gives systematically high values for Θ_o^{el} of IV and III-V semiconductors and it was modified to

$$v_m = .89 \left(\frac{c_{11}\, c_{44}^2}{\rho^3} \right)^{1/6} \qquad \ldots\ldots\ldots \qquad (26)$$

Anisotropic solids present a particular difficulty as the spread of the velocities is high. Blackman (1951) obtained the following semitheoretical formulae for Θ_o^{el}, designed to cover the cases where $(c_{11} - c_{12})/ c_{11}$ is very small

$$\Theta_o^{el} = \left(\frac{h}{k} \right)^3 \frac{.525}{\rho^{3/2}} \quad \frac{3N}{4\pi V} \left((c_{11} - c_{12})(c_{11} + c_{12} + 2\, c_{44})\, c_{44} \right)^{1/2}$$

This formula also was found (Varshni 1964) to give too high values for Θ_o^{el} of Groups IV and III-V solids, and the constant .525 was changed to .4174. By this method calculations can be quickly made, and can provide an accuracy of 5 to 10%.

de Launay's Tables

A convenient method for calculating Θ_o^{el}, which does not require the use of computer, makes use of tables prepared by de Launay (1954). In this method the effect of the electron gas was taken into account.

The expression is

$$\Theta_o^{el} = \frac{9N}{4\pi V}\left(\frac{h}{k}\right)^3\left(\frac{c_{44}}{\rho}\right)^{3/2}\cdot\frac{9}{18+\sqrt{3}}\,f(s,t).$$

The factor $f(s,t)$ has been calculated numerically and tabulated. It is a function of the anisotropy of the crystal and has the value of unity when the elastic constants satisfy the condition for isotropy

$$c_{11} - c_{12} = 2c_{44},$$

and

$$c_{12} = c_{44}.$$

The variables s and t are defined as follows

$$s = \frac{c_{11} - c_{44}}{c_{12} + c_{44}}$$

and

$$t = \frac{c_{12} - c_{44}}{c_{44}}.$$

Thus for any value of s and t one can look up in the tables the corresponding value for $f(s,t)$ and therefore calculate Θ_o^{el}. Sometimes interpolation is necessary.

CHAPTER IV

THREE METHODS FOR CALCULATING THE DEBYE TEMPERATURE

Hopf-Lechner Method

The oldest and best known of the general methods is due to Hopf and Lechner (1914), which is based on replacing v_i^{-3} of the integrand of equation (9) by a function more suited to calculation. To explain the method it is best to refer to Eq. (23) again, written in a more convenient form.

If

$$z = \frac{\rho v^2 - c_{44}}{c_{11} - c_{44}}$$

and

$$K = \frac{c_{12} + c_{44}}{c_{11} - c_{44}} \qquad \ldots\ldots\ldots \qquad (27)$$

then equation (23) becomes

$$\begin{vmatrix} z - p^2 & Kpq & Kpr \\ Kqp & z - q^2 & Kqr \\ Krp & Krq & z - r^2 \end{vmatrix} = 0 \qquad \ldots\ldots\ldots \qquad (28)$$

or

$$z^3 - z^2 + b_1 z - b_2 = 0 \qquad \ldots\ldots\ldots \qquad (29)$$

in which

$$b_1 = (1 - K^2)(p^2 q^2 + q^2 r^2 + r^2 p^2) \qquad \ldots\ldots\ldots \qquad (30)$$

and

$$b_2 = (1 - 3K^2 + 2K^3) p^2 q^2 r^2 \qquad \ldots\ldots\ldots \qquad (31)$$

In this notation, Eq. (9) becomes

$$\frac{3}{v_m^3} = \left(\frac{\rho}{c_{11} - c_{44}}\right)^{3/2} \int \sum_{i=1}^{3} \frac{1}{(z_i + \zeta)^{3/2}} \frac{d\Omega}{4\pi} \qquad \ldots\ldots \qquad (32)$$

where $\zeta = c_{44}/(c_{11} - c_{44})$

As it stands, Eq. (32) is not integrable analytically. Hopf and Lechner (1914) devised an approximate method to evaluate the integral.

Since the values of velocity will vary over a definite range, the function $(z + \zeta)^{-3/2}$ was approximated over this range by a power series, i.e.

$$(z + \zeta)^{-3/2} = \sum_{n=0}^{5} a_n z^n \qquad \ldots\ldots\ldots \qquad (33)$$

The range of z chosen by Hopf and Lechner was from $z = 0$ to $z = 1$,

which means that ρv^2 varies from c_{44} to c_{11}. The coefficients a_n were chosen such that the two functions, Eq. (33), are equal at

$$z_m = 0.2\,m$$

where

$$m = 0, 1, \ldots 5$$

For a more accurate evaluation, the polynomial should be fitted over the extreme values of z that actually occur in a particular crystal (Durant 1936; Blackman 1955). It was pointed out by Blackman (1955) that the extreme values of the velocity will be found for cubic crystals to be associated with a few special directions in the crystal, and they will be contained in the set of the six different velocities along the [100], [110], and [111] directions as shown below.

[100] direction

$$\rho v_1^2 = c_{11} \quad \ldots\ldots\ldots \quad (34)$$

$$\rho v_2^2 = c_{44} \quad \ldots\ldots\ldots \quad (35)$$

$$\rho v_3^2 = c_{44} \quad \ldots\ldots\ldots \quad (36)$$

[110] direction

$$\rho v_1^2 = \frac{1}{2}(c_{11} + c_{12} + 2c_{44}) \quad \ldots\ldots\ldots \quad (37)$$

$$\rho v_2^2 = c_{44} \quad \ldots\ldots\ldots \quad (38)$$

$$\rho v_3^2 = \frac{1}{2}(c_{11} - c_{12}) \quad \ldots\ldots\ldots \quad (39)$$

[111] direction

$$\rho v_1^2 = \frac{1}{3}(c_{11} + 2c_{12} + 4c_{44}) \quad \ldots\ldots\ldots \quad (40)$$

$$\rho v_2^2 = \frac{1}{3}(c_{11} - c_{12} + c_{44}) \quad \ldots\ldots\ldots \quad (41)$$

$$\rho v_3^2 = \frac{1}{3}(c_{11} - c_{12} + c_{44}) \quad \ldots\ldots\ldots \quad (42)$$

The maximum and minimum values of z thus obtained for the various elements are shown in Table II , and for alkali halides in table VIII . Hopf and Lechner (1914) used a fifth degree polynomial; Fuchs (1936a, b) found it necessary to employ an eigth degree polynomial for the case of alkalies. A ninth degree polynomial has been considered by Sutton (1955). Here we have carried out the evaluation for a tenth degree polynomial.

A Tenth Degree Polynomial Approximation

For a tenth degree polynomial approximation Eq. (33) becomes

$$(z + \zeta)^{-3/2} = \sum_{n=0}^{10} a_n z^n \quad \ldots\ldots\ldots \quad (43)$$

In order to find the coefficients a_n the range of z from z maximum (z_{max}) to z minimum (z_{min}) for each solid (see Tables II and VIII) was divided into ten equal parts. Then the two functions of Eq. (43) were calculated for each of the eleven values of z in this inverval. This resulted into 11 simultaneous linear equations in a_n. If

$$\Delta z = \frac{z_{max} - z_{min}}{10}$$

the equations are

$$\left(z_{min} + \zeta\right)^{-3/2} = \sum_{n=0}^{10} a_n z_{min}^n$$

$$\left((z_{min} + \Delta z) + \zeta\right)^{-3/2} = \sum_{n=0}^{10} a_n (z_{min} + \Delta z)^n$$

. .

. .

. .

$$\left(z_{max} + \zeta\right)^{-3/2} = \sum_{n=0}^{10} a_n z_{max}^n \qquad \ldots\ldots\ldots \quad (44)$$

By solving these simultaneous equations we obtain all the coefficients a_n. Let the integral of Eq. (31) be called F then we can write

$$\left(\frac{c_{11}-c_{44}}{\rho}\right)^{3/2} F = \int \sum_{i=1}^{3} \frac{1}{(z_i+\zeta)^{3/2}} \frac{d\Omega}{4\pi} = \int \sum_{n=0}^{10} a_n \sum_{i=1}^{3} z_i^n \frac{d\Omega}{4\pi} \ldots (45)$$

In order to evaluate the R. H. S. we must express it in terms of the direction cosines and the elastic constants. Now if z_1, z_2 and z_3 are the three real roots of the secular equation, Eq. (28), then

$$(z - z_1)(z - z_2)(z - z_3) = 0$$

$$z^3 - (z_1+z_2+z_3)z^2 + (z_1z_2+z_2z_3+z_1z_3)z - z_1z_2z_3 \equiv z^3 - z^2 + b_1z - b_2 = 0 \quad \ldots \quad (46)$$

Where b_1 and b_2 are defined by Eq. (30) and (31). From the above identity we have

$$z_1 + z_2 + z_3 = 1 \qquad \ldots\ldots\ldots \qquad (47)$$

$$z_1z_2 + z_2z_3 + z_1z_3 = b_1 \qquad \ldots\ldots\ldots \qquad (48)$$

$$z_1z_2z_3 = b_2 \qquad \ldots\ldots\ldots \qquad (49)$$

Using these equations we obtain for the sums of the type $(z_1^n + z_2^n + z_3^n)$ the following relations

$$\sum_{i=1}^{3} z_i^0 = 3$$

$$\sum_{i=1}^{3} z_i^1 = 1$$

$$\sum_{i=1}^{3} z_i^2 = 1 - 2b_1$$

$$\sum_{i=1}^{3} z_i^3 = 1 - 3b_1 + 3b_2$$

$$\sum_{i=1}^{3} z_i^4 = - 4b_1 + 4b_2 + 2b_1^2$$

$$\sum_{i=1}^{3} z_i^5 = 1 - 5b_1 + 5b_2 + 5b_1^2 - 5b_1b_2$$

$$\sum_{i=1}^{3} z_i^6 = 1 - 6b_1 + 6b_2 + 9b_1^2 - 12b_1b_2 - 2b_1^3 + 3b_2^2$$

$$\sum_{i=1}^{3} z_i^7 = 1 - 7b_1 + 7b_2 + 14b_1^2 - 21b_1b_2 - 7b_1^3 + 7b_2^2 + 7b_1^2b_2$$

$$\sum_{i=1}^{3} z_i^8 = 1 - 8b_1 + 8b_2 + 20b_1^2 - 32b_1b_2 - 16b_1^3 + 12b_2^2 + 24b_1^2b_2$$
$$- 8b_1b_2^2 + 2b_1^4$$

$$\sum_{i=1}^{3} z_i^9 = 1 - 9b_1 + 9b_2 + 27b_1^2 - 45b_1b_2 - 30b_1^3 + 18b_2^2 + 54b_1^2b_2$$
$$- 27b_1b_2^2 + 9b_1^4 - 9b_1^3b_2 + 3b_2^3$$

$$\sum_{i=1}^{3} z_i^{10} = 1 - 10b_1 + 10b_2 + 35b_1^2 - 60b_1b_2 - 50b_1^3 + 25b_2^2 + 100b_1^2b_2$$

$$- 60b_1b_2^2 + 25b_1^4 - 40b_1^3b_2 + 10b_2^3 + 15b_1^2b_2^2 - 2b_1^5 . \quad \ldots\ldots (50)$$

Let

$$\kappa_1 = (1 - K^2)$$

and

$$\kappa_2 = (1 - 3K^2 + 2K^3) \quad \ldots\ldots\ldots (51)$$

where K is defined by Eq. (27).

The powers and the combinations of b_1 and b_2 appearing in the preceeding set of equations, Eqs (50), are found in terms of κ_1, κ_2 and the direction cosines p, q, and r, and are presented in the following set of equations,

$$b_1 = \kappa_1(p^2q^2 + p^2r^2 + q^2r^2)$$

$$b_1^2 = \kappa_1^2(p^4q^4 + p^4r^4 + q^4r^4 + 2p^2q^2r^2)$$

$$b_1^3 = \kappa_1^3[p^6q^6 + p^6r^6 + q^6r^6 + 3(p^4q^4r^2 + p^4q^2r^4 + p^2q^4r^4) - 3p^4q^4r^4]$$

$$b_1^4 = \kappa_1^4[p^8q^8 + p^8r^8 + q^8r^8 + 4(p^6q^6r^2 + p^6q^2r^6 + p^2q^6r^6) - 4(p^6q^6r^4$$

$$+ p^6q^4r^6 + p^4q^6r^6) + 6p^4q^4r^4]$$

$$b_1^5 = \kappa_1^5[p^{10}q^{10} + p^{10}r^{10} + q^{10}r^{10} + 5(p^8q^8r^2 + p^8q^2r^8 + p^2q^8r^8)$$

$$- 5(p^8q^8r^4 + p^8q^4r^8 + p^4q^8r^8) - 20p^6q^6r^6 + 10(p^6q^6r^4 + p^6q^4r^6$$

$$+ p^4q^6r^6)\ ]$$

$$b_2 = \kappa_2 p^2 q^2 r^2$$

$$b_2^2 = \kappa_2^2 p^4 q^4 r^4$$

$$b_2^3 = \kappa_2^3 p^6 q^6 r^6$$

$$b_1 b_2 = \kappa_1 \kappa_2 (p^4q^4r^2 + p^4q^2r^4 + p^2q^4r^4)$$

$$b_1^2 b_2 = \kappa_1^2 \kappa_2 (p^6q^6r^2 + p^6q^2r^6 + p^2q^6r^6 + 2p^4q^4r^4)$$

$$b_1 b_2^2 = \kappa_1 \kappa_2^2 (p^6q^6r^4 + p^6q^4r^6 + p^4q^6r^6)$$

$$b_1^3 b_2 = \kappa_1^3 \kappa_2 [p^8q^8r^2 + p^8q^2r^8 + p^2q^8r^8 + 3(p^6q^6r^4 + p^6q^4r^6 + p^4q^6r^6)$$

$$- 3p^6q^6r^6]$$

$$b_1^2 b_2^2 = \kappa_1^2 \kappa_2^2 (p^8q^8r^4 + p^8q^4r^8 + p^4q^8r^8 + 2p^6q^6r^6) \qquad \ldots\ldots\ldots \quad (52)$$

The powers and the combinations of the coefficients κ_1 and κ_2 appearing above are expressed in terms of K by the following set of equations,

$$\kappa_1 = 1 - K^2$$

$$\kappa_1^2 = 1 - 2K^2 + K^4$$

$$\kappa_1^3 = 1 - 3K^2 + 3K^4 - K^6$$

$$\kappa_1^4 = 1 - 4K^2 + 6K^4 - 4K^6 + K^8$$

$$\kappa_1^5 = 1 - 5K^2 + 10K^4 - 10K^6 + 5K^8 - 10K^{10}$$

$$\kappa_2 = 1 - 3K^2 + 2K^3$$

$$\kappa_2^2 = 1 - 6K^2 + 4K^3 + 9K^4 - 12K^5 + 4K^6$$

$$\kappa_2^3 = 1 - 9K^2 + 6K^3 + 27K^4 - 36K^5 - 15K^6 + 54K^7 - 36K^8 + 8K^9$$

$$\kappa_1\kappa_2 = 1 - 4K^2 + 2K^3 + 3K^4 - 2K^5$$

$$\kappa_1^2\kappa_2 = 1 - 5K^2 + 2K^3 + 7K^4 - 4K^5 - 3K^6 + 2K^7$$

$$\kappa_1 \kappa_2^2 = 1 - 7K^2 + 4K^3 + 15K^4 - 16K^5 - 5K^6 + 12K^7 - 4K^8$$

$$\kappa_1^3 \kappa_2 = 1 - 6K^2 + 2K^3 + 12K^4 - 6K^5 - 10K^6 + 6K^7 + 3K^8 - 2K^9$$

$$\kappa_1^2 \kappa_2^2 = 1 - 8K^2 + 4K^3 + 22K^4 - 20K^5 - 20K^6 + 28K^7 + K^8 - 12K^9 + 4K^{10} \ldots \quad (53)$$

Now we can substitute the explicit expressions for b_1 and b_2, equations (52) and (53) into equations (50), and carry out the integration, which will involve about 60 terms, term by term. The evaluation of each integral was done by the use of gamma functions.

In spherical polar coordinates the direction cosines p, q and r are

$$p = \sin\theta \cos\varphi$$

$$q = \sin\theta \sin\varphi$$

$$r = \cos\theta$$

The integration is over the unit sphere and the element of solid angle $d\Omega$ is $(r^2 = 1)$

$$d\Omega = \sin\theta \, d\theta \, d\varphi$$

As an illustration we show the evaluation for one of the terms.

$$\int p^8 q^8 r^4 \frac{d\Omega}{4\pi} = \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} \sin^8\theta \cos^8\varphi \sin^8\theta \sin^8\varphi \cos^4\theta \sin\theta \, d\theta \, d\varphi$$

$$= \frac{1}{4\pi} \int_0^{\pi} \sin^{17}\theta \cos^4\theta \, d\theta \int_0^{2\pi} \sin^8\varphi \cos^8\varphi \, d\varphi = \frac{1}{415701}$$

All the different terms and their values after integration are listed below

$$\int p^2 q^2 \frac{d\Omega}{4\pi} = \frac{1}{15}$$

$$\int p^4 q^4 \frac{d\Omega}{4\pi} = \frac{1}{105}$$

$$\int p^6 q^6 \frac{d\Omega}{4\pi} = \frac{5}{2703}$$

$$\int p^8 q^8 \frac{d\Omega}{4\pi} = \frac{7}{21879}$$

$$\int p^{10} q^{10} \frac{d\Omega}{4\pi} = \frac{3}{46183}$$

$$\int p^2 r^2 \frac{d\Omega}{4\pi} = \frac{1}{15}$$

$$\int p^4 r^4 \frac{d\Omega}{4\pi} = \frac{1}{105}$$

$$\int p^6 r^6 \frac{d\Omega}{4\pi} = \frac{5}{2703}$$

$$\int p^8 r^8 \frac{d\Omega}{4\pi} = \frac{7}{21879}$$

$$\int p^{10} r^{10} \frac{d\Omega}{4\pi} = \frac{3}{46183}$$

$$\int q^2 r^2 \frac{d\Omega}{4\pi} = \frac{1}{15}$$

$$\int q^4 r^4 \frac{d\Omega}{4\pi} = \frac{1}{105}$$

$$\int q^6 r^6 \frac{d\Omega}{4\pi} = \frac{5}{2703}$$

$$\int q^8 r^8 \frac{d\Omega}{4\pi} = \frac{7}{21879}$$

$$\int q^{10} r^{10} \frac{d\Omega}{4\pi} = \frac{3}{46183}$$

$$\int p^2 q^2 r^2 \frac{d\Omega}{4\pi} = \frac{1}{105}$$

$$\int p^4 q^4 r^4 \frac{d\Omega}{4\pi} = \frac{1}{5005}$$

$$\int p^6 q^6 r^6 \frac{d\Omega}{4\pi} = \frac{5}{969,969}$$

$$\int p^4 q^4 r^2 \frac{d\Omega}{4\pi} = \frac{1}{1155}$$

$$\int p^6 q^6 r^2 \frac{d\Omega}{4\pi} = \frac{1}{9009}$$

$$\int p^8 q^8 r^2 \frac{d\Omega}{4\pi} = \frac{7}{415701}$$

$$\int p^6 q^6 r^4 \frac{d\Omega}{4\pi} = \frac{1}{51051}$$

$$\int p^8 q^8 r^4 \frac{d\Omega}{4\pi} = \frac{1}{415701}$$

$$\int p^4 q^2 r^4 \frac{d\Omega}{4\pi} = \frac{1}{1155}$$

$$\int p^6 q^2 r^6 \frac{d\Omega}{4\pi} = \frac{1}{9009}$$

$$\int p^8 q^2 r^8 \frac{d\Omega}{4\pi} = \frac{7}{415701}$$

$$\int p^6 q^4 r^6 \frac{d\Omega}{4\pi} = \frac{1}{51051}$$

$$\int p^8 q^4 r^8 \frac{d\Omega}{4\pi} = \frac{1}{415701}$$

$$\int p^2 q^4 r^4 \frac{d\Omega}{4\pi} = \frac{1}{1155}$$

$$\int p^2 q^6 r^6 \frac{d\Omega}{4\pi} = \frac{1}{9009}$$

$$\int p^2 q^8 r^8 \frac{d\Omega}{4\pi} = \frac{7}{415701}$$

$$\int p^4 q^6 r^6 \frac{d\Omega}{4\pi} = \frac{1}{51051}$$

$$\int p^4 q^8 r^8 \frac{d\Omega}{4\pi} = \frac{1}{415701}$$

With the above values for the integrals the set of equations (52) after being integrated becomes

$$\int b_1 \frac{d\Omega}{4\pi} = \frac{1}{5} \kappa_1$$

$$\int b_1^2 \frac{d\Omega}{4\pi} = \frac{1}{21} \kappa_1^2$$

$$\int b_1^3 \frac{d\Omega}{4\pi} = \frac{61}{5005} \kappa_1^3$$

$$\int b_1^4 \frac{d\Omega}{4\pi} = \frac{831}{255,255} \kappa_1^4$$

$$\int b_1^5 \frac{d\Omega}{4\pi} = \frac{4345}{4,849,845} \kappa_1^5$$

$$\int b_2 \frac{d\Omega}{4\pi} = \frac{1}{105} \kappa_2$$

$$\int b_2^2 \frac{d\Omega}{4\pi} = \frac{1}{5005} \kappa_2^2 \qquad \int b_1^2 b_2 \frac{d\Omega}{4\pi} = \frac{11}{15015} \kappa_1^2 \kappa_2$$

$$\int b_2^3 \frac{d\Omega}{4\pi} = \frac{5}{969,969} \kappa_2^3 \qquad \int b_1 b_2^2 \frac{d\Omega}{4\pi} = \frac{1}{17017} \kappa_1 \kappa_2^2$$

$$\int b_1 b_2 \frac{d\Omega}{4\pi} = \frac{1}{385} \kappa_1 \kappa_2 \qquad \int b_1^2 b_2^2 \frac{d\Omega}{4\pi} = \frac{85}{4,849,845} \kappa_1^2 \kappa_2^2$$

$$\int b_1^3 b_2 \frac{d\Omega}{4\pi} = \frac{205}{969,969} \kappa_1^3 \kappa_2 \quad \cdots (54)$$

Thus the final result for the tenth degree polynomial, after combining Eqs (45), (53) and (54) is given below

$$F = \left(\frac{\rho}{c_{11} - c_{44}}\right)^{3/2} \left\{ \int \left[3a_0 + \sum_{n=1}^{10} a_n (z_1^n + z_2^n + z_3^n)\right] \frac{d\Omega}{4\pi} \right\}$$

$$= \left(\frac{\rho}{c_{11} - c_{44}}\right)^{3/2} \left\{ 3a_0 + a_1 + \frac{1}{4,849,845} \times \right.$$

$$\left[a_2 (2,909,907 + 1,939,938\, K^2) \right.$$

$$+ a_3 (2,078,505 + 2,494,206\, K^2 + 277,134\, K^3$$

$$\left. + a_4 (1,616,615 + 2,401,828\, K^2 + 369,512\, K^3 + 461,890\, K^4) \right.$$

$$+ a_5(1,322,685 + 2,099,500\,K^2 + 335,920\,K^3 + 965,770\,K^4 + 125,970\,K^5)$$

$$+ a_6(1,119,195 + 1,773,270\,K^2 + 263,568\,K^3 + 1,296,522\,K^4 + 267,444\,K^5 + 129,846\,K^6)$$

$$+ a_7(969,969 + 1,487,738\,K^2 + 194,446\,K^3 + 1,433,474\,K^4 + 348,194\,K^5 + 366,282\,K^6 + 49,742\,K^7)$$

$$+ a_8(855,855 + 1,256,584\,K^2 + 140,752\,K^3 + 1,429,180\,K^4 + 362,064\,K^5 + 621,528\,K^6 + 143,184\,K^7 + 40,698\,K^8)$$

$$+ a_9(765,765 + 1,075,032\,K^2 + 102,384\,K^3 + 1,343,628\,K^4 + 332,748\,K^5 + 828,648\,K^6 + 240,084\,K^7 + 142,506\,K^8 + 19,050\,K^9)$$

$$+ a_{10}(692,875 + 933,210\,K^2 + 75,920\,K^3 + 1,222,620\,K^4 + 284,600\,K^5 + 960,300\,K^6 + 308,840\,K^7 + 289,070\,K^8 + 68,620\,K^9 + 13,790\,K^{10})\Big]\Big\} \quad \ldots\ldots\ldots \quad (55)$$

Up to the a_8 term the above expression agrees with the corrected expression due to Fuchs (1936a,b). An error in one of the coefficients in Fuchs (1936a) has been corrected (Fuchs 1936b).

Debye temperatures were calculated for eighth, ninth, and tenth degree polynomials. The results are shown in Tables III and VI and are referred to as 8HL, 9HL, and 10HL respectively. All calculations were carried out in a 'double precision' on an IBM 360.

Houston-Bhatia-Tauber Method

Houston (1948) proposed a method for integrating functions of complete cubic symmetry over the unit sphere on the basis of an expansion in Kubic Harmonics K_m, which have the same symmetry properties. They were first introduced by von der Lage and Bethe (1947). Houston used Kubic Harmonics for an approximate determination of the frequency spectrum of cubic crystals. Subsequently Bhatia and Tauber (1954) used the same method in order to determine the Debye characteristic temperature at 0°K. They used a 3-term approximation. Betts, Bhatia and Wyman (1956) presented formulae using 6-term approximation, while Tenerz (1956) used a 5-term one. Later Betts (1961) derived a 9- and 15-term approximation. Formulae for hexagonal, trigonal and tetragonal symmetries have also been worked out by Betts, Bhatia and Horton (1956) and for orthorhombic by Joshi (1961).

Kubic Harmonics of Cubic Symmetry

A Kubic harmonic is defined as a homogeneous polynomial solution of Laplace's equation which obeys certain symmetry properties with respect to the operations of the cubic symmetry group. Following von der Lage and Bethe (1947) we say that a Kubic Harmonic is of type α if it is

invariant under all the operations of the cubic symmetry group. Betts, Bhatia and Wyman (1956) have presented a method for generating the Kubic Harmonics of α type. We summarize here their results.

Suppose $n = r+s$ (r and s being positive integers) and the function A_{rs} being defined as

$$A_{rs} = \frac{(2r+2s)!\,r!\,s!}{(r+s)!} \sum_{a=0}^{r} \sum_{b=0}^{s} \frac{(-1)^{r+s-a-b}(a+b)!\,x^{2r-2a}\,y^{2s-2b}\,z^{2a+2b}}{a!\,b!\,(2a+2b)!\,(2r-2a)!\,(2s-2b)!} \quad \ldots (56)$$

then the Kubic Harmonics of degree 2n are

$$K_{rs} = S A_{rs}(x^2, y^2, z^2) \quad \ldots\ldots (57)$$

where S means symmetrization operation.

Thus the lowest Kubic Harmonics up to degree 8, can be written as

$$\begin{aligned} K_0 &= 1, \\ K_1 &= 0, \\ K_2 &= S(2x^4 - 6x^2y^2), \\ K_3 &= S(x^6 - 15x^4y^2 + 180x^2y^2z^2), \\ K_4 &= S(2x^8 - 56x^6y^2 + 70x^4y^4) \end{aligned} \quad \ldots\ldots (58)$$

The Kubic Harmonics K_m satisfy the orthogonality conditions

$$\int_0^{\pi} \int_0^{2\pi} K_m K_n \sin\theta d\theta d\varphi = 4\pi \gamma_m \delta_{m,n} \quad \ldots\ldots\ldots (59)$$

where γ_m is a normalization constant and $\delta_{m,n}$ is the usual Kronecker delta function, equal to unity when $m = n$ and zero otherwise.

Calculation of Θ_o^{el} by Kubic Harmonics

For the calculation of the Debye temperature we must evaluate the integral for the mean velocity v_m, Eq.(9). Suppose $I(\theta, \varphi)$ has complete cubic symmetry, then for calculating v_m^{-3}

$$I(\theta, \varphi) = \sum_{i=1}^{3} v_i (\theta, \varphi)^{-3} \quad \ldots\ldots\ldots (60)$$

and by Eq. (9) we need evaluate

$$\frac{3}{v_m^3} 4\pi = J = \int_0^{\pi} \int_0^{2\pi} I(\theta, \varphi) \sin\theta d\theta d\varphi \quad \ldots\ldots\ldots (61)$$

Houston's method consists in expanding $I(\theta, \varphi)$ in the Kubic Harmonics having the same symmetry, which we denote by $K_m(\theta, \varphi)$

$$I(\theta, \varphi) = \sum_{m=0} A_m K_m(\theta, \varphi)$$

$$= A_0 K_0 + A_1 K_1 + A_2 K_2 + \ldots \qquad \ldots\ldots\ldots (62)$$

The degree of the polynomial is $2m$ when expressed in terms of x, y, z, except for the case of K_1 ($K_1 = 0$). Clearly the number of terms retained in the expansion (62) defines the degree of approximation.

By integrating Eq. (62) over the unit sphere we get

$$J = \int_0^{\pi} \int_0^{2\pi} I(\theta, \varphi) \sin\theta \, d\theta \, d\varphi = \int_0^{\pi} \int_0^{2\pi} (A_0 K_0 + A_1 K_1 + A_2 K_2 + \ldots) \sin\theta \, d\theta \, d\varphi$$

and since $K_0 = 1$

$$J = \int_0^{\pi} \int_0^{2\pi} (A_0 K_0 + A_1 K_0 K_1 + A_2 K_0 K_2 + \ldots) \sin\theta \, d\theta \, d\varphi .$$

Now using the property of orthogonality over the unit sphere, Eq. (59), we get

$$J = \int_0^{\pi} \int_0^{2\pi} I(\theta, \varphi) \sin\theta \, d\theta \, d\varphi = 4\pi A_0 \qquad \ldots\ldots\ldots (63)$$

Thus the problem of finding v_m^{-3} reduces to obtaining the value for A_0.

Consider again the equations (60) and (62). From Eq. (60) we can always find $I(\theta, \varphi)$ for any direction by finding the three roots of Christoffel's equation of elasticity, Eq. (23). If we know $I_i(\theta, \varphi)$, $(i = 1, n)$ for a number of directions n then we can have the following n simultaneous linear equations in $A_0, A_1, \ldots A_n$,

$$I_1(\theta, \varphi) = A_0K_0 + A_1K_1 + A_2K_2 + \ldots A_nK_n$$

$$I_2(\theta, \varphi) = A_0K_0 + A_1K_1 + A_2K_2 + \ldots A_nK_n$$

$$\vdots \qquad \vdots$$

$$I_n(\theta, \varphi) = A_0K_0 + A_1K_1 + A_2K_2 + \ldots A_nK_n \qquad \ldots\ldots\ldots (64)$$

We must keep in mind that the K_m's are functions of direction and have different values in different equations. They must be computed each time separately. The above system of Eq. (64) can now be solved for A_0 exactly by eliminating $A_1, A_2, \ldots A_n$ successively.

Knowing A_0, Θ_o^{el} can be calculated from

$$\Theta_o^{el} = \frac{h}{k}\left(\frac{9N\rho}{4\pi M A_0}\right)^{1/3} \qquad \ldots\ldots\ldots (65)$$

3-, 6-, 9- and 15-term approximations

On solving the equation of elasticity theory for the velocities $v_i(\theta,\varphi)$ along the directions [100], [110], [111], [210], [211], and [221] one finds the following expressions for $I(\theta,\varphi)$ in terms of the elastic constants

$$I(100) = \rho^{3/2}\{2c_{44}^{-3/2} + (c_{44}+a)^{-3/2}\},$$

$$I(110) = \rho^{3/2}\{c_{44}^{-3/2} + [c_{44}+\tfrac{1}{2}(a-\beta)]^{-3/2} + [c_{44}+\tfrac{1}{2}(a+\beta)]^{-3/2}\},$$

$$I(111) = \rho^{3/2}\{2[c_{44}+\tfrac{1}{3}(a-\beta)]^{-3/2} + [c_{44}+\tfrac{1}{3}(a+2\beta)]^{-3/2}\},$$

$$I(210) = \rho^{3/2}\{c_{44}^{-3/2} + [c_{44}+\tfrac{1}{2}a+\tfrac{1}{10}(9a^2+16\beta^2)^{1/2}]^{-3/2}$$

$$+ [c_{44}+\tfrac{1}{2}a-\tfrac{1}{10}(9a^2+16\beta^2)^{1/2}]^{-3/2}\},$$

$$I(211) = \rho^{3/2}\{[c_{44} + \frac{1}{6}(a-\beta)]^{-3/2} + [c_{44} + \frac{1}{12}(5a+\beta)$$

$$+ \frac{1}{12}(9a^2 + 33\beta^2 - 6a\beta)^{1/2}]^{-3/2} + [c_{44} + \frac{1}{12}(5a+\beta)$$

$$- \frac{1}{12}(9a^2 + 33\beta^2 - 6a\beta)^{1/2}]^{-3/2}\},$$

$$I(221) = \rho^{3/2}\{[c_{44} + \frac{4}{9}(a-\beta)]^{-3/2} + [c_{44} + \frac{1}{18}(5a+4\beta)$$

$$+ \frac{1}{18}(9a^2 + 48\beta^2 + 24a\beta)^{1/2}]^{-3/2} + [c_{44} + \frac{1}{18}(5a+4\beta)$$

$$- \frac{1}{18}(9a^2 + 48\beta^2 + 24a\beta)^{1/2}]^{-3/2}\}, \quad \ldots\ldots\ldots (60)$$

where ρ is the average density of the solid and

$$a = c_{11} - c_{44}$$

$$\beta = c_{12} + c_{44}$$

The six lowest Kubic Harmonics of type a written explicitely ($x^2 + y^2 + z^2 = 1$) are

$$K_0 = 1,$$

$$K_1 = 0,$$

$$K_2 = x^4 + y^4 + z^4 - \frac{3}{5} K_0,$$

$$K_3 = x^2 y^2 z^2 + \frac{1}{22} K_2 - \frac{1}{105} K_0,$$

$$K_4 = x^8 + y^8 + z^8 - \frac{28}{5} K_3 - \frac{210}{143} K_2 - \frac{1}{3} K_0,$$

$$K_5 = x^{10} + y^{10} + z^{10} - \frac{45}{19} K_4 - \frac{126}{17} K_3 - \frac{210}{143} K_2 - \frac{3}{11} K_0$$

$$K_6 = x^4 y^4 z^4 + \frac{6}{115} K_5 - \frac{1}{2 \cdot 7 \cdot 19} K_4 - \frac{54}{5 \cdot 17 \cdot 19} K_3$$

$$+ \frac{3}{11 \cdot 13 \cdot 17} K_2 - \frac{1}{5 \cdot 7 \cdot 11 \cdot 13} K_0 \qquad \ldots\ldots\ldots \quad (67)$$

Knowing the $K_m'^{s}$ and the $I(\theta, \varphi)$ for each direction we can find A_0^n, where n means the number of terms retained in the expansion.

It must be noted that from a set of six directions we can have more than one combination of them for determining A_0^n, $n < 6$, each combination giving different values A_0^n (Betts, Bhatia and Wyman 1956). The expressions for A_0 from a 3- and 6-term approximation are

$$A_0^3 = \frac{1}{35} [10\, I(100) + 16\, I(110) + 9\, I(111)] \qquad \ldots\ldots\ldots \quad (68)$$

$$A_0^6 = \frac{1}{1,081,080}\left[117,603\, I(100) + 76,544\, I(110) + 17,496\, I(111)\right.$$

$$\left. + 381,250\, I(210) + 311,040\, I(211) + 177,147\, I(221)\right] \quad \ldots\ldots\ldots (69)$$

To further extend the method a way of choosing more directions is to project the 1/48th of the unit sphere on a plane (Betts 1961), as shown below.

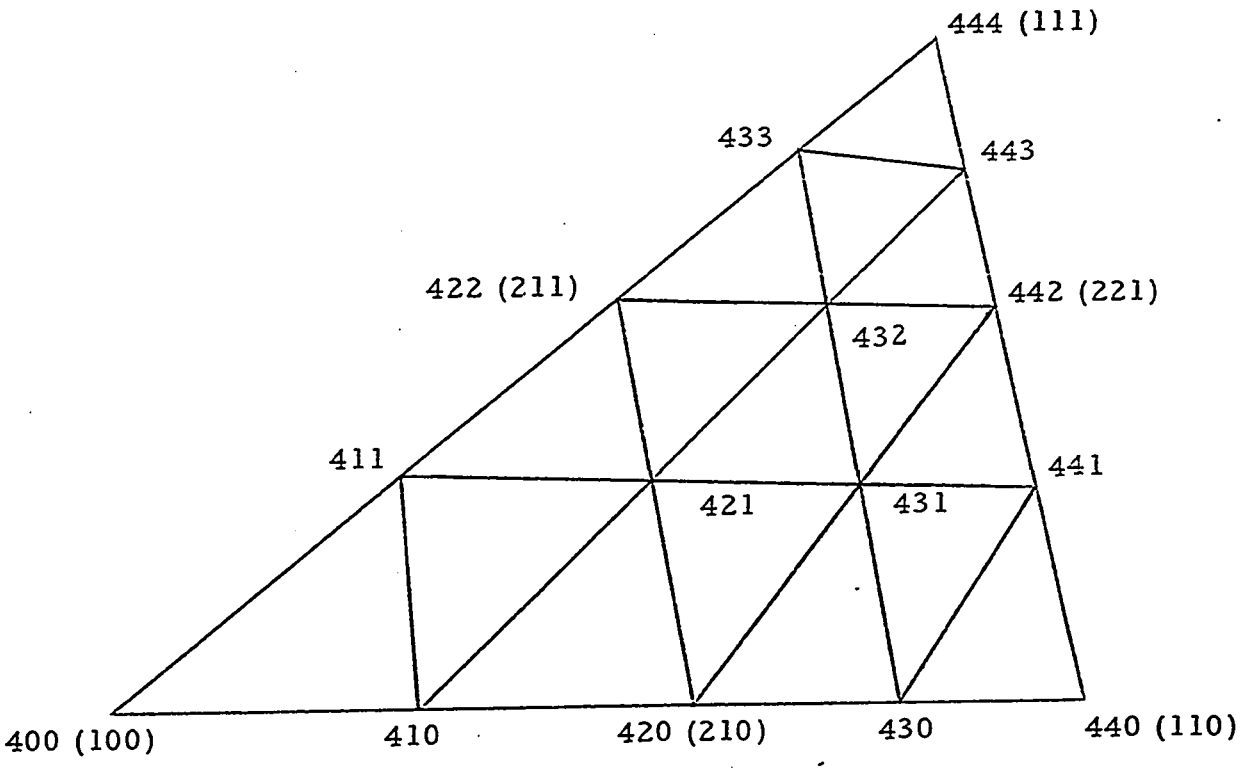

Fig. 1. The distribution of directions over the 1/48th of the unit sphere as it appears in its plane projection.

The procedure is to divide the large triangle into smaller and smaller triangles each time using all the corner points. From figure (1) we can see, for example, that for Houston's formula, Eq. (68), the three directions lie at the corners of the largest triangle.

Having so located the various directions we can choose any set of them spread over the triangle so as to have a good sample of the velocities in the solid angle. By taking in addition to the directions appearing in the 6-term approximation the directions [411], [431] and [433] one gets a 9-term approximation, and further with the additional directions [410], [411], [430], [421], [432], and [443] a 15-term approximation.

The resulting formulae are (Betts 1961)

$$A_0^9 = 0.05637817\, I(100) + 0.04952710\, I(110) - 0.05588614\, I(111)$$

$$+ 0.17827058\, I(210) + 0.10294771\, I(211) + 0.20711638\, I(411)$$

$$+ 0.21376348\, I(431) + 0.17478397\, I(433) + 0.07309875\, I(221) \quad \ldots\ldots (70)$$

and

$$A_0^{15} = 0.0436705\ I(100) + 0.0229221\ I(410) + 0.3400264\ I(210)$$

$$- 0.8133145\ I(430) + 0.9623617\ I(110) + 0.2285255\ I(411)$$

$$- 0.5323867\ I(421) + 2.2314783\ I(431) - 1.9823060\ I(441)$$

$$+ 0.8005275\ I(211) - 3.2370533\ I(432) + 2.3075765\ I(221)$$

$$+ 2.5033260\ I(433) - 1.7484174\ I(443) - 0.1269366\ I(111) \quad \ldots\ldots \quad (71)$$

We may mention here a misprint in Betts' (1961) paper; the tenth term in Eq. (7) of Betts should have I(211), as in the above Eq. (71), rather than I(411). The coefficients of the I's can be regarded as correct to seven significant figures (Betts 1961).

In this work calculations were carried out for 3-, 6-, 9- and 15-term approximations, which are referred to as 3HBT, 6HBT, 9HBT and 15HBT respectively.

For 3 and 6 direction approximations it is possible to obtain A_0 in an analytical form in terms of the elastic constants, Eqs.(68) and (69). However, for 9 and 15 direction approximations it becomes necessary to solve the cubic equation numerically. As a test for the 9- and 15-term approximation we found A_0^3 and A_0^6 by both ways, that is, using

the analytical expressions, Eqs (68) and (69) and by solving the secular equation numerically. Both results agreed to five significant figures.

The calculated values of Debye temperatures by the four HBT methods are recorded in Tables III and VII .

Fedorov Method

Fedorov recently (1963, 1965a,b, 1968) has presented a general theory for the propagation of plane elastic waves in homogeneous crystalline solids.

Using this theory Fedorov and Bystrova (1966) have developed two approximations, I_1 and I_2, for the integral F, Eq. (9). These are as follows.

First approximation:

$$I_1 = a^{-3/2}\left\{ 2 + r_a r_b \left[0.1 r_1 (1 - 0.06 r_a) + \frac{57.2 - 8.4 r_a + 0.48 r_b}{1001} \right] \right\}$$

$$+ c^{-3/2}\left\{ 1 - \frac{r_b r_c}{1001} \left[57.2 (1 - r_2) + 0.5 r_b - r_c (7.2 - 6.7 r_2) \right] \right\} \quad \cdots\cdots\cdots \quad (72)$$

Second approximation:

$$I_2 = I_1 + \frac{r_b^4}{1001} \left[a^{-3/2} (0.17 r_1 + 0.26 r_1^2 + 4.18 r_1^3 - 5.72 r_1^4) \right.$$

$$\left. - c^{-3/2} (0.17 r_2 + 0.7 r_2^2 + 5.86 r_2^3 - 5.28 r_2^4) \right] \quad \cdots\cdots\cdots \quad (73)$$

Here $r_a = \frac{c_3}{a}$, $r_b = \frac{c_3}{b}$, $r_c = \frac{c_3}{c}$

$$r_1 = \frac{b}{a}, \qquad r_2 = \frac{b}{c}$$

$$a = c_1 + 0.2c_3, \qquad b = c_2 + 0.4c_3, \qquad c = a+b,$$

and c_1, c_2, c_3 are expressed in terms of the normal elastic constants of cubic crystals and the density as follows:

$$c_1 = \frac{c_{44}}{\rho},$$

$$c_2 = \frac{c_{12} + c_{44}}{\rho},$$

$$c_3 = \frac{c_{11} - c_{12} - 2c_{44}}{\rho}$$

Calculations of the Debye temperatures were carried out using both the approximations, which are called 1F and 2F respectively, and the results are shown in Tables III and VI

CHAPTER V

DATA AND RESULTS

Data

The experimental data employed in the calculations is summarized in Table I for the elements and in Table V for the alkali halides. If for any solid more than one measurement has been carried out on the elastic constants and the different sets of values are in reasonable agreement with each other then the most recent measurement has been followed. For rubidium, lithium chloride, sodium fluoride, potassium fluoride and rubidium chloride two sets of elastic constants, while for sodium chloride three sets of elastic onstants have been recently reported which differ from each other; calculations were carried out for all sets and these are represented by Rb-1 and Rb-2 in Tables I, II, III and IV, LiCl-1 and LiCl-2, NaF-1 and NaF-2, KF-1 and KF-2, RbCl-1 and RbCl-2, and NaCl-1, NaCl-2 and NaCl-3 in Tables V, VI, VII and VIII. In those cases where the given value was obtained by extrapolation in the quoted reference, this fact has been indicated by 'Extr.' in the last column.

Tables II and VIII show the anisotropy η ($= 2c_{44}/c_{11} - c_{12}$), z_{min}, z_{max}, K, the experimental values of Debye temperatures together with their sources, and theoretical Θ_o^{el} . The way these theoretical

values were obtained is explained later.

For the elements Θ_o^{el} was calculated using the lattice constant a_1 in terms of which the density may be expressed as

$$\rho = \frac{p\,M}{N a_1^3} \qquad \ldots\ldots\ldots \qquad (74)$$

where $p = 2$ for body-centered cubic (b. c. c.), 4 for face-centered cubic (f. c. c.) and 8 for diamond lattices. Thus

$$\Theta_o^{el} = \frac{h}{k}\left(\frac{3p}{4\pi}\right)^{1/3} \frac{v_m}{a_1} \qquad \ldots\ldots\ldots \qquad (75)$$

For a number of elements (see Table I) the lattice constants were calculated from the room temperature value (Gray 1963) either by the method of Corruccini and Gniewek (1961), or using the thermal expansion data given in section 4f of Gray (1963). In Table I is shown which methods were employed for which elements.

For the alkali halides Θ_o^{el} was calculated using the average density ρ of the solid.

For a diatomic solid in the equation of Θ_o^{el} , the atomic weight is replaced by half the molecular weight M ($M = M_1 + M_2$, M_1 and M_2

being the atomic weights of the individual atoms). Thus

$$\Theta_o^{el} = \frac{h}{k}\left(\frac{6\,N\,\rho}{4\pi\,M}\right)^{1/3} v_m \qquad \ldots\ldots\ldots \quad (76)$$

Similarly, for Θ_o^{el} from the Houston-Bhatia-Tauber method, Eq. (65), we get

$$\Theta_o^{el} = \frac{h}{k}\left(\frac{18\,N\,\rho}{4\pi\,M\,A_0}\right)^{1/3} \qquad \ldots\ldots\ldots \quad (77)$$

where M is the molecular weight.

In the case of LiF, KCl and KI the density at $0^\circ K$ was not available. In these cases the molecular volume at the room temperature was calculated from the lattice constant (at the room temperature). From this, using the thermal expansion data (Yates and Panter, 1962) the molecular volume at $0^\circ K$ was obtained.

DISCUSSION

In the harmonic approximation, it is well known that near $T = 0$

$$\Theta_o^{c} = \Theta_o^{el}$$

where Θ_o^{c} is the equivalent Debye temperature derived from the heat capacity as $T \rightarrow 0$ and Θ_o^{el} is the corresponding Debye temperature calculated from the elastic constants at $T = 0$. If elastic

Elements:

TABLE I

Summary of experimental data used in calculations. (The lattice constant (a_1) and the elastic constants are at the temperature indicated in the 4th column. In the 3rd column, b stands for b.c.c., f for f.c.c., and d for diamond.)

Group	Element	Lattice	T (°K)	a_1 (10^{-8} cm)	c_{11} (10^{11} dyn/cm²)	c_{12} (10^{11} dyn/cm²)	c_{44} (10^{11} dyn/cm²)	Source of the elastic constants
0	Ar	f	0	5.3110[a]	0.3732	0.1262	0.1771	Moeller and Squire (1966)[f]
1*a*	Li	b	78	3.50[b]	1.481	1.248	1.077	Nash and Smith (1959)
	Na	b	78	4.2349[c]	0.815	0.679	0.578	Diederich and Trivisonno (1966)
	K	b	4.2	5.225[d]	0.416	0.341	0.286	Marquardt and Trivisonno (1965)
	Rb-1	b	0	5.585[d]	0.316±0.017	0.257±0.038	0.211±0.020	Roberts and Meister (1966), Extr.
	Rb-2	b	0	5.585[d]	0.358	0.3032	0.221	Gutman and Trivisonno (1967), Extr.
1*b*	Cu	f	0	3.6029[e]	17.62	12.494	8.177	Overton and Gaffney (1955)
	Ag	f	0	4.0691[e]	13.149	9.733	5.109	Neighbours and Alers (1958)
	Au	f	0	4.0649[e]	20.163	16.967	4.544	Neighbours and Alers (1958)
3*a*	Al	f	0	4.0328[e]	11.430	6.192	3.162	Kamm and Alers (1964)
4*a*	Diamond	d	300	3.5670[b]	107.6	12.50	57.58	McSkimin and Bond (1957)
	Si	d	77	5.4294[e]	16.772	6.497	8.035	McSkimin and Andreatch, Jr. (1964)
	Ge	d	77	5.6524[e]	13.11	4.923	6.816	McSkimin and Andreatch (1963)
	Pb	f	0	4.9146[e]	5.554	4.542	1.942	Waldorf and Alers (1962)
5*b*	V	b	0	3.0352[e]	23.24	11.936	4.595	Alers (1960)
	Nb	b	4.2	3.2961[e]	25.27	13.32	3.097	Carroll (1965)
	Ta	b	0	3.2979[e]	26.632	15.816	8.736	Featherston and Neighbours (1963)
6*b*	Mo	b	0	3.1470[e]	45.002	17.292	12.503	Featherston and Neighbours (1963)
	W-α	b	0	3.1620[e]	53.255	20.495	16.313	Featherston and Neighbours (1963)
8	Fe	b	0	2.8607[e]	23.7	13.5	11.95	Lord and Beshers (1965), Extr.
	Ni	f	0	3.5160[e]	26.12	15.08	13.17	Alers *et al.* (1960)
	Pd	f	0	3.8808[e]	23.41	17.61	7.12	Rayne (1960)
	Ir	f	0	3.8336[e]	59.6	25.2	27.0	MacFarlane *et al.* (1966)
	Pt	f	0	3.9160[e]	35.8	25.36	7.74	MacFarlane *et al.* (1965)
Act.	Th	f	0	5.0612[e]	7.79	4.82	5.13	Armstrong *et al.* (1959), Extr.

[a] Moeller and Squire (1966).
[b] Gray (1963).
[c] Calculated from the room temperature value (Gray 1963) by the method of Corruccini and Gniewek (1961).
[d] Pearson (1958).
[e] Calculated from the room temperature value (Gray 1963) using the thermal expansion data given in Section 4f of Gray (1963).
[f] Corrected values from a reprint.

TABLE II

Elements: Values of η, z_{min}, z_{max}, K and experimental and theoretical Debye temperatures

Element	T (°K)	η	z_{min}	z_{max}	K	Θ_0^c expt. (°K)	Source of Θ_0^c	Θ_0^{el} theor. (°K)
Ar	0	1.4340	−0.27333	1.36444	1.546660	93.3±0.6	Beaumont *et al.* (1961)	91.2
Li	78	9.2446	−2.37748	4.16997	5.754950	344 ±2.5[a]	Martin (1965)	317.8
Na	78	8.5000	−2.15190	3.86920	5.303797	152.5±2	Martin (1965)	144.3
K	4.2	7.6267	−1.91154	3.54872	4.823077	90.6+1.4 −0.3	Martin (1965)	89.1
Rb-1	0	7.1525	−1.72857	3.30476	4.457143	55.6±0.5	Martin (1965)	54.5
Rb-2	0	8.0657	−1.41314	2.88418	3.826277			54.2
Cu	0	3.1904	−0.59451	1.79269	2.189029	345.6±1.0	Martin (1966)	344.0
Ag	0	2.9912	−0.42301	1.56401	1.846020	226.6±1.0	Martin (1966)	226.2
Au	0	2.8436	−0.18862	1.25149	1.377233	162.4±2	Martin (1966)	161.0
Al	0	1.2073	−0.06567	1.08757	1.131350	427.7±1.0	Phillips (1959)	430.5
						436.4±0.7	Dixon *et al.* (1965)	
Diamond	300	1.2109	−0.20052	1.26736	1.401040	2219 ±20	Desnoyers and Morrison (1958)	2239.6
Si	77	1.5640	−0.33164	1.44218	1.663271	645 ±5	Flubacher *et al.* (1959)	648.9
Ge	77	1.6651	−0.43255	1.57674	1.865110	374 ±2	Flubacher *et al.* (1959)	373.4
Pb	0	3.8379	−0.39756	1.53008	1.795127	106.7±0.5	Keesom and van der Hoeven, Jr. (1963)	104.9
V	0	0.8130	0	0.94331	0.886618	399		399.1
Nb	4.2	0.5183	0	0.87020	0.740405	277		275.7
Ta	0	1.6154	−0.18596	1.24795	1.371927	258	Heiniger *et al.* (1966)	263.7
Mo	0	0.9024	0	0.95840	0.916797	460		474.5
W	0	0.9959	0	0.99819	0.996373	390		384.4
Fe	0	2.3431	−0.58298	1.77730	2.165957	472.7±6.0[b]		472.4
						485.6±1.3[c]	Dixon *et al.* (1965)	
Ni	0	2.3859	−0.59073	1.78764	2.181467	477.4±6.2[b]	Dixon *et al.* (1965)	475.9
						489.9±2.0[c]		
Pd	0	2.4552	−0.25905	1.34541	1.518109	270	Heiniger *et al.* (1966)	275.6
Ir	0	1.5698	−0.30061	1.40082	1.601227	420		429.6
Pt	0	1.4828	−0.08981	1.11974	1.179615	234.9±0.4[d]	Dixon *et al.* (1965)	238.3
Th	0	3.4545	−1.37030	2.82707	3.740602	170	Smith and Wolcott (1956)	163.7

[a] Refers to a partially transformed sample probably containing about 80% faulted hexagonal close-packed phase.
[b] Low temperature specific heat data fitted to $C = \gamma T + \beta T^3 + \alpha T^{3/2}$ by the method of least squares.
[c] In the equation given in footnote *b*, the spin wave contribution to the specific heat, calculated from the exchange interaction term derived from neutron scattering experiments, was subtracted from the calorimetric result and the residual part analyzed to find γ and Θ_0.
[d] ADDED IN PROOF: Recently Berg (Phys. Chem. Solids, 30, 69 (1969)) has determined $\Theta_0 = 240.1$ °K.

TABLE III

Elements: Calculated values of Debye temperatures in °K

Element	Hopf-Lechner			Houston-Bhatia-Tauber				Fedorov	
	8HL	9HL	10HL	3HBT	6HBT	9HBT	15HBT	1F	2F
Ar	91.176	91.178	91.180	90.892	91.189	91.181	91.181	91.209	91.184
Li	311.15	314.69	318.44	272.21	330.31	326.47	317.21	371.36	355.99
Na	141.32	142.75	144.26	125.14	149.02	147.34	144.28	165.65	159.13
K	87.44	88.19	88.98	78.26	91.46	90.49	89.28	100.27	96.61
Rb-1	53.51	53.93	54.37	48.20	55.75	55.18	54.62	60.65	58.54
Rb-2	52.91	53.44	54.04	47.12	55.91	55.27	54.31	61.605	59.294
Cu	342.62	343.08	343.69	329.68	345.58	344.38	344.38	351.27	347.21
Ag	225,10	225.43	225.89	217.35	227.19	226.44	226.46	230.12	227.87
Au	158.43	159.27	160.27	154.97	162.30	161.72	161.74	163.84	162.50
Al	430.33	430.42	430.51	430.05	430.57	430.56	430.56	430.57	430.56
Diamond	2239.6	2239.6	2239.6	2238.1	2239.6	2239.6	2239.6	2239.7	2239.6
Si	648.81	648.83	648.86	645.61	648.99	648.87	648.87	649.33	648.94
Ge	373.32	373.33	373.35	371.01	373.45	373.35	373.35	373.79	373.44
Pb	103.61	103.96	104.47	98.51	105.93	105.31	105.30	108.55	106.81
V	398.88	399.12	399.10	398.57	399.17	399.18	399.18	399.20	399.18
Nb	274.28	277.87	274.88	271.93	276.18	276.59	276.59	277.43	276.52
Ta	263.53	263.62	263.71	261.81	263.85	263.77	263.77	263.99	263.80
Mo	474.48	474.52	474.52	474.37	474.53	474.53	474.53	474.53	474.53
W-α	384.39	384.39	384.39	384.39	384.39	384.39	384.39	384.39	384.39
Fe	471.93	472.09	472.29	462.79	473.05	472.43	472.44	475.87	473.49
Ni	475.42	475.59	475.81	465.79	476.64	475.97	475.98	479.70	477.14
Pd	274.29	274.74	275.30	268.07	276.50	275.90	272.92	278.13	276.61
Ir	429.57	429.59	429.61	427.32	429.71	429.62	429.62	429.93	429.67
Pt	237.52	237.83	238.15	237.07	238.50	238.44	238.44	238.53	238.45
Th	163.28	163.47	163.65	156.92	164.37	163.83	163.81	168.14	165.72

constant data at a higher temperature are employed, the calculated value of the Debye temperature need not be equal to Θ_o^c .

A few years ago, Ludwig (1958) and Leibfried and Ludwig (1961) suggested that owing to anharmonic effects, Θ_o^c in fact differs from Θ_o^{el} . They based their results on special models and found a difference of about 2-3%. Subsequently, however, it was shown by Barron and Klein (1962) that Leibfried and Ludwig's derivation of $\Theta_o^c \neq \Theta_o^{el}$ was in error. More recently, the problem has been considered by Feldman (1964), who has obtained the correction due to the vibrational anharmonicity on the specific heat of a Bravais crystal near $T = 0$. He explicitly shows that this correction maintains the equality of Θ_o^c and Θ_o^{el} to the first order in λ , λ being an ordering parameter.

Elements

Comparison of Calculated values by the Three Methods

Other than from the method of calculation, uncertainty in Θ_o^{el} may be due to errors in the low-temperature elastic constants. The calculated value of Θ_o^{el} is more sensitive to changes in c_{44} and c_{11} than to changes in c_{12}. This can easily be seen from the approximate expression due to Blackman (1935a,b), Eq. (26), where v_m

is given only as the sixth root of a product of c_{11} and c_{44}^2 multiplied by a constant. From this one can easily see that 1% change in c_{11} or c_{44} will result in about .2% and .4% changes, respectively, in Θ_o^{el}. The same change in c_{12} will produce a negligible change in Θ_o^{el}.

The calculated values of Θ_o^{el} in Table III have been given to a greater number of significant figures than is warranted by the accuracy of the experimental data; this has been done to bring out the small changes which occur when successively better approximations are employed.

A comparison of the values obtained by 10HL, 15HBT, and 2F (which may be considered to be the best values for the respective methods) shows that for elements with $\eta \sim 1$, the three sets are close to each other, but for highly anisotropic materials ($\eta > 2.5$) 2F values are too high as compared with the other two. In fact, for such substances 2F results are not even as good as 6HBT ones. We may note here that in both cases, 6HBT and 2F, Θ_o^{el} can be expressed in an analytical form as a function of the elastic constants and the numerical work involved is of the same order of magnitude. It appears that the second approximation of Fedorov is not satisfactory for highly anisotropic materials with $\eta > 1$.

There is very good agreement between 10HL and 15HBT values; only in three cases (Li, Au, and Nb) is the difference between the two values greater than 1%. Broadly speaking, the HL values tend to increase from 8 9 10, and similarly HBT values tend to decrease from 6 9 15 (omit 3HBT). These trends are by no means universal and one can readily spot a few exceptions. The closeness of 10HL and 15HBT values, and the opposite "asymptotic" trends of HL and HBT values, however, suggest that an average of 10HL and 15HBT values may be considered as the "best theoretical value". Such an average is given in the last column of Table II and is compared with the experimental value.

Comparison of the Experimental and Theoretical Debye Temperatures

It can be seen in Tables II and IV that there is no general trend in the relative magnitude between Θ_o^{el} and Θ_o^{c}. Most of the elements have $\Theta_o^{c} > \Theta_o^{el}$, though only by a small amount.

Next we compare the theoretical and experimental Θ_o's for each element.

Argon

The agreement between the observed and calculated values is reasonable.

Lithium

A proper comparison between experiment and theory is not possible for two reasons. Firstly lithium undergoes a martensitic type of transition to a close-packed hexagonal structure at about 70° K and the observed value is for a partially transformed sample. Secondly the calculations were carried out from elastic constant data at 78°K. Consequently it is not surprising that there is a large difference between the observed and the calculated value.

Sodium

The observed value is about 7° K higher than the calculated one, but in this case also the calculated value is based on 78°K data and the difference could be partially or wholly on account of this.

Potassium

The agreement between the two values is satisfactory.

Rubidium

The calculated values by both sets of elastic constants are nearly the same and close to the experimental value; thus the experimental Θ_o does not show preference to either set of elastic constants.

Copper, Silver, and Gold

The agreement between the theoretical and experimental values is excellent.

Aluminium

The calculated value agrees better with that of Phillips (1959) than that of Dixon et al. (1965).

Diamond, Silicon, Germanium, and Lead

Agreement is fair. It may be noted that for diamond, elastic constants at 300°K were used in the calculation. However, in view of the high value of the Debye temperature of diamond, one expects that the difference between these values and those at 0°K would be negligible. To a lesser degree, similar considerations hold for silicon and germanium.

Transition Metals

There is considerable scatter in the experimental Θ_o^c values as reported by different workers. Most of the quoted values in Table III are "best estimates" due to Heiniger, Buchner, and Muller (1966), who have recently reviewed experimental results on the low temperature specific heat of the transition metals. We shall consider these elements together.

Vanadium and Niobium

The experimental values agree well with the theoretical values.

Tantalum, Tungsten, Palladium, and Platinum

There is a difference of 3° to 5° between the theoretical and experimental values; considering the spread of experimental values (see tables in Heiniger et al. 1966), this disagreement is perhaps not too serious. For tungsten, the calculated values by all the 9 approximations are identical to 5 significant figures, a reflection of the fact that its η is very close to 1.

Molybdenum and Iridium

The differences between the theoretical and the observed values are rather large (14.5° and 9.6° respectively) and better measurements of Θ_o^c are desirable.

Iron and Nickel

Dixon et al. (1965) have analyzed their experimental data in two ways as explained in footnotes b and c of Table II. The calculated values agree better with the set in which α, β, and γ were determined by the method of least squares.

Thorium

The observed value is too high and a redetermination would be worthwhile.

TABLE IV

Elements: Comparison among the calculated values of Θ_o^{el} by the four methods and the experimental values Θ_o^c. (Debye temperatures are in $^\circ$K.)

Element	T $^\circ$K	10HL	15HBT	2F	Numerical Integration (Wanner)	Experimental
Ar	0	91.180	91.181	91.184	91.2	93.3 $\pm$ 0.6
Li	78	318.44	317.21	355.99	317.8	344 $\pm$ 2.5
Na	78	144.26	144.28	159.13	144.3	152.5 $\pm$ 2
K	4.2	88.98	89.28	96.61	89.1	90.6 $\pm$ 1.4
Rb-1	0	54.37	54.62	58.54	54.5	55.6 $\pm$ 0.5
Rb-2	0	54.04	54.31	59.294	54.2	
Cu	0	343.69	344.38	347.21	344.0	345.6 $\pm$ 1.0
Ag	0	225.89	226.46	227.87	226.2	226.6 $\pm$ 1.0
Au	0	160.27	161.74	162.50	161.0	162.4 $\pm$ 2
Al	0	430.51	430.56	430.56	430.5	427.7 $\pm$ 1.0
						436.4 $\pm$ 0.7

Element	T °K	10HL	15HBT	2F	Numerical Integration	Experimental
Diamond	300	2239.6	2239.6	2239.6	2239.6	2219 ± 20
Si	77	648.86	648.87	648.94	648.9	645 ± 5
Ge	77	373.35	373.35	373.44	373.4	374 ± 2
Pb	0	104.47	105.30	106.81	104.9	106.7 ± 0.5
V	0	399.10	399.18	399.18	399.1	399
Nb	4.2	274.88	276.59	276.52	275.7	277
Ta	0	263.71	263.77	263.80	263.7	258
Mo	0	474.52	474.53	474.53	474.5	460
W	0	384.39	384.39	384.39	384.4	390
Fe	0	472.29	472.44	473.49	472.4	472.7 ± 6.0
						485.6 ± 1.3
Ni	0	475.81	475.98	477.14	475.9	477.4 ± 6.2
						489.9 ± 2.0

Element	T °K	10HL	15HBT	2F	Numerical Integration	Experimental
Pd	0	275.30	272.92	276.61	275.6	270
Ir	0	429.61	429.62	429.67	429.6	420
Pt	0	238.15	238.44	238.45	238.3	234.9 $\pm$ 0.4
Th	0	163.65	163.81	165.72	163.7	170

Recently, Wanner (1970) has used the same data for the elastic constants as those used here and has calculated Θ_o^{el} by numerical integration taking 200 different directions in 1/16 of the unit sphere. Table IV shows Θ_o^{el} as obtained by Wanner and the 10HL, 15HBT, 2F and Θ_o^{c} from experiment. The agreement between Θ_o^{el} from numerical integration and from the other methods is very good in all cases, except for the highly anisotropic elements Li, Na, K, and Rb. Wanner's values for all elements, except the ones having the diamond lattice structure, are slightly higher than our "best theoretical value" (Θ_o^{el} theoret.).

Alkali Halides

The general remarks about the relative merits of the three methods mentioned above apply also here. For the alkali halides (Tables VI and VII), values of Θ_o^{el} due to 2F (Fedorov) seem to be greater than the ones obtained by 10HL and 15HBT when $\eta > 1$ and less when $\eta < 1$, with the exception of RbCl and RbBr, though only by about .2%. The same behaviour is observed for the elements (Table III), which show too high values of Θ_o^{el} when $\eta > 2.5$.

The "best theoretical value" for Θ_o^{el} has been computed in the same way as for the elements.

TABLE V

Alkali Halides: Summary of the data used in calculations. (The source for the density and the elastic constants is the same, unless otherwise indicated. The elastic constants are at the temperature indicated in the 2nd column.)

Solid	T (^oK)	Molecular Wt (a. m. u.)	Density ρ g/cm^3	c_{11} (10^{11} dyn/cm^2)	c_{12} (10^{11} dyn/cm^2)	c_{44} (10^{11} dyn/cm^2)	Source of data
LiF	0.0	25.9374	2.6757[a]	12.460	4.240	6.490	Briscoe and Squire (1957)
LiCl-1	4.2	42.3920	2.1110	6.074	2.270	2.692	Lewis et al. (1967)
LiCl-2	4.2	42.3920	2.1321	5.860	2.086	2.671	Marshall et al. (1967)
LiBr	0.0	86.8480	3.5768	4.721	1.590	2.052	Marshall & Cleavelin(1969)
NaF-1	4.2	41.9882	2.8510	10.850	2.290	2.899	Lewis et al. (1967)
NaF-2	0.0	41.9882	2.8558[b]	11.039	2.242	2.947	Vallin & Marklund (1966)
NaCl-1	4.2	58.4428	2.2170	5.733	1.123	1.331	Lewis et al. (1967)
NaCl-2	4.2	58.4428	2.1669	5.838	1.194	1.327	Peterson et al. (1967)
NaCl-3	4.2	58.4428	2.2159	5.834	1.192	1.337	Fugate and Schuele (1966)
NaBr	4.2	102.8988	3.299	4.800	0.986	1.070	Lewis et al. (1967)
NaI	4.2	149.8942	3.7620	3.761	0.798	0.781	Claytor & Marshall (1960)

Solid	T (°K)	Molecular Wt (a.m.u.)	Density ρ g/cm^3	c_{11} (10^{11} dyn/cm^2)	c_{12} (10^{11} dyn/cm^2)	c_{44} (10^{11} dyn/cm^2)	Source of data
KF-1	4.2	58.1004	2.5300	7.570	1.350	1.336	Lewis et al. (1967)
KF-2	4.2	58.1004	2.5858	7.585	1.473	1.293	Marshall & Muller (1967)
KCl	4.2	74.5550	2.0448[a]	4.832	0.540	0.663	Norwood & Briscoe (1958)
KBr	298.0	119.0110	2.744	3.468	0.580	0.507	Slage & McKinstry (1967)
KI	4.2	166.0064	3.2077[a]	3.380	0.220	0.368	Norwood & Briscoe (1958)
RbF	295.0	104.4684	3.8675[c]	5.525	1.395	0.925	Haussuhl (1960)
RbCl-1	4.2	120.9230	2.8200	4.297	0.649	0.493	Lewis et al. (1967)
RbCl-2	4.2	120.9230	2.8641	4.499	0.676	0.497	Marshall et al. (1967)
RbBr	4.2	165.3790	3.4340	3.863	0.474	0.4085	Lewis et al. (1967)
RbI	4.2	212.3744	3.6680	3.210	0.360	0.2920	Lewis et al. (1967)
CsCl	298.0	168.3580	3.9880	3.664	0.882	0.804	Slage & Mckinstry (1967)
CsBr	4.2	212.8140	4.6550	3.437	1.035	0.999	Vallin et al. (1964)
CsI	4.2	259.8094	4.7120	2.737	0.793	0.825	Vallin et al. (1964)

[a] Calculated from room temperature lattice constant (Gray 1963) and thermal expansion data from Yates and Panter (1962)

[b] Calculated from the value of the lattice constant at 0°K as given by Vallin and Marklund (1966)

[c] Calculated from the room temperature lattice constant (Gray 1963).

TABLE VI

Alkali Halides: Calculated values of Debye Temperature in °K

	Hopf-Lechner			Fedorov	
	8HL	9HL	10HL	1F	2F
LiF	733.03	733.04	733.06	733.64	733.16
LiCl-1	428.82	428.83	428.85	428.96	428.86
LiCl-2	425.89	425.90	425.91	426.03	425.93
LiBr	274.06	274.07	274.07	274.10	274.07
NaF-1	491.81	491.84	491.85	492.07	491.83
NaF-2	496.52	496.55	496.56	496.81	496.55
NaCl-1	320.79	320.82	320.84	321.39	320.80
NaCl-2	322.37	322.41	322.43	323.02	322.38
NaCl-3	321.88	321.92	321.94	322.50	321.89
NaBr	224.32	224.34	224.36	224.83	224.32

	8HL	9HL	10HL	1F	2F
Na I	167.46	167.49	167.50	168.02	167.46
KF-1	332.62	332.73	332.79	335.67	332.58
KF-2	327.32	327.44	327.52	330.53	327.31
KCl	235.67	235.85	235.97	242.63	235.83
KBr	164.92	165.02	165.09	168.18	164.96
KI	130.23	130.42	130.56	138.21	131.00
RbF	211.52	211.60	211.66	213.17	211.57
RbCl-1	168.20	168.42	168.58	175.40	168.77
RbCl-2	169.52	169.77	169.95	177.53	170.25
RbBr	135.72	135.94	136.10	143.41	136.53
RbI	107.04	107.29	107.48	115.71	108.41
CsCl	159.36	159.38	159.39	159.66	159.37
CsBr	149.46	149.47	149.47	149.47	149.47
CsI	126.20	126.20	126.21	126.21	126.21

TABLE VII

Alkali Halides: Calculated values of Debye temperatures in °K.

	Houston-Bhatia-Tauber			
Solid	3HBT	6HBT	9HBT	15HBT
LiF	729.48	733.20	733.07	733.07
LiCl-1	427.52	428.89	428.85	428.85
LiCl-2	424.62	425.95	425.91	425.91
LiBr	273.56	274.08	274.07	274.07
NaF-1	489.75	491.77	491.85	491.85
NaF-2	494.33	496.48	496.57	496.57
NaCl-1	318.02	320.69	320.85	320.85
NaCl-2	319.45	322.26	322.44	322.44
NaCl-3	319.06	321.78	321.95	321.95
NaBr	222.14	224.23	224.37	224.37
NaI	165.42	167.37	167.52	167.52
KF-1	325.49	332.12	332.84	332.84
KF-2	319.95	326.80	327.58	327.57
KCl	226.08	234.60	236.08	236.04
KBr	159.42	164.40	165.15	165.14
KI	122.33	129.07	130.72	130.61
RbF	207.23	211.27	211.70	211.70
RbCl-1	159.50	167.12	168.76	168.68

Solid	3HBT	6HBT	9HBT	15HBT
RbCl-2	160.24	168.33	170.16	170.05
RbBr	127.59	134.59	136.30	136.18
RbI	99.239	105.80	107.74	107.55
CsCl	157.93	159.31	159.40	159.40
CsBr	149.32	149.47	149.47	149.47
CsI	126.11	126.21	126.21	126.21

TABLE VIII

Alkali Halides: Values of z_{min}, z_{max}, K, η and theoretical and experimental Debye temperatures.

Solid	T °K	z_{min}	z_{max}	K	η	Θ_o^{el} theor. (°K)	Θ_o^{c} exp. (° K)	Source
LiF	0.0	-0.398660	1.531550	1.797320	1.5791	733.07	737 ± 9	Martin (1955)
							722 ± 6	Scales (1958)
LiCl-1	4.2	-0.233590	1.311450	1.467179	1.4154	428.85	422 ± 6	Moyer (1965)
LiCl-2	4.2	-0.245850	1.327790	1.491690	1.4155	425.47		
LiBr	0.0	-0.182280	1.243040	1.364556	1.3108	274.72		
NaF-1	4.2	0	1.000000	0.652622	0.6773	491.85		
NaF-2	0.0	0	1.000000	0.641251	0.6700	496.57		
NaCl-1	4.2	0	1.000000	0.557474	0.5774	320.85	320.6 ± 1.5	Barron et al. (1957)
NaCl-2	4.2	0	1.000000	0.558856	0.5715	322.43	320	Morrison et al. (1955)
NaCl-3	4.2	0	1.000000	0.562375	0.5760	321.94		
NaBr	4.2	0	1.000000	0.551206	0.5611	224.36		

Solid	T °K	z_{min}	z_{max}	K	η	Θ_o^{el} theor. (°K)	Θ_o^{c} exp. (°K)	Source
NaI	4.2	0	1.000000	0.529866	0.5272	167.51	164.2 ± 1	Barron et al. (1957)
							164.3 ± 1.5	Martin (1964)
							163.2	Claytor and Marshall (1960)
KF-1	4.2	0	1.000000	0.430863	0.4296	332.82		
KF-2	4.2	0	1.000000	0.439606	0.4231	327.54		
KCl	4.2	0	1.000000	0.288558	0.3090	236.00	233 ± 3	Harrison (1968)
							235.1±0.5	Barron et al. (1957)
							233 ± 3	Keesom & Pearlman (1953)
							229 ± 2	Seward & Narayanamurti (1966)
KBr	298.0	0	1.000000	0.367106	0.3511	165.11	174.3±.7	Barron et al. (1957)
							173.8±1.5	Martin (1964)
KI	4.2	0	1.000000	0.195219	0.2329	130.58	132.3± 1	Barron et al. (1957)
							133.1±1.5	Martin (1964)
							128.3	Scales (1958)
RbF	295.0	0	1.000000	0.504348	0.4479	211.68		

Solid	T °K	z_{min}	z_{max}	K	η	Θ_o^{el} theor. (°K)	Θ_o^{c} exp. (° K)	Source
RbCl-1	4.2	0	1.000000	0.300210	0.2703	168.73	165	Alexander & Pohl(1967)
RbCl-2	4.2	0	1.000000	0.293103	0.2600	170.00		
RbBr	4.2	0	1.000000	0.255464	0.2411	136.14	131	Alexander & Pohl (1967)
RbI	4.2	0	1.000000	0.223441	0.2049	107.52	103	Alexander & Pohl (1957)
CsCl	298.0	0	1.000000	0.589510	0.5780	159.39		
CsBr	4.2	0	1.000000	0.834290	0.8318	149.47		
CsI	4.2	0	1.000000	0.846234	0.8488	126.21	127.67	Marshall & Kundel (1969)

In Table VIII it is seen that η varies in a rather regular manner, that is, it decreases for all the alkali compounds as the size of the halide ion is increased. This results in $\eta > 1$ for the lithium halides and $\eta < 1$ for the rest. An exception to this behaviour of the halide ion is shown by the cesium halides, where the trend is reversed. It must be noted that these three cesium halides have a b. c. c. lattice while the rest have an f. c. c one.

Comparison of the Experimental and Theoretical Debye Temperatures

The alkali halides show a trend toward $\Theta_o^{el} > \Theta_o^{c}$, except KI, while in the case of the elements there is no such trend, as a matter of fact most of them show $\Theta_o^{c} > \Theta_o^{el}$.

From Table VIII it can be seen that Θ_o^{el} and Θ_o^{c} agree with experiment to within less than 2% in almost all cases. The exceptions are NaI, KBr, RbCl, RbBr and RbI. In these cases the disagreement is about 3% or more.

Next we compare the theoretical and experimental Θ_o^{c}'s for each group of the alkali halides.

Lithium Halides

LiF: The calculated value is within the experimental error of the observed value due to Martin (1955) and outside the experimental

error of the value due to Scales (1958).

LiCl: The two sets of elastic constants give Θ_o^{el} differing only by about 1%, both lying within the experimental error of Θ_o^{c}.

LiBr: There is no Θ_o^{c} available, so that no comparison with experiment can be made.

Sodium Halides

NaF: The calculated values by both sets of elastic constants differ between them by about 1%, but there is no experimental value to compare with.

NaCl: Θ_o^{el} from the three sets of elastic constants agree amongst themselves to within .3% and fall within the experimental error of Θ_o^{c}.

NaBr: There is no Θ_o^{c} to compare with.

NaI: The theoretical value is too high and does not fall within the experimental error of any of the three observed values. The difference is about 3%.

Potassium Halides

KF: The two calculated values differ between themselves by about 2%, but there is no Θ_o^{c} to compare with.

KCl: The agreement with the experiment is satisfactory in three cases but Θ_o^c due to Seward and Narayanamurti (1966) is lower by 3.5%.

KBr: The two experimental values are close to each other, and are $\sim 9^\circ$ greater than the theoretical value; the difference appears to be due to the fact that room temperature elastic constant data was used.

KI: Agreement is fair, except with the observed value due to Scales (1958) which is rather low.

Rubidium Halides

As mentioned earlier, the calculated values are rather high by about 3% for RbCl, and 4% for RbBr and RbI. The two values calculated for RbCl agree amongst themselves to within 1.2%.

Cesium Halides

The cesium halides as a group are the most isotropic as compared to other groups. The calculated values by the three methods converge very quickly to the final value, and are very close to each other, especially in the case of CsI for which the agreement with experiment is about 1%. Unfortunately there are no experimental results available for the other cesium halides.

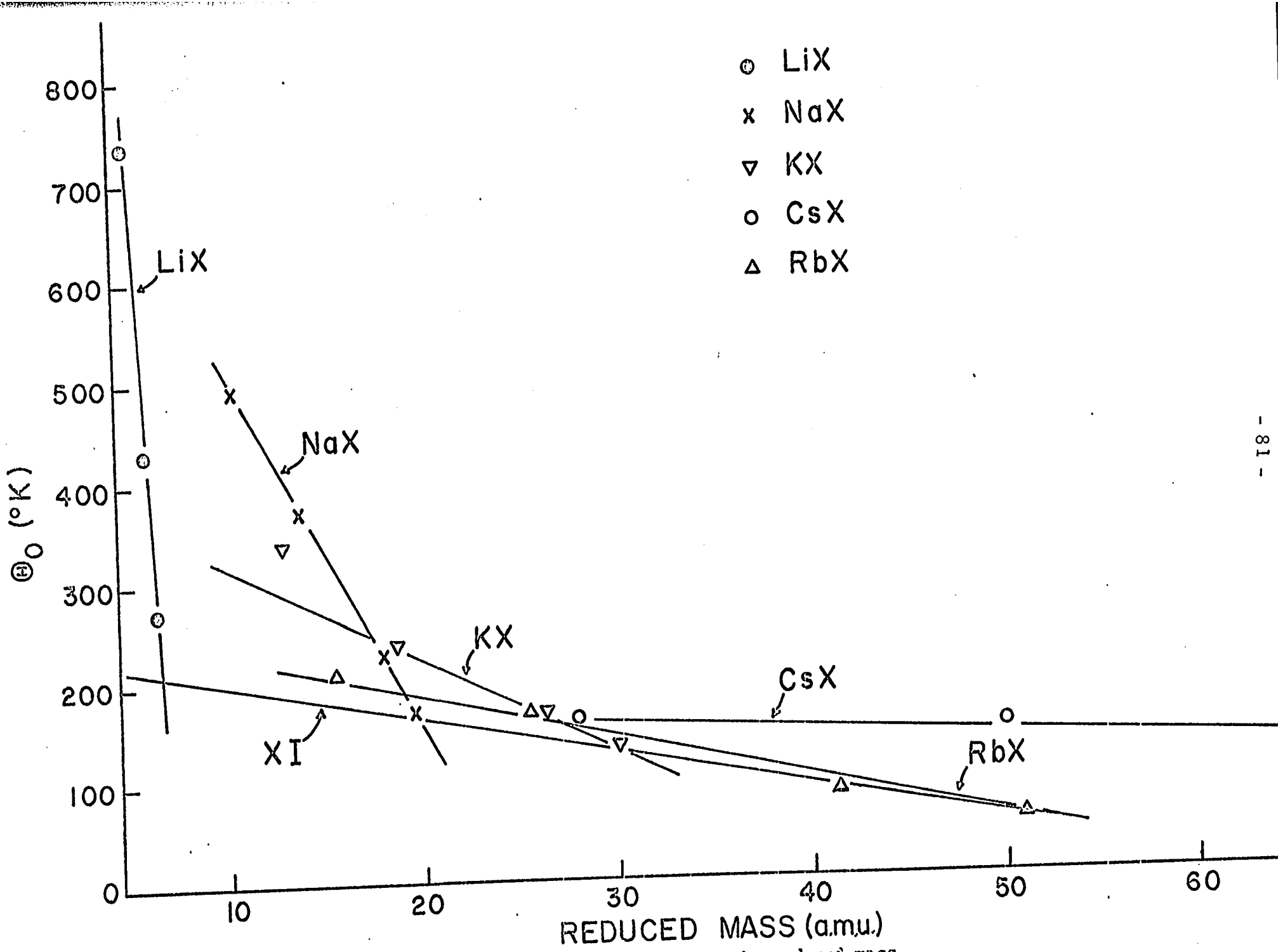

Fig. 2. Debye temperature vs. the reduced mass.

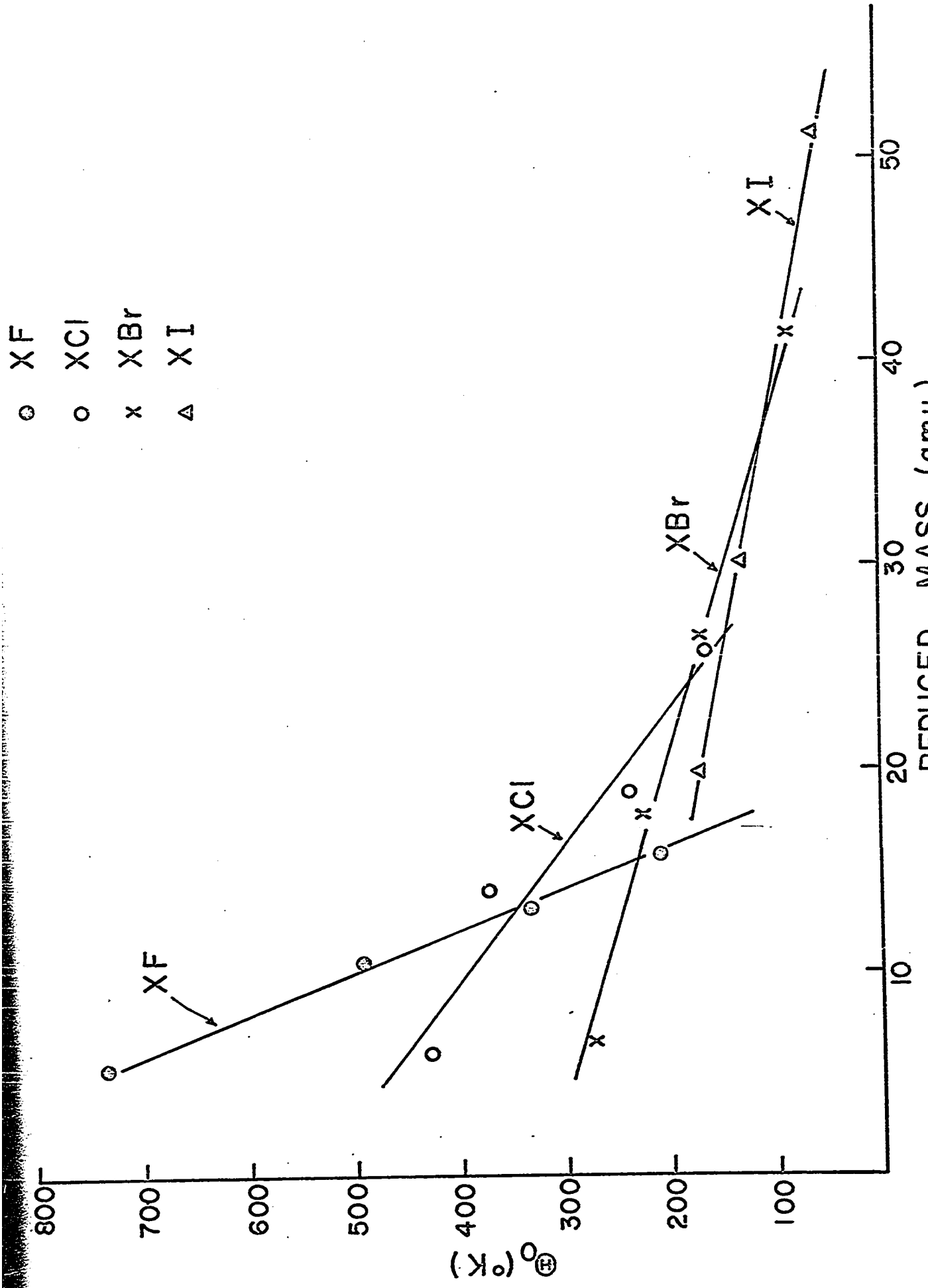

Fig. 3. Debye temperature vs. the reduced mass.

Regularities in the Debye Temperatures

Because the frequency spectrum and consequently the specific heat and the Debye temperature of a solid are dependent upon the relative masses of the vibrating ions we have plotted the Debye temperature of the alkali halides vs. their reduced mass.

The two figures, 2 and 3, show the same points but grouped differently.

In Fig. 2 the grouping is done on the basis of the alkali ion. It is observed that all the members of a group fall on a straight line. This regularity is most pronounced for Li and Na halides, where the points are almost exactly on the line, while for the Cs halides it is less so, but still good. We note that as the mass of the halide ion becomes larger the effect of the reduced mass on the Debye temperature is more pronounced for the lighter alkali ions (Li^+, Na^+), and less so for heavier ones, especially Rb^+ and Cs^+. Thus the absolute value of the slope decreases as we pass from Li to Cs halides.

In figure 3, where the grouping is done on the basis of the halide ion, a similar behaviour is observed. Again all groups fall on different straight lines, only the Cl compounds are not too regular, and the absolute value of the slope decreases as we pass from F to I compounds.

These two figures can be used for estimating Debye temperatures of alkali halides for which data is not available. For example, from fig. 2. we estimate Θ_o of LiI to be $\simeq 200 \pm 25\,^{\circ}K$. The second correlation (Fig. 3) gives $210 \pm 5\,^{\circ}K$.

REFERENCES

Alers, G. A. 1960, Phys. Rev. 119, 1532.

Alers, G. A. 1965, Physical Acoustics, Edited by W. P. Mason, Vol. IIIB (Academic Press New York).

Alers, G. A., Neighbours, J. R. and Sato, H. 1960, J. Phys. Chem. Solids 13, 40.

Alexander, C. T., and Pohl, R. O. 1967, Quoted in Lewis et al. (1967).

Armstrong, P. E., Carlson, O. N. and Smith, J. F. 1959, J. Appl. Phys. 30, 36.

Barron, T. H. K., Berg, W. T., and Morrison, J. A. 1957, Proc. Roy. Soc. (London), A 242, 478.

Barron, T. H. K. and Klein, M. L. 1962, Phys. Rev. 127, 1997.

Beaumont, R. H., Chihara, H. and Morrison, J. A. 1961, Proc. Phys. Soc. 78, 1462.

Betts, D. D., Bhatia, A. B., and Horton G. K., 1956, Phys. Rev. 104, 43.

Betts, D. D. 1961, Can. J. Phys. 39, 233.

Betts, D. D., Bhatia, A. B., and Wyman, M. 1956, Phys. Rev. 104, 37.

Bhatia, A. B. and Tauber, G. E. 1954, Phil Mag. 45, 1211: Errata 46, 108 (1955).

Bijl, D. 1957, Prog. Low Temp. Phys., 2, 395.

Blackman, M. 1935a. Proc. Roy. Soc., A148, 384.

Blackman, M. 1935b. Proc. Roy. Soc., A149, 126.

Blackman, M. 1941, Repts. Prog. Phys., 8, 11.

Blackman, M. 1951, Phil. Mag., 42, 1441.

Blackman, M. 1955, Handbuch der Physik 7/1 325 (Springer-Verlag, Berlin).

Born, M. 1915, Dynamik der Kristallgitter (Teubner, Leipzig).

Born, M. 1923, Atomtheorie des festen Zustandes (Leipzig).

Born, M., and von Karman, T. 1912, Physik. Z. 13, 297.

Born, M., and von Karman, T. 1913, Phys. Zeit, 14, 15.

Brillouin, L. 1946, "Wave Propagation in Periodic Structures" McGraw-Hill, New York.

Briscoe, C. V., and Squire, C. F. 1957, Phys. Rev. 106, 1175.

Carroll, K. J. 1965, J. Appl. Phys. 36, 3689.

Claytor, R. N., and Marshall, B. J. 1960, Phys. Rev. 120, 332.

Corruccini, R. J. and Gniewek, J. J. 1961, N.B.S. Monograph 29 (National Bureau of Standards, Washington).

Debye, P. J. W., 1912, Ann. Physik. Lpz. [4] 39, 789, translation in "The Collected Papers of P. J. W. Debye" (Interscience, New York).

de Launay, J. 1954, J. Chem. Phys., 22, 1676.

Desnoyers, J. E., and Morrison, J. A. 1958, Phil. Mag. 3, 42.

Diederich, M. E., and Trivisonno, J. 1966, J. Phys. Chem. Solids, 27, 637.

Dixon, M., Hoare, F. E., Holden, T. M., and Moody, D. E. 1965, Proc. Roy. Soc. A285, 561.

Durand, M. 1936, Phys. Rev. 50, 449.

Einstein, A. 1907, Ann. Physik [4] 22, 180.
Einstein, A., 1911, Ann. Physik, 35, 679.

Featherston, F. H. and Neighbours, J. R. 1963, Phys. Rev. 130, 1324.

Fedorov, F. I. 1963, Soviet-Phys.-Crystallography 8, 159, 312.

Fedorov, F. I. 1965a, Soviet-Phys.-Crystallography 10, 125.

Fedorov, F. I. 1965b, Soviet-Phys.-Doklady 10, 896.

Fedorov, F. I. 1968, Theory of Elastic Waves in Crystals (Plenum Press, New York).

Fedorov, F. I. and Bystrova, T. G. 1966, Soviet Phys. - Crystallography 11, 333.

Feldman, J. L. 1964, Proc. Phys. Soc. 84, 361.

Flubacher, P., Leadbetter, A. J. and Morrison, J. A. 1959, Phil. Mag. 4, 273.

Fuchs, K. 1936a, Proc. Roy. Soc. A153, 622.

Fuchs, K. 1936b, Proc. Roy. Soc. A157, 44.

Fugate, R. Q., and Schule, D. E. 1966, J. Phys. Chem. Solids, 27, 493.

Gray, D. E. 1963, American Institute of Physics Handbook (McGraw-Hill, New York).

Gutman, E. J., and Trivisonno, J. 1967, J. Phys. Chem. Solids 28, 805.

Harrison, J. P. 1968, Rev. Scient. Instr., 39, 145.

Haussuhl, S. 1960, Z. Phys., 159, 223.

Heiniger, F., Bucher, E., and Muller, J. 1966, Phys. Kondens. Materie 5, 243.

Hopf, L., and Lechner, G. 1914, Verh. Deutsch. Ges. 16, 643.

Houston, W. V. 1948, Revs. Mod. Phys. 20, 161.

Kamm, G. N., and Alers, G. A. 1964, J. Appl. Phys. 35, 327.

Keesom, P. H., and Pearlman, N. 1953, Phys. Rev., 91, 1354.

Keesom, P. H., and van der Hoeven Jr., B. J. C. 1963, Phys. Letters. 3, 360.

Leibfried, G., and Ludwig, W. 1961, Solid State Physics 12, 275.

Lewis, J. T., Lehoczky, A., and Briscoe, C. V. 1967, Phys. Rev., 161, 877.

Lord, Jr., A. E., and Beshers, D. N. 1965, J. Appl. Phys. 36, 1620.

Ludwig, W. 1958, J. Phys. Chem. Solids 4, 282.

Joshi, S. K. 1961, Phys. Rev. 121, 40.

MacFarlane, R. E., Rayne, J. A. and Jones, C. K. 1965, Phys. Letters, 18, 91.

MacFarlane, R. E., Rayne, J. A., and Jones, C. K. 1966, Phys. Letters, 20, 234.

Marquardt, W. R., and Trivisonno, J. 1965, J. Phys. Chem. Solids, 26, 273.

Marshall, B. J., and Cleavelin, C. R. 1969, J. Phys. Chem. Solids, 30, 1905.

Marshall, B. J., and Kunkel, J. T. 1969, J. App. Phys., 40, 5191.

Marshall, B. J., and Miller, R. E. 1967, J. Appl. Phys., 38, 4749.

Marshall, B. J., Pederson, D. D., and Dorris, G. G. 1967, J. Phys. Chem. Solids, 28, 1061.

Martin, D. L. 1955, Phil. Mag., 46, 751.

Martin, D. L. 1964, Proc. Phys. Soc. (London), 83, 99.

Martin, D. L. 1965, Phys. Rev. 139, A150.

Martin, D. L. 1966, Phys. Rev. 141, 576.

McSkimin, H. J., and Andreatch, P. 1963, J. Appl. Phys. 34, 651.

McSkimin, H. J., and Bond, W. L. 1957, Phys. Rev., 105, 116.

McSkimin, H. J. and Andreatch Jr., P. 1964, J. Appl. Phys. 35, 2161.

Moeller, H. R., and Squire, C. F. 1966, Phys. Rev. 151, 689.

Morrison, Paterson and Dugsdale 1955, Can. J. Chem. 33, 375.

Moyer, D. F. 1965, J. Phys. Chem. Solids, 26, 1459.

Musgrave, M. J. P. 1954, Proc. Roy. Soc., A226, 339.

Nash, H. C., and Smith, C. S. 1959, J. Phys. Chem. Solids 9, 113.

Neighbours, J. R., and Alers, G. A. 1958, Phys. Rev. 111, 707.

Nernst, W., and Lindemann, F. A. 1911, Z. Electrochem. 17, 817.

Norwood, M. H., and Briscoe, C. V. 1958, Phys. Rev., 112, 45.

Overton Jr., W. C., and Gaffney, J. 1955, Phys. Rev. 98, 969.

Pearson, W. B. 1958, A Handbook of Lattice Spacings and Structures of Metals and Alloys (Pergamon Press).

Peterson, G., Vallin, J., Calais, J. L., and Mansikka K, 1967, Ark. Fys., 34, 371.

Phillips, N. E. 1959, Phys. Rev. 114, 676.

Quimby, S. L., and Sutton, P. M. 1953, Phys. Rev. 91, 1122.

Rayne, J. A. 1960, Phys. Rev. 118, 1545.

Reuss, A. 1929, Z. Angew. Math. Mech., 9, 49.

Roberts, C. A. and Meister, R. 1966, J. Phys. Chem. Solids 27, 1401.

Scales, W. W. 1958, Phys. Rev., 112, 49.

Seward, W. D., and Narayanamurti, V. 1966, Phys. Rev., 148, 463.

Slage, D. D., and McKinstry, H. A. 1967, J. Appl. Phys. 38, 451.

Slage, D. D., and McKinstry, H. A. 1967, J. Appl. Phys. 38, 437.

Smith, P. L., and Wolcott, N. M. 1956, Conférence de Physique des basses températures (Institut du Froid, Paris 1956) p. 283.

Sutton, P. M. 1955, Phys. Rev. 99, 1826.

Tenerz, E. 1956, Ark. Fysik 11, 247.

Vallin, J., Beckenant, O., and Salama K. 1964, J. Appl. Phys., 35, 1222.

Vallin, J., Marklund, K., Sikstrom, J. O., and Beckman, D. 1966, Ark. Fys., 32, 515.

Varshni, Y. P. 1964, R. C. A. Victor Techn. Rep. (Unpublished).

Voigt, W. 1910, "Lehrbuch der Kristallphysik" p. 962, Teubner, Leibzig.

von der Lage, F. C., and Bethe, H. A. 1947, Phys. Rev. 71, 612.

Waldorf, D. L., and Alers, G. A. 1962, J. Appl. Phys. 33, 3266.

Wanner, R., 1970, Can. J. Phys. 48, 1270.

Yates, B., and Panter, P. H. 1962, Proc. Phys. Soc., 80, 373.

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