DEBYE TEMPERATURE OF SOME CUBIC ELEMENTS AND ALKALI HALIDES

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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 $0^\circ K$ ($\Theta_c^C$). This temperature can also be calculated from the elastic stiffness constants ($\Theta_o^{el}$) (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 $\Theta_o^{el}$ 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 $\nu_E$, which was characteristic for the solid. This rather simple model gave surprisingly 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 $\nu_E$. 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 cal-
culations 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 frequen-
cies, long wavelengths, but for high frequencies, at which the wave-
length is comparable to the distance between two atoms, it is only approxi-
imately correct. The atomic nature of the lattice was taken into ac-
count 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 \( \nu_D \) for the modes of vibration. This then leads to a characteristic temperature \( \Theta_D \), where \( \Theta_D = \frac{h \nu_D}{k} \).

Born (1915) proposed that instead of a single cut off frequency \( \nu_D \) 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 \( \Theta_D \). 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

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

where \( \nabla^2 \) 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

$$u = A e^{i \left( \frac{2\pi n}{L} x + \frac{2\pi n}{L} y + \frac{2\pi n}{L} z - \omega t \right)}$$

or

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

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

and

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

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

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

or

$$n = \pm \frac{L}{v} \sqrt{\omega^2} \quad \ldots \ldots \quad (4)$$

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 conti-
nuous 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 fre-
quency. Therefore the number of modes \( g(\nu) \, d\nu \) within a range \( \nu \)
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

\[
g(\nu) \, d\nu = \frac{4 \pi V \nu^2}{\nu^3} \, d\nu \quad \ldots \ldots \ldots \quad (5)
\]

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

\[
g(\nu) \, d\nu = 4 \pi V (n_L^{-3} + 2n_T^{-3}) \nu^2 \, d\nu \quad \ldots \ldots \ldots \quad (6)
\]

Since there are only \( 3N \) degrees of freedom available to the \( N \) dis-
crete atoms, there must be a limit to the frequency range of the solid
specified by a maximum cutoff frequency \( \nu_D \), such that

\[
\int_0^{\nu_D} g(\nu) \, d\nu = 3N \quad \ldots \ldots \ldots \quad (7)
\]
and therefore we get for \( v_D \)

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

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

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

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 \( v_D \) becomes

\[
v_D = \left( \frac{3N}{4\pi V} \right)^{1/3} v_m
\]

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

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 \( \Theta_0 \) at \( 0^\circ K \), is defined to be
\[ \Theta_0 = \frac{h}{k} v_D \] ........... (11)

or

\[ \Theta_0 = \frac{h}{k} \left( \frac{3N}{4\pi V} \right)^{1/3} v_m \] ........... (11a)

or

\[ \Theta_0 = \frac{h}{k} \left( \frac{1}{4\pi} \frac{n}{v_c} \right)^{1/3} v_m \] ........... (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 \( \Theta_0 \) takes the form

\[ \Theta_0 = \frac{h}{k} \left( \frac{3N}{4\pi} \frac{\rho}{M} \right)^{1/3} v_m \] ........... (12)

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

In the above relations it is seen that \( \Theta_0 \) 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 inde-
dependent of frequency, the $\Theta_0$ determined from calorimetric measu-
rements (Debye theory) is the same with that determined from sound
velocities, called $\Theta_0^{el}$. 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)

$$
g(v) = \begin{cases} 
\frac{9N}{3} v^2 & \text{for } v \leq v_D \\
\frac{v}{v_D} & \\
0 & \text{for } v > v_D 
\end{cases}
$$

(13)

**Debye Specific Heat**

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

$$
\bar{u} = \frac{1}{2} \hbar v + \frac{\hbar v}{e^{\hbar v/(kT)} - 1}
$$

(14)

Hence the molar internal energy of a solid will be

$$
E = \int_0^{v_{max}} \bar{u} g(v) \, dv
$$

(15)
According to the Debye theory \( \nu_{\text{max}} = \nu_D \) and by Eq. (14) Eq. (15) becomes:

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

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

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

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

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 \( n \geq 1 \):

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

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

\[
C_v = 3R \left[ \frac{4n^4}{5} \frac{1}{x^3} - \frac{3x}{e^x - 1} - 12x \sum_{k=1}^{\infty} e^{-kx} \left( \frac{1}{kx} + \frac{3}{2kx^2} + \frac{6}{3kx^3} + \frac{6}{4kx^4} \right) \right] \quad (18)
\]
High Temperature Limit

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

$$C_v \to 3R \quad \cdots \cdots \quad (19)$$

Low Temperature Limit

At low temperatures $x \to \infty$ 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

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

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 $\Theta_D$ 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 $\Theta_0^{el}$ 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:
\[
\begin{vmatrix}
A_{11} - \rho v^2 & A_{12} & A_{13} \\
A_{12} & A_{22} - \rho v^2 & A_{23} \\
A_{13} & A_{23} & A_{33} - \rho v^2
\end{vmatrix} = 0 \ldots (21)
\]

where \(\rho\) 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:

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

\[
A_{22} = p^2 c_{66} + q^2 c_{22} + r^2 c_{44} + 2qrc_{24} + 2rpc_{46} + 2pqc_{26},
\]

\[
A_{33} = p^2 c_{55} + q^2 c_{44} + r^2 c_{33} + 2qrc_{34} + 2rpc_{35} + 2pqc_{45},
\]

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

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

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

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 $\Theta_0$

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 \( \frac{3}{v^3} \), and \( \theta_o^{\text{el}} \) becomes:

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

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 et 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

\[
\frac{3}{v_m} = \frac{1}{3} \frac{1}{v_L} + \frac{2}{3} \frac{1}{v_T}
\]

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

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

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

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

provided

\[
\delta = \frac{(c_{12} - c_{11} + 2 c_{44})}{(c_{11} - c_{44})}
\]

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):
\[ v_m = \left( \frac{c_{11}c_{44}^2}{\rho^3} \right)^{1/6} \]  

\[ .......... \quad (25) \]

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

\[ v_m = 0.89 \left( \frac{c_{11}c_{44}^2}{\rho^3} \right)^{1/6} \]

\[ .......... \quad (26) \]

Anisotropic solids present a particular difficulty as the spread of the velocities is high. Blackman (1951) obtained the following semitheoretical formulae for \( \Theta_o^{el} \), designed to cover the cases where

\[ \frac{(c_{11} - c_{12})}{c_{11}} \] is very small

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

This formula also was found (Varshni 1964) to give too high values for \( \Theta_o^{el} \) 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 \( \Theta_o^{el} \), 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

$$
\Theta^\text{el}_0 = \frac{9N}{4\pi V} \left( \frac{h}{k} \right)^3 \left( \frac{c_{44}}{\rho} \right)^{3/2} \cdot \frac{9}{18 + \sqrt{3}} f(s,t).
$$

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 \( \Theta^\text{el}_0 \). 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

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

then equation (23) becomes

$$\begin{vmatrix}
  z - p^2 & Kpq & Kpr \\
  Kqp & z - q^2 & Kqr \\
  Krp & Krq & z - r^2
\end{vmatrix} = 0 \quad \cdots \quad (28)$$
or
\[ z^3 - z^2 + b_1 z - b_2 = 0 \]  \hspace{1cm} (29)

in which
\[ b_1 = (1 - K^2) \left( \frac{2}{p^2} + \frac{2}{q^2} + \frac{2}{r^2} + \frac{2}{p^2} \right) \]  \hspace{1cm} (30)

and
\[ b_2 = (1 - 3K^2 + 2K^3) \left( \frac{2}{p^2} + \frac{2}{q^2} + \frac{2}{r^2} \right) \]  \hspace{1cm} (31)

In this notation, Eq. (9) becomes
\[
\frac{3^3}{v_m} = \left( \frac{\rho}{c_{11} - c_{44}} \right)^{3/2} \int \frac{1}{(z_i + \zeta)^{3/2}} \frac{d\Omega}{4\pi} \quad \cdots \quad (32)
\]

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

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.
\[
(z + \zeta)^{-3/2} = \sum_{n=0}^{5} a_n z^n \]  \hspace{1cm} (33)

The range of \( z \) chosen by Hopf and Lechner was from \( z = 0 \) to \( z = 1 \),
which means that \( \rho v^2 \) varies from \( c_{44} \) to \( c_{11} \). The coefficients \( a_n \) were chosen such that the two functions, Eq. (33), are equal at

\[
\frac{z}{m} = 0.2 \text{ m}
\]

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

\[
\rho v_1^2 = c_{11} \quad \text{........... (34)}
\]

\[
\rho v_2^2 = c_{44} \quad \text{........... (35)}
\]

\[
\rho v_3^2 = c_{44} \quad \text{........... (36)}
\]

[110] direction

\[
\rho v_1^2 = \frac{1}{2} (c_{11} + c_{12} + 2c_{44}) \quad \text{........... (37)}
\]

\[
\rho v_2^2 = c_{44} \quad \text{........... (38)}
\]
\[ \rho v_3^2 = \frac{1}{2} (c_{11} - c_{12}) \]  

(39)

[111] direction

\[ \rho v_1^2 = \frac{1}{3} (c_{11} + 2c_{12} + 4c_{44}) \]  

(40)

\[ \rho v_2^2 = \frac{1}{3} (c_{11} - c_{12} + 4c_{44}) \]  

(41)

\[ \rho v_3^2 = \frac{1}{3} (c_{11} - c_{12} + 4c_{44}) \]  

(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 eighth 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

\[ (z + \zeta)^{-3/2} = \sum_{n=0}^{10} a_n z^n \]  

(43)
In order to find the coefficients \( a_n \) the range of \( z \) from \( z_{\text{max}} \) to \( z_{\text{min}} \) 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 interval.

This resulted into 11 simultaneous linear equations in \( a_n \). If

\[
\Delta z = \frac{z_{\text{max}} - z_{\text{min}}}{10}
\]

the equations are

\[
(z_{\text{min}} + \zeta)^{-3/2} = \sum_{n=0}^{10} a_n z_{\text{min}}^n
\]

\[
(z_{\text{min}} + \Delta z + \zeta)^{-3/2} = \sum_{n=0}^{10} a_n (z_{\text{min}} + \Delta z)^n
\]

\[
(z_{\text{max}} + \zeta)^{-3/2} = \sum_{n=0}^{10} a_n z_{\text{max}}^n
\]

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

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

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

$$z^3 - (z_1 + z_2 + z_3)z^2 + (z_1 z_2 + z_2 z_3 + z_3 z_1)z - z_1 z_2 z_3 = z^3 - z^2 + b_1 z - b_2 = 0 \ldots \quad (46)$$

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

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

$$z_1 z_2 + z_2 z_3 + z_3 z_1 = b_1 \quad \ldots \ldots \quad (48)$$

$$z_1 z_2 z_3 = b_2 \quad \ldots \ldots \quad (49)$$

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_1 b_2 \\
\sum_{i=1}^{3} z_i^6 = 1 - 6b_1 + 6b_2 + 9b_1^2 - 12b_1 b_2 - 2b_1^3 + 3b_2^2 \\
\sum_{i=1}^{3} z_i^7 = 1 - 7b_1 + 7b_2 + 14b_1^2 - 21b_1 b_2 - 7b_1^3 + 7b_2^2 + 7b_1 b_2 \\
\sum_{i=1}^{3} z_i^8 = 1 - 8b_1 + 8b_2 + 20b_1^2 - 32b_1 b_2 - 16b_1^3 + 12b_2^2 + 24b_1 b_2 - 8b_1 b_2^2 + 2b_1^4 \\
\sum_{i=1}^{3} z_i^9 = 1 - 9b_1 + 9b_2 + 27b_1^2 - 45b_1 b_2 - 30b_1^3 + 18b_2^2 + 54b_1 b_2 - 27b_1 b_2^2 + 9b_1^4 - 9b_1^2 b_2 + 3b_2^3
\[
\sum_{i=1}^{3} z^i = 1 - 10b_1 + 10b_2 + 35b_1^2 - 60b_1b_2 - 50b_1^3 + 25b_2^2 + 100b_1b_2^2
\]
\[
- 60b_1b_2^2 + 25b_1^4 - 40b_1^3b_2 + 10b_1^3 + 15b_1b_2^2 - 2b_1^5.
\] ........ (50)

Let
\[ \kappa_1 = (1 - K^2) \]

and
\[ \kappa_2 = (1 - 3K^2 + 2K^3) \] ........... (51)

where \( K \) is defined by Eq. (27).

The powers and the combinations of \( b_1 \) and \( b_2 \) appearing in the preceding set of equations, Eqs (50), are found in terms of \( \kappa_1, \kappa_2 \) and the direction cosines \( p, q, \) and \( r, \) and are presented in the following set of equations,

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

\[ b_2 = \kappa_1(p^4 q^4 + p^4 r^4 + q^4 r^4 + 2p^2 q^2 r^2) \]

\[ b_3 = \kappa_1^3[p^6 q^6 + p^6 r^6 + q^6 r^6 + 3(p^4 q^2 r^2 + p^4 q^4 r^4 + p^4 r^4 q^4) - 3p^4 q^4 r^4] \]

\[ b_4 = \kappa_1^4[p^8 q^8 + p^8 r^8 + q^8 r^8 + 4(p^6 q^2 r^2 + p^6 q^4 r^4 + p^6 r^4 q^4) - 4(p^6 q^4 r^4 + p^4 q^2 r^4 + p^2 q^4 r^2) + 6p^4 q^4 r^4] \]
\[ b_1 = \kappa_1 \left[ p^{10} q^{10} r^{10} + p q r + 5(p q r + p q r + p q r) \right] 
- 5(p q r + p q r + p q r) - 20p q r + 10(p q r + p q r) + 466 \\
+ 466 \] 

\[ b_2 = \kappa_2 p q r \]

\[ b_2^2 = \kappa_2^2 p^2 q^2 r^2 \]

\[ b_2^3 = \kappa_2^3 p^3 q^3 r^3 \]

\[ b_1 b_2 = \kappa_1 \kappa_2 (p q r + p q r + p q r) \]

\[ b_1^2 b_2 = \kappa_1^2 \kappa_2 (p q r + p q r + p q r) \]

\[ b_1^3 b_2 = \kappa_1^3 \kappa_2 (p q r + p q r + p q r) \]

\[ b_3 b_2 = \kappa_1^3 \kappa_2 \left[ p^{10} q^{10} r^{10} + p q r + 288 + 3(p q r + p q r + p q r) \right] \]

\[ b_1^2 b_2 = \kappa_1^2 \kappa_2 (p q r + p q r + p q r) \]  

\[ \cdots \cdots \cdots \ \ (52) \]
The powers and the combinations of the coefficients $k_1$ and $k_2$

appearing above are expressed in terms of $K$ by the following set

of equations,

$$k_1^1 = 1 - K^2$$

$$k_1^2 = 1 - 2K^2 + K^4$$

$$k_1^3 = 1 - 3K^2 + 3K^4 - K^6$$

$$k_1^4 = 1 - 4K^2 + 6K^4 - 4K^6 + K^8$$

$$k_1^5 = 1 - 5K^2 + 10K^4 - 10K^6 + 5K^8 - 10K^{10}$$

$$k_2^1 = 1 - 3K^2 + 2K^3$$

$$k_2^2 = 1 - 6K^2 + 4K^3 + 9K^4 - 12K^5 + 4K^6$$

$$k_2^3 = 1 - 9K^2 + 6K^3 + 27K^4 - 36K^5 + 15K^6 + 54K^7 - 36K^8 + 8K^9$$

$$k_1k_2^1 = 1 - 4K^2 + 2K^3 + 3K^4 - 2K^5$$

$$k_1k_2^2 = 1 - 5K^2 + 2K^3 + 7K^4 - 4K^5 + 3K^6 + 2K^7$$
\[ \kappa_1^2 \kappa_2^2 = 1 - 7K^2 + 4K^3 + 15K^4 - 16K^5 - 5K^6 + 12K^7 - 4K^8 \]

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

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

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.
\[ \int p^8 q^8 r^4 \frac{d\Omega}{4\pi} = \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} \sin^8 \theta \cos^8 \phi \sin^8 \theta \sin^8 \phi \cos^4 \theta \sin \theta d\theta d\phi \]

\[ = \frac{1}{4\pi} \int_0^{\pi} \sin^17 \theta \cos^4 \theta d\theta \int_0^{2\pi} \sin^8 \phi \cos^8 \phi d\phi = \frac{1}{415701} \]

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

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

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

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

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

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

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

\[ \int p^4 r^4 \frac{d\Omega}{4\pi} = \frac{1}{105} \]
\[
\int \frac{6 \cdot 6 \, d\Omega}{4\pi} = \frac{5}{2703}
\]
\[
\int \frac{8 \cdot 8 \, d\Omega}{4\pi} = \frac{7}{21879}
\]
\[
\int \frac{10 \cdot 10 \, d\Omega}{4\pi} = \frac{3}{46183}
\]
\[
\int \frac{2 \cdot 2 \, d\Omega}{4\pi} = \frac{1}{15}
\]
\[
\int \frac{4 \cdot 4 \, d\Omega}{4\pi} = \frac{1}{105}
\]
\[
\int \frac{6 \cdot 6 \, d\Omega}{4\pi} = \frac{5}{2703}
\]
\[
\int \frac{8 \cdot 8 \, d\Omega}{4\pi} = \frac{7}{21879}
\]
\[
\int \frac{10 \cdot 10 \, d\Omega}{4\pi} = \frac{3}{46183}
\]
\[
\int \frac{2 \cdot 2 \cdot 2 \, d\Omega}{4\pi} = \frac{1}{105}
\]
\[
\int \frac{4 \cdot 4 \cdot 4 \, d\Omega}{4\pi} = \frac{1}{5005}
\]
\[
\int \frac{6 \cdot 6 \cdot 6 \, d\Omega}{4\pi} = \frac{5}{969,969}
\]
\[ \int \frac{d\Omega}{4\pi} \stackrel{4\ 4\ 2\ p\ q\ r}{p\ q\ r} = \frac{1}{1155} \]

\[ \int \frac{d\Omega}{4\pi} \stackrel{6\ 6\ 2\ p\ q\ r}{p\ q\ r} = \frac{1}{9009} \]

\[ \int \frac{d\Omega}{4\pi} \stackrel{8\ 8\ 2\ p\ q\ r}{p\ q\ r} = \frac{7}{415701} \]

\[ \int \frac{d\Omega}{4\pi} \stackrel{6\ 6\ 4\ p\ q\ r}{p\ q\ r} = \frac{1}{51051} \]

\[ \int \frac{d\Omega}{4\pi} \stackrel{8\ 8\ 4\ p\ q\ r}{p\ q\ r} = \frac{1}{415701} \]

\[ \int \frac{d\Omega}{4\pi} \stackrel{4\ 2\ 4\ p\ q\ r}{p\ q\ r} = \frac{1}{1155} \]

\[ \int \frac{d\Omega}{4\pi} \stackrel{6\ 2\ 6\ p\ q\ r}{p\ q\ r} = \frac{1}{9009} \]

\[ \int \frac{d\Omega}{4\pi} \stackrel{8\ 2\ 8\ p\ q\ r}{p\ q\ r} = \frac{7}{415701} \]

\[ \int \frac{d\Omega}{4\pi} \stackrel{6\ 4\ 6\ p\ q\ r}{p\ q\ r} = \frac{1}{51051} \]

\[ \int \frac{d\Omega}{4\pi} \stackrel{8\ 4\ 8\ p\ q\ r}{p\ q\ r} = \frac{1}{415701} \]

\[ \int \frac{d\Omega}{4\pi} \stackrel{2\ 4\ 4\ p\ q\ r}{p\ q\ r} = \frac{1}{1155} \]
\[ \int p^2 q^2 r^2 \frac{d\Omega}{4\pi} = \frac{1}{9009} \]

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

\[ \int p^4 q^2 r^2 \frac{d\Omega}{4\pi} = \frac{1}{51051} \]

\[ \int p^4 q^2 r^2 \frac{d\Omega}{4\pi} = \frac{1}{415701} \]

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

\[ \int b^1 \frac{d\Omega}{4\pi} = \frac{1}{5} \kappa_1 \]

\[ \int b^2 \frac{d\Omega}{4\pi} = \frac{1}{21} \kappa_1^2 \]

\[ \int b^3 \frac{d\Omega}{4\pi} = \frac{61}{5005} \kappa_1^3 \]

\[ \int b^4 \frac{d\Omega}{4\pi} = \frac{831}{255,255} \kappa_1^4 \]

\[ \int b^5 \frac{d\Omega}{4\pi} = \frac{4345}{4,849,845} \kappa_1^5 \]

\[ \int b^2 \frac{d\Omega}{4\pi} = \frac{1}{105} \kappa_2 \]
\[
\int b_2^2 \frac{d\Omega}{4\pi} = \frac{1}{5005} \kappa_2^2 \\
\int b_1^2 b_2 \frac{d\Omega}{4\pi} = \frac{11}{15015} \kappa_1 \kappa_2 \\
\int b_3^2 \frac{d\Omega}{4\pi} = \frac{5}{969,969} \kappa_2^3 \\
\int b_1^2 b_2^2 \frac{d\Omega}{4\pi} = \frac{1}{17017} \kappa_1 \kappa_2^2 \\
\int b_1^2 b_2 \frac{d\Omega}{4\pi} = \frac{1}{385} \kappa_1 \kappa_2 \\
\int b_2^2 \frac{d\Omega}{4\pi} = \frac{85}{4,849,845} \kappa_2^2 \\
\int b_1^3 b_2 \frac{d\Omega}{4\pi} = \frac{205}{969,969} \kappa_1 \kappa_2^2 
\] ...

(54)

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

\[
F = \left( \frac{\rho}{c_{11} - c_{44}} \right)^{3/2} \left[ \int \left[ 3 a_0^+ + \sum_{n=1}^{10} a_n \left( n_1^n + n_2^n + n_3^n \right) \right] \frac{d\Omega}{4\pi} \right] \\
= \left( \frac{\rho}{c_{11} - c_{44}} \right)^{3/2} \left[ 3 a_0^+ + a_1^+ + \frac{1}{4,849,845} x \right] \\
\left[ a_2(2,909,907 + 1,939,938 \ K^2) \\
+ a_3(2,078,505 + 2,494,206 \ K^2 + 277, 134 \ K^3) \\
+ a_4(1,616,615 + 2,401,828 \ K^2 + 369, 512 \ K^3 + 461, 890 \ K^4) \right]
\]
\[ + a_5 (1, 322, 685 + 2, 099, 500 \, K^2 + 335, 920 \, K^3 + 965, 770 \, K^4 + 125, 970 \, K^5) \]
\[ + a_6 (1, 119, 195 + 1, 773, 270 \, K^2 + 263, 568 \, K^3 + 1, 296, 522 \, K^4 + 267, 444 \, K^5 + 129, 846 \, K^6) \]
\[ + a_7 (969, 969 + 1, 487, 738 \, K^2 + 194, 446 \, K^3 + 1, 433, 474 \, K^4 + 348, 194 \, K^5 + 366, 282 \, K^6 + 49, 742 \, K^7) \]
\[ + a_8 (855, 855 + 1, 256, 584 \, K^2 + 140, 752 \, K^3 + 1, 429, 180 \, K^4 + 362, 064 \, K^5 + 621, 528 \, K^6 + 143, 184 \, K^7 + 40, 698 \, K^8) \]
\[ + a_9 (765, 765 + 1, 075, 032 \, K^2 + 102, 384 \, K^3 + 1, 343, 628 \, K^4 + 332, 748 \, K^5 + 828, 648 \, K^6 + 240, 084 \, K^7 + 142, 506 \, K^8 + 19, 050 \, K^9) \]
\[ + a_{10} (692, 875 + 933, 210 \, K^2 + 75, 920 \, K^3 + 1, 222, 620 \, K^4 + 284, 600 \, K^5 + 960, 300 \, K^6 + 308, 840 \, K^7 + 289, 070 \, K^8 + 68, 620 \, K^9 + 13, 790 \, K^{10}) \]
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 $0^\circ K$. 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 $\alpha$ 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 \( \alpha \) type. We summarize here their results.

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

\[
A_{rs} = \frac{(2r+2s)!}{(r+s)!} \frac{r}{\sum_{a=0}^{r+s-a-b}(a+b)!} \frac{s}{\sum_{b=0}^{r+s-a-b}(a+b)!} x^{2r-2a} y^{2s-2b} z^{2a+2b} \]

then the Kubic Harmonics of degree \( 2n \) are

\[
K_{rs} = S A_{rs} (x^2, y^2, z^2) \]

where \( S \) means symmetrization operation.

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

\[
K_0 = 1,
K_1 = 0,
K_2 = S(2x^4 - 6x^2 y^2),
K_3 = S(x^6 - 15x^4 y^2 + 180x^2 y^4 z^2),
K_4 = S(2x^8 - 56x^6 y^2 + 70x^4 y^4 z^4) \]

\[
\ldots \ldots \ldots \ldots (58)
\]
The Kubic Harmonics $K_m$ satisfy the orthogonality conditions

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

where $\gamma_m$ 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 $\Theta_e$ 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 $v_m^{-3}$

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

and by Eq. (9) we need evaluate

$$
\frac{3}{v_m^3} 4\pi = J = \int_0^\pi \int_0^{2\pi} I(\theta, \varphi) \sin \theta d\theta d\phi \quad \ldots \ldots (61)
$$
Houston's method consists in expanding $I(\theta, \varphi)$ in the Kubic Harmonics having the same symmetry, which we denote by $K_m(\theta, \varphi)$

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

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

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

$$J = \int_{0}^{\pi} \int_{0}^{2\pi} I(\theta, \varphi) \sin \theta \, d\theta \, d\varphi = 4\pi A_0 \quad \ldots \ldots (63)$$
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 \( A_0, A_1, \ldots A_n \).

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

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

\[
\vdots
\]

\[
I_n(\theta, \varphi) = A_0K_0 + A_1K_1 + A_2K_2 + \ldots A_nK_n
\]

\[ \ldots \ldots (64) \]

We must keep in mind that the \( K_i \)'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 \( A_0 \), \( \Theta_0 \) can be calculated from

\[
\Theta_0 = \frac{h}{k} \left( \frac{9N \rho}{4\pi M A_0} \right)^{1/3}
\]

\[ \ldots \ldots \quad (65) \]

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

\[
I(100) = \rho^{3/2} \left[ 2c_{44}^{-3/2} + \left( c_{44}^+ + a \right)^{-3/2} \right],
\]

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

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

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

\[
+ \left[ c_{44}^+ + \frac{1}{2} a - \frac{1}{10} (9a^2 + 16\beta^2)^{1/2} \right]^{-3/2} \right].
\]
\[ I(211) = \rho^{3/2} \left[ \left( c_{44} + \frac{1}{6} (\alpha - \beta) \right)^{-3/2} + \left( c_{44} + \frac{1}{12} (5 \alpha + \beta) \right) \right. \]
\[ + \frac{1}{12} (9\alpha^2 + 33\beta^2 - 6\alpha \beta)^{1/2} \left. \right]^{-3/2} + \left[ c_{44} + \frac{1}{12} (5\alpha + \beta) \right) \]
\[ - \frac{1}{12} (9\alpha^2 + 33\beta^2 - 6\alpha \beta)^{1/2} \right]^{-3/2} \]
\[ I(221) = \rho^{3/2} \left[ \left( c_{44} + \frac{4}{9} (\alpha - \beta) \right)^{-3/2} + \left( c_{44} + \frac{1}{18} (5\alpha + 4\beta) \right) \right. \]
\[ + \frac{1}{18} (9\alpha^2 + 48\beta^2 + 24\alpha \beta)^{1/2} \left. \right]^{-3/2} + \left[ c_{44} + \frac{1}{18} (5\alpha + 4\beta) \right) \]
\[ - \frac{1}{18} (9\alpha^2 + 48\beta^2 + 24\alpha \beta)^{1/2} \right]^{-3/2} \]}{60}

where \( \rho \) is the average density of the solid and

\[ \alpha = c_{11} - c_{44} \]
\[ \beta = c_{12} + c_{44} \]

The six lowest Kubic Harmonics of type \( \alpha \) written explicitly \((x^2 + y^2 + z^2 = 1)\) are

\[ K_0 = 1, \]
\[ K_1 = 0, \]
\[ K_2 = x^4 + y^4 + z^4 - \frac{3}{5} K_0, \]

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

\[ K_4 = x^8 + y^8 + z^8 - \frac{28}{5} K_3 - \frac{210}{143} K_2^2 - \frac{1}{3} K_0, \]

\[ K_5 = x^{10} + y^{10} + z^{10} - \frac{45}{19} K_4 - \frac{126}{17} K_3 - \frac{210}{143} K_2^2 - \frac{3}{11} K_0 \]

\[ K_6 = x^4 y^4 z^4 + \frac{6}{115} K_5^2 - \frac{1}{2\cdot7\cdot19} K_4^2 - \frac{54}{5\cdot17\cdot19} K_3^2 \]

\[ + \frac{3}{11\cdot13\cdot17} K_2^2 - \frac{1}{5\cdot7\cdot11\cdot13} K_0 \] \hspace{1cm} (67)

Knowing the \( K_n \)'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

\[ A_0 = \frac{1}{35} \left[ 10 I(100) + 16 I(110) + 9 I(111) \right] \] \hspace{1cm} (68)
\[ A_0^6 = \frac{1}{1,081,080} \left[ 117,603 I(100) + 76,544 I(110) + 17,496 I(111) \right. \\
+ 381,250 I(210) + 311,040 I(211) + 177,147 I(221) \right] \quad \ldots \ldots (69) \]

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)

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

\[ + 0.17827058 I(210) + 0.10294771 I(211) + 0.20711638 I(411) \]

\[ + 0.21376348 I(431) + 0.17478397 I(433) + 0.07309875 I(221) \ldots \ldots (70) \]

and
\[ A_{15}^0 = 0.0436705 \ I(100) + 0.0229221 \ I(410) + 0.3400264 \ I(210) \]

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

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

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

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

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:

$$I_1 = a^{-3/2} \left\{ \begin{array}{l}
2 + r_a r_b \left[ 0.1 r_1 (1 - 0.06r_1) + \frac{57.2 - 8.4 r_a + 0.48 r_b}{1001} \right] \\
+ c^{-3/2} \left[ 1 - \frac{r_b r_c}{1001} \left[ 57.2 (1 - r_2) + 0.5 r_b - r_c (7.2 - 6.7 r_2) \right] \right] \end{array} \right\} \ldots \ldots \ldots (72)$$

Second approximation:

$$I_2 = I_1 + \frac{r_b^4}{1001} \left[ a^{-3/2} (0.17 r_1 + 0.26 r_1^2 + 4.18 r_1^3 - 5.72 r_1^4) \\
- c^{-3/2} (0.17 r_2 + 0.7 r_2^2 + 5.86 r_2^3 - 5.28 r_2^4) \right] \ldots \ldots \ldots (73)$$

Here $r_a = \frac{c_3}{a}$, $r_b = \frac{c_3}{b}$, $r_c = \frac{c_3}{c}$
\[ r_1 = \frac{b}{a}, \quad r_2 = \frac{b}{c} \]

\[ a = c_1 + 0.2c_3, \quad b = c_2 + 0.4c_3, \quad c = a + b, \]

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 constants 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 \( \eta (= 2 c_{44}/(c_{11} - c_{12})) \), \( z_{\text{min}} \) to \( z_{\text{max}} \), K, the experimental values of Debye temperatures together with their sources, and theoretical \( \Theta_{e}^{\text{el}} \). The way these theoretical
values were obtained is explained later.

For the elements \( \Theta^e_0 \) was calculated using the lattice constant \( a_1 \) in terms of which the density may be expressed as

\[
\rho = \frac{p M}{N a_1^3} \quad \ldots \ldots \quad (74)
\]

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

\[
\Theta^e_0 = \frac{\hbar}{k} \left( \frac{3p}{4\pi} \right)^{1/3} \frac{v}{m a_1} \quad \ldots \ldots \quad (75)
\]

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 \( \Theta^e_0 \) was calculated using the average density \( \rho \) of the solid.

For a diatomic solid in the equation of \( \Theta^e_0 \), 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

\[ \Theta_0^c = \frac{h}{k} \left( \frac{6 N \rho}{4 \pi M} \right)^{1/3} v_m \]  

\[ \Theta_0^el = \frac{h}{k} \left( \frac{18 N \rho}{4 \pi M A_0} \right)^{1/3} \]  

(76)  \hspace{2cm} (77)

Similarly, for \( \Theta_0^c \) from the Houston-Bhatia-Tauber method, Eq. (65), we get

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 \( T = 0 \)

\[ \Theta_0^c = \Theta_0^el \]

where \( \Theta_0^c \) is the equivalent Debye temperature derived from the heat capacity as \( T \to 0 \) and \( \Theta_0^el \) is the corresponding Debye temperature calculated from the elastic constants at \( T = 0 \). If elastic
Elements:

Summary of experimental data used in calculations. (The lattice constant \(a_i\) 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.)

<table>
<thead>
<tr>
<th>Group</th>
<th>Element</th>
<th>Lattice</th>
<th>(T) (°K)</th>
<th>(a_i) (10^{-8} cm)</th>
<th>(c_{11}) dyn/cm²</th>
<th>(c_{12}) dyn/cm²</th>
<th>(c_{44}) dyn/cm²</th>
<th>Source of the elastic constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Ar</td>
<td>f</td>
<td>0</td>
<td>5.311⁴⁺</td>
<td>0.3732</td>
<td>0.1262</td>
<td>0.1771</td>
<td>Moeller and Squier (1960)⁷</td>
</tr>
<tr>
<td>1a</td>
<td>Li</td>
<td>b</td>
<td>78</td>
<td>3.30⁴⁺</td>
<td>1.481</td>
<td>1.248</td>
<td>1.077</td>
<td>Nash and Smith (1959)</td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>b</td>
<td>78</td>
<td>4.23⁴⁺</td>
<td>0.815</td>
<td>0.679</td>
<td>0.578</td>
<td>Diederich and Trivisonno (1966)</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>b</td>
<td>4.2</td>
<td>5.28⁴⁺</td>
<td>0.416</td>
<td>0.341</td>
<td>0.286</td>
<td>Marquardt and Trivisonno (1965)</td>
</tr>
<tr>
<td></td>
<td>Rb-1</td>
<td>b</td>
<td>0</td>
<td>5.58⁴⁺</td>
<td>0.316±0.017</td>
<td>0.257±0.038</td>
<td>0.211±0.020</td>
<td>Roberts and Meister (1966), Extr.</td>
</tr>
<tr>
<td></td>
<td>Rb-2</td>
<td>b</td>
<td>0</td>
<td>5.58⁴⁺</td>
<td>0.358</td>
<td>0.3032</td>
<td>0.221</td>
<td>Gutman and Trivisonno (1967), Extr.</td>
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<td>1b</td>
<td>Cu</td>
<td>f</td>
<td>0</td>
<td>3.60⁴⁺</td>
<td>17.62</td>
<td>12.494</td>
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<td>4.06⁴⁺</td>
<td>13.149</td>
<td>9.733</td>
<td>5.109</td>
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<td>Au</td>
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<td>4.08⁴⁺</td>
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<td>16.967</td>
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<td>2a</td>
<td>Al</td>
<td>f</td>
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<td>4.03⁴⁺</td>
<td>11.430</td>
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<td>3.162</td>
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<td>4a</td>
<td>Diamond</td>
<td>d</td>
<td>300</td>
<td>3.36⁴⁺</td>
<td>107.6</td>
<td>12.50</td>
<td>37.58</td>
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</tr>
<tr>
<td>4a</td>
<td>Si</td>
<td>d</td>
<td>77</td>
<td>5.42⁴⁺</td>
<td>16.772</td>
<td>6.497</td>
<td>8.035</td>
<td>McSkimin and Andreatch, Jr. (1959)</td>
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<tr>
<td>6b</td>
<td>Ge</td>
<td>d</td>
<td>77</td>
<td>5.52⁴⁺</td>
<td>13.11</td>
<td>4.923</td>
<td>6.816</td>
<td>McSkimin and Andreatch (1963)</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>f</td>
<td>0</td>
<td>4.91⁴⁺</td>
<td>5.554</td>
<td>4.542</td>
<td>1.942</td>
<td>Waldorf and Aleris (1962)</td>
</tr>
<tr>
<td>5b</td>
<td>V</td>
<td>b</td>
<td>0</td>
<td>3.03⁴⁺</td>
<td>23.24</td>
<td>11.936</td>
<td>4.595</td>
<td>Aleris (1960)</td>
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<tr>
<td></td>
<td>Nb</td>
<td>b</td>
<td>4.2</td>
<td>3.29⁴⁺</td>
<td>25.27</td>
<td>13.32</td>
<td>3.097</td>
<td>Carroll (1965)</td>
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<tr>
<td>6b</td>
<td>Ta</td>
<td>b</td>
<td>0</td>
<td>3.29⁴⁺</td>
<td>26.632</td>
<td>15.816</td>
<td>8.736</td>
<td>Featherston and Neighbours (1963)</td>
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<tr>
<td></td>
<td>Mo</td>
<td>b</td>
<td>0</td>
<td>3.14⁴⁺</td>
<td>45.002</td>
<td>17.292</td>
<td>12.503</td>
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<td>0</td>
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<td>20.495</td>
<td>16.313</td>
<td>Featherston and Neighbours (1963)</td>
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<tr>
<td>8</td>
<td>Fe</td>
<td>b</td>
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<td>2.86⁴⁺</td>
<td>23.7</td>
<td>13.5</td>
<td>11.95</td>
<td>Lord andBesesh (1965), Extr.</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>f</td>
<td>0</td>
<td>3.51⁴⁺</td>
<td>26.12</td>
<td>15.08</td>
<td>13.17</td>
<td>Aleris et al. (1960)</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>f</td>
<td>0</td>
<td>3.88⁴⁺</td>
<td>23.41</td>
<td>17.61</td>
<td>7.12</td>
<td>Rayno (1960)</td>
</tr>
<tr>
<td></td>
<td>Ir</td>
<td>f</td>
<td>0</td>
<td>3.83⁴⁺</td>
<td>59.6</td>
<td>25.2</td>
<td>27.0</td>
<td>MacFarlane et al. (1966)</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>f</td>
<td>0</td>
<td>3.91⁴⁺</td>
<td>35.8</td>
<td>25.36</td>
<td>7.74</td>
<td>MacFarlane et al. (1965)</td>
</tr>
<tr>
<td></td>
<td>Th</td>
<td>f</td>
<td>0</td>
<td>5.06⁴⁺</td>
<td>7.79</td>
<td>4.82</td>
<td>5.13</td>
<td>Armstrong et al. (1959), Extr.</td>
</tr>
</tbody>
</table>

*Moeller and Squier (1960).  
*Gray (1953).  
*Calculated from the room temperature value (Gray 1963) by the method of Ceccarelli and Chmieluk (1961).  
*Calculated from the room temperature value (Gray 1963) using the thermal expansion data given in Section 4f of Gray (1963).  
*Corrected values from a reprint.
## TABLE II

**Elements**: Values of $\eta$, $z_{\text{min}}$, $z_{\text{max}}$, $K$ and experimental and theoretical Debye temperatures

<table>
<thead>
<tr>
<th>Element</th>
<th>$T$ (°K)</th>
<th>$\eta$</th>
<th>$z_{\text{min}}$</th>
<th>$z_{\text{max}}$</th>
<th>$K$</th>
<th>$\Theta_0^{\text{expt.}}$ (°K)</th>
<th>Source of $\Theta_0^c$</th>
<th>$\Theta_0^{\text{theor.}}$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0</td>
<td>1.434</td>
<td>-0.2733</td>
<td>1.3644</td>
<td>1.546660</td>
<td>93.3 ± 0.6</td>
<td>Beaumont et al. (1961)</td>
<td>91.2</td>
</tr>
<tr>
<td>Li</td>
<td>78</td>
<td>9.2446</td>
<td>-2.37748</td>
<td>4.16997</td>
<td>5.754950</td>
<td>344 ± 2.5*</td>
<td>Martin (1966)</td>
<td>317.8</td>
</tr>
<tr>
<td>Na</td>
<td>78</td>
<td>8.5000</td>
<td>-2.15190</td>
<td>3.86920</td>
<td>5.303797</td>
<td>152.5 ± 2</td>
<td>Martin (1966)</td>
<td>144.3</td>
</tr>
<tr>
<td>K</td>
<td>4.2</td>
<td>7.6267</td>
<td>-1.91154</td>
<td>3.34872</td>
<td>4.823077</td>
<td>90.6 ± 1.4</td>
<td>Martin (1966)</td>
<td>89.1</td>
</tr>
<tr>
<td>Rb-1</td>
<td>0</td>
<td>7.1525</td>
<td>-1.72857</td>
<td>3.30476</td>
<td>4.457143</td>
<td>55.6 ± 0.5</td>
<td>Martin (1965)</td>
<td>54.5</td>
</tr>
<tr>
<td>Rb-2</td>
<td>0</td>
<td>8.0657</td>
<td>-1.41314</td>
<td>2.88418</td>
<td>3.826277</td>
<td>345.6 ± 1.0</td>
<td>Martin (1966)</td>
<td>344.0</td>
</tr>
<tr>
<td>Cu</td>
<td>3.1904</td>
<td>2.9912</td>
<td>-0.42301</td>
<td>1.56401</td>
<td>1.846020</td>
<td>226.6 ± 1.0</td>
<td>Martin (1966)</td>
<td>226.2</td>
</tr>
<tr>
<td>Ag</td>
<td>0</td>
<td>2.8436</td>
<td>-0.18862</td>
<td>1.25149</td>
<td>1.377233</td>
<td>162.4 ± 2</td>
<td>Phillips (1939)</td>
<td>161.0</td>
</tr>
<tr>
<td>Au</td>
<td>0</td>
<td>1.2073</td>
<td>-0.06567</td>
<td>1.08757</td>
<td>1.131350</td>
<td>427.7 ± 1.0</td>
<td>Phillips (1939)</td>
<td>430.5</td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
<td>1.2109</td>
<td>-0.20052</td>
<td>1.26736</td>
<td>1.401040</td>
<td>436.4 ± 0.7</td>
<td>Dixon et al. (1965)</td>
<td>2239.6</td>
</tr>
<tr>
<td>Diamond</td>
<td>300</td>
<td>1.2109</td>
<td>-0.20052</td>
<td>1.26736</td>
<td>1.401040</td>
<td>2219 ± 20</td>
<td>Desnoyers and Morrison (1958)</td>
<td>348.9</td>
</tr>
<tr>
<td>Si</td>
<td>77</td>
<td>1.5640</td>
<td>-0.33164</td>
<td>1.44218</td>
<td>1.663271</td>
<td>645 ± 2</td>
<td>Flubacher et al. (1959)</td>
<td>648.9</td>
</tr>
<tr>
<td>Ge</td>
<td>77</td>
<td>1.6651</td>
<td>-0.42353</td>
<td>1.57674</td>
<td>1.865110</td>
<td>374 ± 2</td>
<td>Flubacher et al. (1939)</td>
<td>374.3</td>
</tr>
<tr>
<td>Pb</td>
<td>0</td>
<td>3.8379</td>
<td>-0.39756</td>
<td>1.53008</td>
<td>1.795127</td>
<td>106.7 ± 0.5</td>
<td>Keesom and van der Hoeven, Jr. (1963)</td>
<td>104.9</td>
</tr>
<tr>
<td>V</td>
<td>0</td>
<td>0.8130</td>
<td>0</td>
<td>0.94331</td>
<td>0.886618</td>
<td>399</td>
<td>Heiniger et al. (1966)</td>
<td>399.1</td>
</tr>
<tr>
<td>Nb</td>
<td>4.2</td>
<td>0.5183</td>
<td>0</td>
<td>0.87020</td>
<td>0.740405</td>
<td>277</td>
<td>Heiniger et al. (1966)</td>
<td>275.7</td>
</tr>
<tr>
<td>Ta</td>
<td>0</td>
<td>1.6154</td>
<td>-0.18596</td>
<td>1.24795</td>
<td>1.371927</td>
<td>238</td>
<td>Heiniger et al. (1966)</td>
<td>263.7</td>
</tr>
<tr>
<td>Mo</td>
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<td>0.9024</td>
<td>0</td>
<td>0.95840</td>
<td>0.916797</td>
<td>460</td>
<td>474.5</td>
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</tr>
<tr>
<td>W</td>
<td>0</td>
<td>0.9959</td>
<td>0</td>
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<td>0.996373</td>
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<tr>
<td>Fe</td>
<td>0</td>
<td>2.3431</td>
<td>-0.58298</td>
<td>1.77730</td>
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<td>472.7 ± 6.0*</td>
<td>Dixon et al. (1965)</td>
<td>472.4</td>
</tr>
<tr>
<td>Ni</td>
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<td>1.78764</td>
<td>2.181467</td>
<td>477.4 ± 6.2*</td>
<td>Dixon et al. (1965)</td>
<td>475.9</td>
</tr>
<tr>
<td>Pd</td>
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<td>2.4552</td>
<td>-0.25905</td>
<td>1.34541</td>
<td>1.518109</td>
<td>270</td>
<td>Heiniger et al. (1966)</td>
<td>275.6</td>
</tr>
<tr>
<td>Ir</td>
<td>0</td>
<td>1.3698</td>
<td>-0.30061</td>
<td>1.40082</td>
<td>1.601227</td>
<td>420</td>
<td>Heiniger et al. (1966)</td>
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<tr>
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<td>-0.08081</td>
<td>1.11974</td>
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<td>234.9 ± 0.4*</td>
<td>Dixon et al. (1965)</td>
<td>238.3</td>
</tr>
<tr>
<td>Th</td>
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<td>3.4545</td>
<td>-1.37030</td>
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<td>3.740602</td>
<td>170</td>
<td>Smith and Wolcott (1956)</td>
<td>163.7</td>
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*Refers to a partially transformed sample probably containing about 80% faulted hexagonal close-packed phase.
*Low temperature specific heat data fitted to $C = \gamma T + \beta T^2 + \alpha T^3$ by the method of least squares.
*In the equation given in footnote $\beta$, 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 $\gamma$ and $\Theta_0^c$.
*ADDED IN PROOF: Recently Berg (Phys. Chem. Solids, 30, 69 (1969)) has determined $\Theta_0 = 2401^\circ$ K.
<table>
<thead>
<tr>
<th>Elements</th>
<th>Hopf-Lechner</th>
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<th>Fedorov</th>
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<td>10HL</td>
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<td>314.69</td>
<td>318.44</td>
</tr>
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</tr>
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</tr>
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<td>Ag</td>
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<td>225.43</td>
<td>225.89</td>
</tr>
<tr>
<td>Au</td>
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<td>159.27</td>
<td>160.27</td>
</tr>
<tr>
<td>Al</td>
<td>430.33</td>
<td>430.42</td>
<td>430.51</td>
</tr>
<tr>
<td>Diamond</td>
<td>2239.6</td>
<td>2239.6</td>
<td>2239.6</td>
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<td>Si</td>
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</tr>
<tr>
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<td>373.32</td>
<td>373.33</td>
<td>373.35</td>
</tr>
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<td>103.96</td>
<td>104.47</td>
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<tr>
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<td>399.12</td>
<td>399.10</td>
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<td>274.88</td>
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<tr>
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<td>474.52</td>
<td>474.52</td>
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<tr>
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<td>472.09</td>
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<tr>
<td>Ni</td>
<td>475.42</td>
<td>475.59</td>
<td>475.81</td>
</tr>
<tr>
<td>Pd</td>
<td>274.29</td>
<td>274.74</td>
<td>275.30</td>
</tr>
<tr>
<td>Ir</td>
<td>429.57</td>
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</tr>
<tr>
<td>Pt</td>
<td>237.52</td>
<td>237.83</td>
<td>238.15</td>
</tr>
<tr>
<td>Th</td>
<td>163.28</td>
<td>163.47</td>
<td>163.65</td>
</tr>
</tbody>
</table>
constant data at a higher temperature are employed, the calculated value of the Debye temperature need not be equal to $\Theta_0^c$.

A few years ago, Ludwig (1958) and Leibfried and Ludwig (1961) suggested that owing to anharmonic effects, $\Theta_0^c$ in fact differs from $\Theta_0^{el}$. 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 $\Theta_0^c \neq \Theta_0^{el}$ 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 $\Theta_0^c$ and $\Theta_0^{el}$ to the first order in $\lambda$, $\lambda$ being an ordering parameter.

Elements

Comparison of Calculated values by the Three Methods

Other than from the method of calculation, uncertainty in $\Theta_0^{el}$ may be due to errors in the low-temperature elastic constants. The calculated value of $\Theta_0^{el}$ 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 $\Theta_{0}^{el}$. The same change in $c_{12}$ will produce a negligible change in $\Theta_{0}^{el}$.

The calculated values of $\Theta_{0}^{el}$ 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, $\Theta_{0}^{el}$ 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 $\Theta^c_0$ and $\Theta^{el}_0$. Most of the elements have $\Theta^c_0 > \Theta^{el}_0$, though only by a small amount.

Next we compare the theoretical and experimental $\Theta_0$'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 $70^\circ K$ and the observed value is for a partially transformed sample. Secondly the calculations were carried out from elastic constant data at $78^\circ K$. Consequently it is not surprising that there is a large difference between the observed and the calculated value.

Sodium

The observed value is about $7^\circ K$ higher than the calculated one, but in this case also the calculated value is based on $78^\circ K$ 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 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 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 \(3^\circ\) to \(5^\circ\) 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 \(\eta\) is very close to 1.

Molybdenum and Iridium

The differences between the theoretical and the observed values are rather large (14.5\(^\circ\) and 9.6\(^\circ\) respectively) and better measurements of \(\Theta^c\) 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 \(a, \beta,\) and \(\gamma\) 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 $\Theta^e_0$ by the four methods and the experimental values $\Theta^C_0$. (Debye temperatures are in $^\circ$ K.)

<table>
<thead>
<tr>
<th>Element</th>
<th>T $^\circ$ K</th>
<th>10HL</th>
<th>15HBT</th>
<th>2F</th>
<th>Numerical Integration (Wanner)</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0</td>
<td>91.18</td>
<td>91.181</td>
<td>91.184</td>
<td>91.2</td>
<td>93.3 ± 0.6</td>
</tr>
<tr>
<td>Li</td>
<td>78</td>
<td>318.44</td>
<td>317.21</td>
<td>355.99</td>
<td>317.8</td>
<td>344 ± 2.5</td>
</tr>
<tr>
<td>Na</td>
<td>78</td>
<td>144.26</td>
<td>144.28</td>
<td>159.13</td>
<td>144.3</td>
<td>152.5 ± 2</td>
</tr>
<tr>
<td>K</td>
<td>4.2</td>
<td>88.98</td>
<td>89.28</td>
<td>96.61</td>
<td>89.1</td>
<td>90.6 ± 1.4</td>
</tr>
<tr>
<td>Rb-1</td>
<td>0</td>
<td>54.37</td>
<td>54.62</td>
<td>58.54</td>
<td>54.5</td>
<td>55.6 ± 0.5</td>
</tr>
<tr>
<td>Rb-2</td>
<td>0</td>
<td>54.04</td>
<td>54.31</td>
<td>59.294</td>
<td>54.2</td>
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</tr>
<tr>
<td>Cu</td>
<td>0</td>
<td>343.69</td>
<td>344.38</td>
<td>347.21</td>
<td>344.0</td>
<td>345.6 ± 1.0</td>
</tr>
<tr>
<td>Ag</td>
<td>0</td>
<td>225.89</td>
<td>226.46</td>
<td>227.87</td>
<td>226.2</td>
<td>226.6 ± 1.0</td>
</tr>
<tr>
<td>Au</td>
<td>0</td>
<td>160.27</td>
<td>161.74</td>
<td>162.50</td>
<td>161.0</td>
<td>162.4 ± 2</td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
<td>430.51</td>
<td>430.56</td>
<td>430.56</td>
<td>430.5</td>
<td>427.7 ± 1.0</td>
</tr>
</tbody>
</table>

<p>|                    |              |       |       |     |                               | 436.4 ± 0.7  |</p>
<table>
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<th>T °K</th>
<th>10HL</th>
<th>15HBT</th>
<th>2F</th>
<th>Numerical Integration</th>
<th>Experimental</th>
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<td>2239.6</td>
<td>2239.6</td>
<td>2219 ± 20</td>
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<td>648.86</td>
<td>648.87</td>
<td>648.94</td>
<td>648.9</td>
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<tr>
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<td>373.35</td>
<td>373.44</td>
<td>373.4</td>
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<td>399.18</td>
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<td>399</td>
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<tr>
<td>Nb</td>
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<td>Ta</td>
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<td>460</td>
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<tr>
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<td>475.98</td>
<td>477.14</td>
<td>475.9</td>
<td>477.4 ± 6.2</td>
</tr>
<tr>
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<td></td>
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<tr>
<td>Element</td>
<td>( T ) °K</td>
<td>( 10H )</td>
<td>( 15H )</td>
<td>( 15HBT )</td>
<td>( 2E )</td>
<td>( 2E )</td>
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<td>----------</td>
<td>----------</td>
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<tr>
<td>Pd</td>
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<td>272.92</td>
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<td>429.67</td>
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<td>238.3</td>
<td>234.9 ± 0.4</td>
<td>234.9 ± 0.4</td>
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<tr>
<td>Th</td>
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<td>165.72</td>
<td>163.81</td>
<td>170</td>
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</tbody>
</table>
Recently, Wanner (1970) has used the same data for the elastic constants as those used here and has calculated $\Theta_o^{el}$ by numerical integration taking 200 different directions in $\frac{1}{16}$ of the unit sphere. Table IV shows $\Theta_o^{el}$ as obtained by Wanner and the 10HL, 15HBT, 2F and $\Theta_o^c$ from experiment. The agreement between $\Theta_o^{el}$ 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" ($\Theta_o^{el}$ theor.).

**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 $\Theta_o^{el}$ 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 $\Theta_o^{el}$ when $\eta > 2.5$.

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

<table>
<thead>
<tr>
<th>Solid</th>
<th>T (°K)</th>
<th>Molecular Wt (a. m. u.)</th>
<th>Density ρ (g/cm^3)</th>
<th>c_{11} (10^{11} dyn/cm^2)</th>
<th>c_{12} (10^{11} dyn/cm^2)</th>
<th>c_{44} (10^{11} dyn/cm^2)</th>
<th>Source of data</th>
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</thead>
<tbody>
<tr>
<td>LiF</td>
<td>0.0</td>
<td>25.9374</td>
<td>2.6757^a</td>
<td>12.460</td>
<td>4.240</td>
<td>6.490</td>
<td>Briscoe and Squire (1957)</td>
</tr>
<tr>
<td>LiCl-1</td>
<td>4.2</td>
<td>42.3920</td>
<td>2.1110</td>
<td>6.074</td>
<td>2.270</td>
<td>2.692</td>
<td>Lewis et al. (1967)</td>
</tr>
<tr>
<td>LiCl-2</td>
<td>4.2</td>
<td>42.3920</td>
<td>2.1321</td>
<td>5.860</td>
<td>2.086</td>
<td>2.671</td>
<td>Marshall et al. (1967)</td>
</tr>
<tr>
<td>LiBr</td>
<td>0.0</td>
<td>86.8480</td>
<td>3.5768</td>
<td>4.721</td>
<td>1.590</td>
<td>2.052</td>
<td>Marshall &amp; Cleavelin (1969)</td>
</tr>
<tr>
<td>NaF-1</td>
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<td>41.9882</td>
<td>2.8510</td>
<td>10.850</td>
<td>2.290</td>
<td>2.899</td>
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</tr>
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<td>41.9882</td>
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<td>2.242</td>
<td>2.947</td>
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</tr>
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<td>NaCl-1</td>
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<td>58.4428</td>
<td>2.2170</td>
<td>5.733</td>
<td>1.123</td>
<td>1.331</td>
<td>Peterson et al. (1967)</td>
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<tr>
<td>NaCl-2</td>
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<td>58.4428</td>
<td>2.1669</td>
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<td>1.194</td>
<td>1.327</td>
<td>Fugate and Schuele (1966)</td>
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<td>0.781</td>
<td>Claytor &amp; Marshall (1960)</td>
</tr>
<tr>
<td>Solid</td>
<td>T (°K)</td>
<td>Molecular Wt (a.m. u.)</td>
<td>Density $\rho$ (g/cm$^3$)</td>
<td>$c_{11}$ (10$^{11}$ dyn/cm$^2$)</td>
<td>$c_{12}$ (10$^{11}$ dyn/cm$^2$)</td>
<td>$c_{44}$ (10$^{11}$ dyn/cm$^2$)</td>
<td>Source of data</td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
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<td>-----------------------------</td>
<td>-------------------------------</td>
<td>-------------------------------</td>
<td>-------------------------------</td>
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<td>2.0448$^a$</td>
<td>4.832</td>
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<td>0.663</td>
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<td>Vallin et al. (1964)</td>
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$^a$ 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>
<thead>
<tr>
<th>Alkali Halides</th>
<th>Calculated values of Debye Temperature in °K</th>
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TABLE VII

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

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<th>3HBT</th>
<th>6HBT</th>
<th>9HBT</th>
<th>15HBT</th>
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<td>6HBT</td>
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<tr>
<td>CsBr</td>
<td>149.32</td>
<td>149.47</td>
<td>149.47</td>
<td>149.47</td>
</tr>
<tr>
<td>CsI</td>
<td>126.11</td>
<td>126.21</td>
<td>126.21</td>
<td>126.21</td>
</tr>
</tbody>
</table>
TABLE VIII: Values of $z_{\text{min}}$, $z_{\text{max}}$, $K$, $\eta$, and theoretical and experimental Debye temperatures.

<table>
<thead>
<tr>
<th>Alkali Halides</th>
<th>$z_{\text{min}}$</th>
<th>$z_{\text{max}}$</th>
<th>$K$</th>
<th>$\eta$</th>
<th>Source</th>
<th>$\Theta_0$ (°K)</th>
<th>$\Theta_0$ (°K)</th>
<th>$\Theta_0$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>-0.339860</td>
<td>1.088150</td>
<td>1.793220</td>
<td>1.351550</td>
<td>Martin (1955)</td>
<td>737 ± 9</td>
<td>733.07</td>
<td>722 ± 6</td>
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<tr>
<td>LiCl-L</td>
<td>0.233590</td>
<td>1.321450</td>
<td>1.467179</td>
<td>1.4154</td>
<td>Scales (1958)</td>
<td>428.85</td>
<td>425.47</td>
<td>422 ± 6</td>
</tr>
<tr>
<td>LiCl-2</td>
<td>-0.244550</td>
<td>1.327790</td>
<td>1.491690</td>
<td>1.4155</td>
<td>Scales (1958)</td>
<td>428.85</td>
<td>425.47</td>
<td>422 ± 6</td>
</tr>
<tr>
<td>LiBr</td>
<td>0.0 ± 0.18280</td>
<td>1.243040</td>
<td>1.364556</td>
<td>1.3108</td>
<td>Scales (1958)</td>
<td>491.85</td>
<td>274.72</td>
<td>496.57</td>
</tr>
<tr>
<td>NaF-1</td>
<td>0.652622</td>
<td>0.6773</td>
<td>0.652622</td>
<td>0.6773</td>
<td>Scales (1958)</td>
<td>491.85</td>
<td>274.72</td>
<td>496.57</td>
</tr>
<tr>
<td>NaCl-1</td>
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<td>0.6773</td>
<td>0.652622</td>
<td>0.6773</td>
<td>Scales (1958)</td>
<td>491.85</td>
<td>274.72</td>
<td>496.57</td>
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<tr>
<td>NaCl-2</td>
<td>0.652622</td>
<td>0.6773</td>
<td>0.652622</td>
<td>0.6773</td>
<td>Scales (1958)</td>
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<td>496.57</td>
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<td>0.652622</td>
<td>0.6773</td>
<td>Scales (1958)</td>
<td>491.85</td>
<td>274.72</td>
<td>496.57</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.652622</td>
<td>0.6773</td>
<td>0.652622</td>
<td>0.6773</td>
<td>Scales (1958)</td>
<td>491.85</td>
<td>274.72</td>
<td>496.57</td>
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<td>Solid</td>
<td>T $^\circ$K</td>
<td>z$_{\text{min}}$</td>
<td>z$_{\text{max}}$</td>
<td>K</td>
<td>$\eta$</td>
<td>$\Theta_0^\text{el\ theor.}$ ($^\circ$K)</td>
<td>$\Theta_0^\text{c\ exp.}$ ($^\circ$K)</td>
<td>Source</td>
</tr>
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<td>-------</td>
<td>------------</td>
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<td>-------</td>
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<td>-------------------------------</td>
</tr>
<tr>
<td>Nal</td>
<td>4.2</td>
<td>0</td>
<td>1.000000</td>
<td>0.529866</td>
<td>0.5272</td>
<td>167.51</td>
<td>164.2 ± 1</td>
<td>Barron et al. (1957)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>164.3 ± 1.5</td>
<td>Martin (1964)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>163.2</td>
<td>Claytor and Marshall (1960)</td>
</tr>
<tr>
<td>KF-1</td>
<td>4.2</td>
<td>0</td>
<td>1.000000</td>
<td>0.430863</td>
<td>0.4296</td>
<td>332.82</td>
<td></td>
<td>Harrison (1968)</td>
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<td>KF-2</td>
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<td>0</td>
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<td>0.439606</td>
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<td>1.000000</td>
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<td>0.3090</td>
<td>236.00</td>
<td>233 ± 3</td>
<td>Harrison (1968)</td>
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<td></td>
<td>235.1 ± 0.5</td>
<td>Barron et al. (1957)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>233 ± 3</td>
<td>Keesom &amp; Pearlman (1953)</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>229 ± 2</td>
<td>Seward &amp; Narayananamurti (1966)</td>
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<td>KBr</td>
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<td>1.000000</td>
<td>0.367106</td>
<td>0.3511</td>
<td>165.11</td>
<td>174.3 ± 0.7</td>
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<td></td>
<td>173.8 ± 1.5</td>
<td>Martin (1964)</td>
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<tr>
<td>KI</td>
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<td>1.000000</td>
<td>0.195219</td>
<td>0.2329</td>
<td>130.58</td>
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<td>Barron et al. (1957)</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>133.1 ± 1.5</td>
<td>Martin (1964)</td>
</tr>
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<td></td>
<td></td>
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<td></td>
<td>128.3</td>
<td>Şcales (1958)</td>
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<td>RbF</td>
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<td>Solid</td>
<td>$T_{\text{oK}}$</td>
<td>$z_{\text{min}}$</td>
<td>$z_{\text{max}}$</td>
<td>K</td>
<td>$\eta$</td>
<td>$\Theta_{o_{\text{e}}}^{\text{thor.}}$ (oK)</td>
<td>$\Theta_{o_{\text{c}}}^{\text{exp.}}$ (oK)</td>
<td>Source</td>
</tr>
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<td>-------</td>
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<td>0.255464</td>
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<td>136.14</td>
<td>107.52</td>
<td>Alexander &amp; Pohl (1957)</td>
</tr>
<tr>
<td>RbI</td>
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<td>1.000000</td>
<td>0.223441</td>
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<td>103.92</td>
<td>149.47</td>
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<tr>
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<td>1.000000</td>
<td>0.589510</td>
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<td>159.39</td>
<td>126.21</td>
<td>Marshall &amp; Kundel (1969)</td>
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<td>0.834290</td>
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<td>149.47</td>
<td>127.67</td>
<td>Marshall &amp; Kundel (1969)</td>
</tr>
<tr>
<td>CsI</td>
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<td>1.000000</td>
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<td>0.8488</td>
<td>126.21</td>
<td>127.67</td>
<td>Marshall &amp; Kundel (1969)</td>
</tr>
</tbody>
</table>
In Table VIII it is seen that \( \eta \) 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 \( \Theta_{o}^{el} \) and \( \Theta_{o}^{c} \) 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 \( \Theta_{o}^{c} \)'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 $\Theta^\text{el}_o$ differing only by about 1%, both lying within the experimental error of $\Theta^C_o$.

LiBr: There is no $\Theta^C_o$ 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: $\Theta^\text{el}_o$ from the three sets of elastic constants agree amongst themselves to within .3% and fall within the experimental error of $\Theta^C_o$.

NaBr: There is no $\Theta^C_o$ 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 $\Theta^C_o$ to compare with.
KCl: The agreement with the experiment is satisfactory in three cases but \( \kappa^c_0 \) 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 $\Theta_o$ of LiI to be $\approx 200 \pm 25^\circ K$. The second correlation (Fig. 3) gives $210 \pm 5^\circ K$. 
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