THE NORMAL MODES OF VIBRATION OF A CRYSTAL LATTICE

Thesis by

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In Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1939

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I wish to acknowledge my sincere gratitude to Prof. W. V. Houston whose valuable suggestions and frequent assistance have made this work possible.

SUMMARY

An atomic model is set up for the purpose of finding the normal modes of vibration of a crystal lattice. The potential energy is assumed to be a quadratic function of the displacements of the atoms from their equilibrium positions. Actual solutions of the secular equation are found for tungsten, a body-centered cubic crystal, whose elastic properties happen to satisfy the condition for isotropy. The interaction between an atom and its fourteen nearest neighbors is considered and central forces and the Cauchy relations are assumed. A method of selecting suitable atomic force constants from macroscopic elastic properties is given.

Numerical methods yield a frequency distribution which is characterized by two rather steep maxima. The result is used in evaluating the specific heat of tungsten as a function of temperature and a better fit with observed values is obtained by this method than by the particular Debye distribution with which it agrees at low frequencies. Calculations are also carried out for the variation of the intensity of reflection of x-rays with temperature, but there are is no experimental data for tungsten to compare with the theory.

PART I, INTRODUCTION TO THE PROPERTIES OF SOLIDS

Various models have been proposed for the description of solid bodies and the consequences worked out in great detail. The increasing complexity of these conceptions of the solid state have generally led to a more complete understanding of its nature and properties, although much remains to be done in a quantitative way. These different theories will be discussed briefly, their experimental verification examined, and the position of the present work indicated.

A solid can be represented a priori either as a continuum or as an arrangement of atoms. The continuum hypothesis considers a solid body as completely filling a region of space with no ultimate sub-structure. The atomic theory pictures a solid as made up of characteristic atoms or molecules bound together by forces between the individual particles. The atomicity of matter is of course supported by an enormous body of evidence and so the idea of a continuum is now admitted only as a convenient mathematical fiction to be used when distances large compared with atomic magnitudes are involved.

A distinction is often made between two types of solids. Amorphous substances are supercooled liquids with no definite arrangement of atoms, while crystalline solids are characterized by a definite atomic lattice, which gives the spatial configuration of the atoms in their equilibrium positions. In a single crystal this orderly arrangement continues throughout the body. On the other hand, a polycrystalline material is composed of small single crystals oriented in a random way with respect to each other. Due to this haphazard internal arrangement, polycrystals may be considered isotropic from a large scale point of view.

Because of their fundamental nature and relative simplicity single crystals afford a basis for a theoretical discussion. Recent progress in growing single crystals and accumulating data about them permits a comparison of observation and theory in some cases. Also, when there is sufficient knowledge about the nature of single crystals, information pertaining to polycrystals can be obtained by averaging over direction in the solid, if surface effects where the small crystals join together are neglected.

The symmetry properties of crystals can be determined from their form and their thermal, electrical, optical, and mechanical behavior. However, to have a complete atomic description of the crystal, it is necessary to know the exact equilibrium positions of the atoms and the forces between them. The question of structure has been solved in most cases by x-ray analysis, but the forces which maintain that structure have been the subject of many assumptions and hypotheses. These must be considered in some detail to provide a background for the work presented later.

SECTION 1, ELASTICITY.

From a macroscopic viewpoint certain phenomenological statements about the forces involved in the crystal are contained in its elastic properties. These are expressed in a form based on the continuum conception of a solid and must be interpreted from the atomic standpoint. The fundamental feature of the elasticity of solids is embodied in Hooke's law, which states that the force necessary to change the shape or size of a solid is directly proportional to the distortion produced, or more precisely that stress is proportional to strain. Hooke's law is only a first approximation, valid in the limit of vanishing strain. The constant of proportionality depends on the material and the nature of the strain.

For a body of volume v subject to a hydrostatic pressure p, the bulk modulus is defined by the relation, $\kappa = -v(dp/dv)$. The reciprocal of the bulk modulus is the compressibility. When a body of length l and cross-sectional area A is stretched or compressed by a force f acting in a certain direction, the constant is called Young's modulus and is given by the equation, $Y = (f/A)/(\Delta l/l)$. In such a case the ratio of the lateral strain to the longitudinal strain is known as Poisson's ratio σ and has a value of $\frac{1}{\cancel{4}_{2}}$ if the volume of the body is unchanged. For a shearing stress the constant involved is the modulus of rigidity, $\eta = (f/A)/\theta$ where A is the area of the plane surface of the body over which the force f acts in twisting it through an angle θ.

These four elastic constants are not independent as there are two relations between them resulting from geometrical considerations.[1] For example, $Y = 9\eta\kappa/(3\kappa + \eta)$ and $\sigma = (3\kappa - 2\eta)/(6\kappa + 2\eta)$. A polycrystalline material whose elastic properties don't depend on direction has then only two independent constants. For a single crystal the direction is significant and the number of constants required depends on the symmetry.

In order to express adequately the elastic phenomena for single crystals, a generalization of Hooke's law is necessary. Voigt[2] has shown that stress and strain are tensors of the second rank and there is a tensor equation connecti~~on~~ng them. Let X_{ij} be the component of stress equal to the force in the i direction on a unit surface normal to the j direction. In common with other tensor indices in this discussion, i and j assume the values, one, two, or three, corresponding to the three coordinate axes. Let e_{kl} be the component of strain equal to the relative displacement of neighboring points in the body or $\partial u_k/\partial x^l$, where u is the actual displacement. The generalization of Hooke's law is contained in the equation,

$$X_{ij} = c_{ij}^{kl}\, e_{kl} \tag{1}$$

the summation convention being used. c_{ij}^{kl} is an elastic constant.

The condition for rotational equilibrium makes X_{ij} a symmetrical tensor, i.e., $X_{ij} = X_{ji}$. The strain tensor can be represented as the sum of a symmetrical and an antisymmetrical tensor. $e_{kl} = \frac{1}{2}(\partial u_k/\partial x^l + \partial u_l/\partial x^k) + \frac{1}{2}(\partial u_k/\partial x^l - \partial u_l/\partial x^k)$. The antisymmetrical part corresponds to rigid body rotation and may be disregarded if only actual strains are to be considered. In that case, $e_{kl} = e_{lk}$, both the stress and strain tensors are symmetrical, and the eighty-one elastic constants can be reduced to thirty-six by redefining them according to the equations:

$$
\begin{aligned}
X_{11} &= c_{11}e_{11} + c_{12}e_{22} + c_{13}e_{33} + c_{14}e_{23} + c_{15}e_{13} + c_{16}e_{12}.\\
X_{22} &= c_{21}e_{11} + c_{22}e_{22} + c_{23}e_{33} + c_{24}e_{23} + c_{25}e_{13} + c_{26}e_{12}.\\
X_{33} &= c_{31}e_{11} + c_{32}e_{22} + c_{33}e_{33} + c_{34}e_{23} + c_{35}e_{13} + c_{36}e_{12}.\\
X_{23} &= c_{41}e_{11} + c_{42}e_{22} + c_{43}e_{33} + c_{44}e_{23} + c_{45}e_{13} + c_{46}e_{12}.\\
X_{13} &= c_{51}e_{11} + c_{52}e_{22} + c_{53}e_{33} + c_{54}e_{23} + c_{55}e_{13} + c_{56}e_{12}.\\
X_{12} &= c_{61}e_{11} + c_{62}e_{22} + c_{63}e_{33} + c_{64}e_{23} + c_{65}e_{13} + c_{66}e_{12}.
\end{aligned} \tag{2}
$$

This means that the sum, $c_{ij}^{kl} + c_{ij}^{lk}$ or $c_{ji}^{kl} + c_{ji}^{lk}$, is denoted by a single constant.

From the stress and strain tensors a scalar can be formed by tensor multiplication and contraction. This is the potential energy V of the strained crystal.

$$V = \frac{1}{2}\,(X_{11}e_{11} + X_{22}e_{22} + X_{33}e_{33} + X_{23}e_{23} + X_{13}e_{13} + X_{12}e_{12}).$$

If the expressions for the stresses are substituted from the generalized Hooke's law equations, a quadratic function in the strains is obtained with the elastic constants as coefficients. Now, if the forces involved are conservative and thus derivable from a potential, the following relations are satisfied:

$$X_{ij} = \partial V/\partial e_{ij}.$$

$$\therefore \quad \partial X_{ij}/\partial e_{kl} = \partial^2 V/\partial e_{ij}\partial e_{kl} = \partial^2 V/\partial e_{kl}\partial e_{ij} = \partial X_{kl}/\partial e_{ij}.$$

This means that $c_{12} = c_{21}$, etc., so that the symmetry of the elastic constants reduces their number from thirty-six to twenty-one. The potential energy can then be written in the form

$$
\begin{aligned}
V = \tfrac{1}{2}\, c_{11}e_{11}^2 + c_{12}e_{11}e_{22} + c_{13}e_{11}e_{33} + c_{14}e_{11}e_{23} + c_{15}e_{11}e_{23} + c_{16}e_{11}e_{12} \\
+ \tfrac{1}{2}\, c_{22}e_{22}^2 + c_{23}e_{22}e_{33} + c_{24}e_{22}e_{23} + c_{25}e_{22}e_{13} + c_{26}e_{22}e_{12} \\
+ \tfrac{1}{2}\, c_{33}e_{33}^2 + c_{34}e_{33}e_{23} + c_{35}e_{33}e_{13} + c_{36}e_{33}e_{12} \\
+ \tfrac{1}{2}\, c_{44}e_{23}^2 + c_{45}e_{23}e_{13} + c_{46}e_{23}e_{12} \\
+ \tfrac{1}{2}\, c_{55}e_{13}^2 + c_{56}e_{13}e_{12} \\
+ \tfrac{1}{2}\, c_{66}e_{12}^2 .
\end{aligned}
\tag{3}
$$

By performing symmetry operations which correspond to various special types of crystals a further reduction in the number of elastic constants is obtained. A triclinic crystal with no symmetry at all has the full complement of twenty-one constants. A monoclinic crystal with one symmetry plane has only thirteen constants. Crystals belonging to the rhombic system have two perpendicular reflection planes and nine elastic constants. Trigonal crystals with a threefold symmetry axis and tetragonal crystals with a fourfold symmetry axis have six constants. For a hexagonal crystal having a sixfold symmetry axis there are five constants. The cubic or regular system has a threefold symmetry axis and two symmetry planes, so that only three constants remain. The symmetry elements mentioned are the minimum number from which others may be derived in some cases. Finally, as stated before, two constants suffice for an isotropic material.

In order to demonstrate the principles involved and to have the results for later use, the reduction of the number of elastic constants will be carried out for a cubic crystal. Let x, y, and z refer to orthogonal coordinate axes coinciding with the edges of the cube. Replacing x by - x corresponds to reflection in the yz plane, which is a symmetry plane of the cube. This means that the form of the potential energy must not be changed by such a symmetry operation.

The definition of strains as relative displacements, $e_{ij} = \partial u_i/\partial x^j$ shows that reversing the direction of the x-axis changes the sign of e_{12} and e_{13} but leaves the others unchanged. Since the form of the potential energy is to be preserved, terms which change sign must vanish because the elastic coefficient is zero. The result is that c_{15}, c_{25}, c_{35}, c_{45}, c_{16}, c_{26}, c_{36}, c_{46}, and c_{56} are all equal to zero for a cubic crystal. In like manner the xy symmetry plane leads to the vanishing of c_{14}, c_{24}, and c_{34}.

A cyclic interchange of the axes is equivalent to a rotation of the cube through an angle of 120° about the body diagonal and such an operation also produces no change in the configuration of the crystal. Replacing x by y, y by z, and z by x results in substituting 1 for 2, 2 for 3, and 3 for 1 in the strain indices. This shows that $c_{11} = c_{22} = c_{33}$, $c_{12} = c_{13} = c_{23}$, and $c_{44} = c_{55} = c_{66}$, so that the elastic constants of a cubic crystal can be represented by the array

$$\begin{array}{cccccc} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ & c_{11} & c_{12} & 0 & 0 & 0 \\ & & c_{11} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & & & & c_{44} & 0 \\ & & & & & c_{44} \end{array} \tag{4}$$

Another way of exhibiting the elastic properties of a crystal is by means of the elastic moduli, s_{ij}^{kl}, defined by the inverse of the generalized Hooke's law, $e_{ij} = s_{ij}^{kl} X_{kl}$. If the determinant of the tensor is considered, c_{ij}^{kl} is equal to the cofactor of s_{ij}^{kl} divided by the value of the determinant of the s_{ij}^{kl}. In the case of the cubic crystal,

$$c_{11} = (s_{11} + s_{12})/(s_{11} + 2\ s_{12})(s_{11} - s_{12}),$$
$$(5) \qquad c_{11} - c_{12} = 1/(s_{11} - s_{12}), \qquad c_{44} = 1/s_{44}.$$

This completes the discussion of elasticity from a macroscopic point of view. It must be emphasized, however, that only a first approximation has been considered and that more complicated features such as the elastic limit, yield point, plasticity, and rupture find no place in a theory based on Hooke's law.

It is now necessary to mention attempts to secure an atomic interpretation of the large scale elastic properties of crystals. The assumption of central forces between atoms in a crystal was first used by Cauchy[3] to reduce the number of elastic constants for a triclinic crystal from twenty-one to fifteen by means of the following relations:

$$c_{23} = c_{44},\ c_{13} = c_{55},\ c_{12} = c_{66}$$
$$(6) \qquad c_{56} = c_{14},\ c_{46} = c_{25},\ c_{45} = c_{36}.$$

In particular for a cubic crystal this requires that $c_{12} = c_{44}$. A detailed derivation will be given later.

For most substances the Cauchy relations are not experimentally verified at all, and consequently the atomic approach was long discredited. The table[4] of observed elastic constants for cubic crystals illustrates the discrepancies, which are quite large except for some of the alkali halides. The units are 10^{11} dynes/cm^2.

	c_{11}	c_{12}	c_{44}
W	51.3	20.6	15.3
Li	1.53	1.19	1.33
Na	0.972	0.829	0.579
Ag	12.0	8.97	4.37
Cu	17.0	12.3	7.52
Au	18.7	15.0	4.37
Fe	23.7	14.1	11.6
Al	10.8	6.21	2.84
KBr	3.33	0.579	0.615
KCl	3.75	0.199	0.656
KJ	2.67	0.427	0.406
NaBr	4.40	1.32	1.34
NaCl	4.77	1.32	1.32

Born[5] has shown that the Cauchy relations do not hold even for central forces when the basic cell of the crystal contains several atoms whose relative positions in the cell may be changed. The crystal is then represented by the superposition of several simple lattices which may be displaced with respect to each other, and this actually occurs for residual rays in the infra-red. Born's theory does not explain the failure of the Cauchy relations for monatomic metals where each atom is a symmetry center and there is no reason for such a relative displacement of lattices. Since the method used by Born is the basis of the present work, it will be considered in detail later.

The present explanation for the disagreement between Cauchy's theory and the observed elastic properties of metals is that the free electrons affect elasticity in a way not at all provided for by simple atomic hypotheses. The application of quantum mechanics to this problem in the form of the Wigner-Seitz method has been fairly successful in computing the binding energy of the crystal, the interatomic distances, and the elastic constants. Since a qualitative conclusion of the theory in regard to the Cauchy relations will be essential here, a brief discussion of the principles involved will be presented.

Fuchs[6] has applied the Wigner-Seitz method to monovalent metals such as sodium and copper. The procedure is to surround each atom by a polyhedron whose faces are the perpendicular bisectors of the lines connecting the atom with its neighbors. The wave equation is then solved in each cell with the boundary condition that the normal derivative of the wave function shall vanish over the surface of the polyhedron. This guarantees the necessary periodicity of the solution.

The total energy of the crystal consists of the kinetic energy of the electrons and the potential energy of both ions and electrons. It is shown that the contribution to the energy due to the valence electrons depends only on the atomic volume, i.e., the volume of the polyhedral cell. On the other hand, the electrostatic energy of the lattice and the exchange energy between the closed shells of ions are functions of the interatomic distances and are changed by any distortion of the crystal even if the volume is unaltered. Therefore, elastic constants involved in a strain where the volume is not changed fit in with the assumptions of Cauchy's theory since electrostatic and exchange effects may be represented by central forces. The failure of the Cauchy relations is then due to any constant depending on the volume of the crystal and thereby on the presence of "free" electrons.

A strain not affecting the volume results when there is a compression in one direction and an equal expansion at right angles. In that case Hooke's law for a cubic crystal becomes $X_{11} = X_{22} = (c_{11} - c_{12})e_{11}$ and the ratio of stress to strain is $(c_{11} - c_{12}) = \frac{1}{2}\, \partial^2 V/\partial e_{11}^2$, when $e_{22} = -e_{11}$. The other illustration is a pure shear where only e_{23} differs from zero and the pertinent equation is $X_{23} = c_{44}e_{23}$ and $c_{44} = \partial^2 V/\partial e_{23}^2$. Finally, an example of strain which does change the volume is a uniform compression where $X_{11} = X_{22} = X_{33} = (c_{11} + 2c_{12})e_{11}$ and the bulk modulus is $(1/3)(c_{11} + 2c_{12})$ or $\frac{1}{3}\, \partial^2 V/\partial e_{11}^2$, when $e_{11} = e_{22} = e_{33}$.

Now the atomic model to be used later in this work does not take the electrons into account and so leads to the Cauchy relations. In order to get some information about atomic forces it is necessary to have suitable elastic constants for such a model. The procedure then is to take the observed values of c_{44} and $c_{11} - c_{12}$ which are not affected by the "free" electrons, and to use the Cauchy relation for the third condition instead of the experimental bulk modulus. This seems to be the only satisfactory method of relating empirical elastic properties to a simple atomic model.

SECTION 2, SPECIFIC HEAT.

There are other problems in crystal physics besides connecting macroscopic elastic constants with atomic forces. The most significant of these is the computation of the specific heat based on certain assumptions about the nature of the solid state. The first attempt at such a theory was the explanation given for the experimental law of Dulong and Petit[7], which states that at room temperature or thereabouts the specific heat of all solid elements is approximately 6.4 calories per mole per degree centigrade. This clearly shows that an atomic phenomenon is involved since the specific heat is the same for an equal number of atoms of different substances.

According to Boltzmann's principle, the probability of finding one of a system of particles in the space dv when thermal equilibrium is established is proportional to $[\exp(-\mathcal{E}/kT)]\,dv$, where $\mathcal{E}$ is the total energy of the particle in the given position, k is Boltzmann's constant, and T is the absolute temperature. Now, when each particle is acted on by elastic forces so that the potential energy is a quadratic function of the displacement from equilibrium, the average energy per degree of freedom turns out to be kT and is entirely independent of the frequency of vibration according to this equipartition theorem[8]. If it is assumed that a solid consists of atoms vibrating in such a manner, the internal energy U is just 3NkT per mole, where N is Avogadro's number. Only the three degrees of translational freedom are considered, the supposition being made that there are no rotational effects.

When the temperature of the solid is raised but the volume is not allowed to change, no work is done against the surroundings and the heat absorbed equals the increase in internal energy. Therefore, the specific heat at constant volume is the rate of change of the internal energy with respect to the temperature. $C_v = (\partial U/\partial T)_v = 3Nk = 3R = 5.96$ calories per mole per degree centigrade; R is the gas constant.

The observed specific heats however are measured at constant pressure and by applying thermodynamical principles the difference between C_p and C_v can be derived.[9] From the first law, $dQ = (\partial U/\partial T)_v dT + [(\partial U/\partial v)_T + p]\,dv$, dQ being the heat absorbed. $C_p - C_v = [(\partial U/\partial v)_T + p](\partial v/\partial T)_p$.
The specific heat at constant pressure exceeds that at constant volume because of the additional energy required to overcome the external pressure and the internal forces when the solid expands.

According to the second law of thermodynamics, dQ/T is an exact differential and so the reciprocity relation applies, i.e., $\{\partial[(1/T)(\partial U/\partial T)_v]/\partial v\}_T = \{\partial[(1/T)(\partial U/\partial v)_T + (p/T)]/\partial T\}_v$, or $(\partial U/\partial v)_T + p = T(\partial p/\partial T)_v$ and $C_p - C_v = T(\partial p/\partial T)_v(\partial v/\partial T)_p$. Now, $(\partial v/\partial T)_p = \alpha v$ and $(\partial p/\partial T)_v = -(\partial p/\partial v)_T(\partial v/\partial T)_p = \kappa\alpha$, where α is the volume coefficient of expansion and κ is the bulk modulus. Therefore,

$$(7) \qquad C_p - C_v = \kappa\alpha^2 vT = (\kappa\alpha^2 A/\rho)T,$$

ρ being the density and A the atomic weight. This formula is used to obtain C_v from the observed values of C_p when the temperature is sufficiently high to make the difference appreciable. Combining this expression with the equipartition value results in the equation:

$$(8) \qquad C_p = 5.96 + (\kappa\alpha^2A/\rho)T,$$

a linear function of the temperature insofar as κ and α are constant. The specific heat at constant pressure would thus have the value 3R at absolute zero and increase slowly with the temperature, the coefficient of T being of the order of 10^{-4} cal. per mole per °C. in the case of tungsten, for example. The values at room temperature are generally in fair agreement with experiment.

There are however, important exceptions to the law of Dulong and Petit. For instance, at room temperature diamond has a specific heat of only 1.5 cal. per mole per °C. It was long realized also that specific heats decrease as the temperature is lowered in a way entirely inconsistent with the equipartition theorem. The stimulus for a detailed investigation of this point was provided by Nernst's heat postulate[10], which states that the entropy is finite at all temperatures. Now, $S(T) - S_0 = \int_0^T dQ/T = \int_0^T (C_V/T)dT$, if S is the entropy and if the volume is unchanged. Unless C_V vanishes at absolute zero, the integral would become logarithmically infinite. To test this conclusion Nernst and his collaborators measured the specific heats of many solids and found a characteristic rapid decrease as the temperature was lowered.

At about the same time the development of the quantum theory applied to radiation by Planck[11] provided a method of improving on the classical theory. Planck postulated that the average energy of a harmonic oscillator is $h\nu/[\exp(h\nu/kT) - 1]$ instead of kT. The new expression depends on ν, the frequency of vibration, and h, a universal constant representing the quantum of action, and was obtained by not letting $h\nu$, the energy, approach zero in the customary way which leads to the equipartition theorem.

This result, first used for the vibrations of electrons concerned in radiation, was soon utilized by Einstein[12] for the atomic vibrations involved in specific heat theory. It was assumed that each atom in the solid has the same frequency of vibration so that the internal energy is

$$U = 3Nh\nu/[\exp(h\nu/kT) - 1]. \tag{9}$$

The specific heat at constant volume is obtained by differentiating U with respect to T.

$$C_v = (3Nh^2\nu^2/kT^2)/[\exp(h\nu/kT) - 1]^2. \tag{10}$$

Let $h\nu/k = \theta$ a characteristic temperature depending on the substance. Then,

$$C_v = 3R(\theta/T)^2/[\exp(\theta/T) - 1]^2. \tag{11}$$

This means that the specific heat would vary in the same way for all substances, a difference in frequency simply resulting in a change of temperature scale. As T increases, C_v approaches the equipartition value 3R, while at low temperatures C_v vanishes exponentially, thus satisfying Nernst's postulate.

In order to connect ν or θ with the observed properties of the solid it is necessary to employ the usual relation for the force constant f. $\nu = (1/2\pi)(f/m)^{\frac{1}{2}}$. Einstein related f to the compressibility by assuming that there are elastic forces between each atom and its twenty-six nearest neighbors in a cubic lattice and that the effect is the same as if the neighboring atoms were uniformly smeared over the surface of a sphere around the central atom. The result was

$$(12)\quad \nu = (\sqrt{6}/2\pi)(\pi/6)^{\frac{1}{3}}(N^2\kappa^3/A^2\rho)^{\frac{1}{6}} = 2.66 \times 10^7(\kappa^3/A^2\rho)^{\frac{1}{6}}.$$

This can be obtained by dimensional analysis except for the numerical factor, which only gives the order of magnitude anyway because of the rough approximations made in the derivation. In the present work a frequency which might be considered as corresponding to Einstein's will be computed for the case where one atom is allowed to vibrate, the rest being held stationary.

This assumption of a single frequency of vibration is the principal objection to Einstein's theory, for any interaction between atoms would lead to a coupled system with many modes of vibration. The fact that oscillations of one atom affect others is demonstrated by the existence of elastic waves in solids. Therefore, it is not surprising that the Einstein formula gives a decrease of specific heat with temperature which is more rapid than that found by experiment. However, the great improvement over the classical theory did justify the use of Planck's formula for vibrating atoms and did indicate the validity of identifying heat motion with elastic vibrations.

A modification of the Einstein formula was presented by Nernst and Lindemann[13], who assumed two characteristic frequencies, ν and $\nu/2$. The equation for the specific heat is then (13)

$$C_v = (3Nh^2\nu^2/kT^2)/[\exp(h\nu/kT) - 1]^2 + (3Nh^2\nu^2/4kT^2)/[\exp(h\nu/2kT) - 1]^2.$$

This result is in somewhat better agreement with observation, although it also requires that the specific heat vanish exponentially at absolute zero. However, no satisfactory derivation was forthcoming and so the formula was considered as an attempt to fit the empirical curves. Recently, Blackman has indicated a more significant interpretation, and the present work will also point out the advantages of the Nernst-Lindemann expression compared with Einstein's formula.

The next advance in explaining the specific heats of solids was made by Debye[14] in his celebrated theory. Instead of assuming one or two fundamental frequencies he made use of a whole spectrum. In order to find the number of frequencies in a given range, the elastic equations for an isotropic continuum were solved. These partial differential equations are set up in the usual way. If the net forces on an infinitesimal cube within the solid are put equal to the product of its mass and its acceleration, the result is $(\partial X_{ij}/\partial x_j) = \rho(d^2u_i/dt^2)$, where X_{ij} is the stress tensor, u_i is the displacement of a portion of the solid at the position x_i, t is the time, and summation over j is implied. Upon substituting for X_{ij} from Hooke's law, there is obtained the equation of motion, $c_{ij}^{kl}(\partial^2u_k/\partial x_l\partial x_j) = \rho(d^2u_i/dt^2)$.

For a cubic crystal, the first of these three equations is

$$c_{11}(\partial^2u_x/\partial x^2) + \tfrac{1}{2}\,c_{44}(\partial^2u_x/\partial y^2 + \partial^2u_x/\partial z^2)$$
$$+ (c_{12} + \tfrac{1}{2}\,c_{44})(\partial^2u\ /\partial x\partial y + \partial^2u_z/\partial x\partial z) = \rho(d^2u_x/dt^2).$$

In the case of an isotropic substance there are only two independent elastic constants, so that $c_{44} = (c_{11} - c_{12})$. (The factor of $\frac{1}{2}$ often appearing on the right side of this equation results from the omission of the same factor in the definition of the strain, e_{12}.) Then the previous equation becomes the x component of the vector relation

$$\tfrac{1}{2}(c_{11} + c_{12})\mathrm{grad}(\mathrm{div}\ \bar{u}) + \tfrac{1}{2}(c_{11} - c_{12})\nabla^2\bar{u} = \rho(d^2\bar{u}/dt^2).$$

Now, $\bar{u}$ can be considered as made up of two parts, one with vanishing curl and the other with zero divergence.

$$\bar{u} = \bar{u}' + \bar{u}'', \text{ where } \bar{u}' = \mathrm{div}\ \phi \text{ and } \mathrm{div}\ \bar{u}'' = 0.$$

When this is substituted in the differential equation, it reduces to the sum of two wave equations which, written separately, are

$$(c_{11}/\rho)\nabla^2\phi = (\partial^2\phi/\partial t^2) \quad \text{and} \quad [\tfrac{1}{2}(c_{11} - c_{12})/\rho]\nabla^2\bar{u}'' = (\partial^2\bar{u}''/\partial t^2).$$

The justification for the separation depends on the fact that the second equation represents transverse waves since $\mathrm{div}\ \bar{u}'' = 0$ is the condition for transversality, while the first equation corresponds to longitudinal waves. The two waves are independent within the body of the solid where they travel with different velocities, $c' = (c_{11}/\rho)^{\frac{1}{2}}$ and $c'' = [\frac{1}{2}(c_{11} - c_{12})/\rho]^{\frac{1}{2}}$.

The situation at this point is very similar to the case of radiation in a hohlraum. In fact, exactly the same type of equation applies. Rayleigh and Jeans[15], using the boundary condition that the tangential component of electric field strength vanishes at the surface of the container, found the following solution for the transverse vibrations in a cubical hohlraum:

$$u''_x = A_x \cos(\pi jx/a)\sin(\pi ky/a)\sin(\pi lz/a)\cos\omega'' t$$

with similar equations for the other two components; A_x is the amplitude, a is the length of one edge of the cube, j, k, and l are integers, and $\omega'' = c(\pi/a)(j^2 + k^2 + l^2)^{\frac{1}{2}}$. The last relation guarantees that the solution satisfies the wave equation. It is evident that the boundary conditions and the transversality condition also hold. Here, c is velocity of light.

Consider the j, k, l space where possible frequencies correspond to points in a cubic lattice representing the various combinations of integers, each point located at the center of a cube of unit volume. A surface of constant frequency in this space is one octant of a sphere with radius equal to $(2a\nu/c)$. The volume of the sphere is equal to n, the number of vibrations with frequency less than ν; boundary effects where the surface of the sphere cuts through the cubic cells are negligible because of the great number of modes of vibration.

$$n = (4\pi/3)a^3\nu^3/c^3 = (4\pi/3)v\nu^3/c^3. \tag{14}$$

It was shown that only the volume v of the hohlraum is essential, the shape being immaterial. To find the number of vibrations between ν and $\nu + d\nu$ differentiate with respect to ν, obtaining

$$dn = (4\pi v\nu^2/c^3)d\nu. \tag{15}$$

This important relation states that the distribution depends on the square of the frequency so that the number of vibrations accumulates rapidly as the frequency increases.

Debye treated the similar elastic problem by solving the wave equation in a spherical solid with convenient boundary conditions and arrived at exactly the same type of distribution for both the transverse and longitudinal waves. Since the former account for twice as many degrees of freedom as the latter, the final expression is (16)

$$dn = 4\pi v\nu^2[(1/c')^3 + (2/c'')^3]d\nu = 4\pi v\nu^2[(\rho/c_{11})^{\frac{3}{2}} + (\rho/c_{11}-c_{12})^{\frac{3}{2}}]d\nu.$$

The elastic constants used here can be related in various ways to observed elastic properties. For example, $c_{11} = 3\kappa(1-\sigma)/(1+\sigma)$ and $c_{12} = 3\kappa\sigma/(1+\sigma)$, where κ is the bulk modulus and σ is Poisson's ratio.

Now for elastic vibrations in a continuum or radiation in a hohlraum there is nothing to limit the frequency permissable, an infinite number of degrees of freedom being possible. Therefore, to find the internal energy, Planck's formula for the energy of an oscillator is multiplied by the number of vibrations in a given frequency range and the product integrated from zero to infinity. In the case of radiation this gives

$$U = (4\pi v/c^3)\int_0^\infty \{h\nu^3/[\exp(h\nu/kT) - 1]\}d\nu = (4\pi vk^4T^4/h^3c^3)\int_0^\infty [x^3/(e^x-1)]dx$$

$= (4\pi^5 vk^4/15h^3c^3)T^4$, where $x = (h\nu/kT)$ and the definite integral has the value $\pi^4/15$. The specific heat at constant volume is

(17) $$C_v = (4\pi^5 vk^4/5h^3c^3)T^3.$$

A similar result is obtained for an elastic continuum. This agrees with experimental data on the specific heats of actual solids at low temperatures where small frequencies or long wave lengths are important, but has no correlation with the observed values at higher temperatures. The deviation must be due to the atomic character of the crystal which puts a lower limit on the allowable wave length. Debye took this into account by assuming a maximum frequency which was computed from a limitation of the degrees of freedom to three times the number of atoms in the solid. The previous frequency distribution was retained up to the point where the correct number of vibrations had been included and then was abruptly terminated.

The procedure is to consider one mole of the solid which has 3N degrees of freedom, N being Avogadro's number. Then, the maximum frequency ν_m is defined by the relation

$$3N = (4\pi/3)v\nu_m^3[(1/c')^3 + (2/c'')^3]$$

Let $h\nu_m/k = \theta$, Debye's characteristic temperature. The equation for the internal energy now becomes

$$(18)\qquad U = (9N/\nu_m^3)\int_0^{\nu_m}\{h\nu^3/[\exp(h\nu/kT) - 1]\}\,d\nu$$

$$= 9R(T/\theta)^3\int_0^{(\theta/T)}[x^3/(e^x - 1)]\,dx.$$

The specific heat is

$$(19)\qquad C_v = 9R(T/\theta)^3\int_0^{(\theta/T)}[x^4e^x/(e^x - 1)^2]\,dx$$

$$= 36R(T/\theta)^3\int_0^{(\theta/T)}[x^3/(e^x - 1)]\,dx \quad - 9R(\theta/T)/[\exp(\theta/T) - 1].$$

The last equation results from an integration by parts.

Debye's formula for the specific heat like Einstein's has the same form for all substances, a difference in θ simply causing a change in the temperature scale. Moreover, at high temperatures the specific heat again reduces to the equipartition value, 3R. At low temperatures the upper limit of the integral may be considered infinite so that $C_v = (12\pi^4R/5)(T/\theta)^3$, the same as for a continuum. This third power law holds with an accuracy of one percent from absolute zero to $T = \theta/12$ according to the theory. The decrease of specific heat with temperature is thus less rapid than that given by the Einstein or Nernst-Lindemann formulae, but the Nernst heat postulate is still satisfied.

The early experiments of Nernst and his collaborators on the specific heats of solids were in agreement with Debye's theory. It was found that a good fit to the observed values could be obtained by choosing properly the values of θ, the single parameter involved. These values of θ agreed fairly well with those computed from elastic data and so it was felt that the question of specific heats of solids was more or less settled. However, more recent work has shown many discrepancies with the Debye theory due partly to inadequate treatment and partly to extraneous effects.

In the first place, Debye started with a partial differential equation that applies only to isotropic substances. Now, in general, single crystals are not isotropic with respect to their elastic properties. Even cubic crystals, which may be considered isotropic for some phenomena, have three independent elastic constants instead of the two associated with isotropic substances. An exception occurs in the case of tungsten whose constants happen to satisfy the relation for isotropy. Polycrystalline material has the same properties in all directions from a large scale point of view but actually is composed of many single crystals randomly oriented. Therefore, the same objections are involved for wave lengths short in comparison with the dimensions of the small crystals and yet large compared with atomic dimensions; in addition, there would be surface effects where the crystals join together. For these reasons it appears that the assumption of isotropy is justifiable merely as a means of simplifying the calculations.

In the second place, Debye made use of two separate and distinct models for a solid which cannot be consistently utilized at the same time. The frequency distribution obtained by solving the equations for a continuum was cut off at a frequency determined by the number of atoms in the body. This added restriction was necessary in order to secure any semblance of agreement with experimental specific heats at high temperatures where wave lengths of the order of magnitude of atomic dimensions become important. However, the atomic nature of the crystal must certainly affect the form of the distribution long before the maximum frequency is reached, and it is not correct to suddenly introduce the atomic model as a last resort. It would seem better to consider the atomic structure of the crystal from the beginning and to try to compute the frequency distribution from the normal modes of vibration of the coupled system of atomic oscillators.

An attempt to do this was first made by Born and von Karman[16]. The procedure can be simply illustrated by means of a one dimensional lattice for which an explicit solution can be obtained. Suppose atoms of the same mass m are equally spaced along a straight line with a distance a between neighbors. The position of the atoms may be specified by positive or negative integers which give the distance in units of a from some atom selected as the origin. It is assumed that each atom is affected only by its immediate neighbors and that the forces acting are proportional to the relative displacements, just as though springs separated the atoms. If the displacement of the jth atom is u_j, the force acting on it is

$$\gamma(u_{j+1} - u_j) - \gamma(u_j - u_{j-1}) = \gamma(u_{j+1} + u_{j-1} - 2\, u_j) = m\ddot{u}_j ,$$

where γ is the force constant and $\ddot{u}_j$ is the acceleration.

Consider the wave solution, $u_j = ue^{i(\nu t + j\varphi)}$, where u is a constant amplitude, ν is the frequency, and φ is the phase difference between the vibrations of successive atoms. The wave length λ is given by the relation, $\varphi/2\pi = a/\lambda$. When the proposed solution is substituted in the difference equation, it is found to be satisfied if

$$-m\nu^2 = \gamma(e^{i\varphi} + e^{-i\varphi} - 2) = 2\gamma(\cos\varphi - 1) = -4\gamma\sin^2\tfrac{1}{2}\varphi.$$

$$\therefore\ \nu = 2(\gamma/m)^{\frac{1}{2}}\sin\tfrac{1}{2}\varphi = \nu_0\sin(\pi a/\lambda),$$

where $\nu_0 = 2(\gamma/m)^{\frac{1}{2}}$ is the maximum frequency possible. This is a dispersion formula giving the frequency as a function of the wave length. The velocity of the wave is the product of the frequency and the wave length and equals $\lambda\nu_0\sin(\pi a/\lambda)$, a constant only for wave lengths long in comparison with the interatomic distance. This indicates one point of departure from the Debye theory.

It was assumed that the number of normal modes of vibration having a frequency less than ν is given by the relation, $n = N(\varphi/2\pi)$, where N is the total number of atoms. This was actually based on a discussion of an infinite lattice where the values of φ are uniformly distributed from 0 to 2π. The dispersion formula then results in the equation,

$n = (N/\pi)\ \mathrm{arc\ sin}(\nu/\nu_0)$ and $dn = \left[(N/\pi)/(\nu_0^2 - \nu^2)^{\frac{1}{2}}\right]d\nu$,

so that there is a concentration of vibrations at the high frequency end of the spectrum.

Born and von Karman next considered a simple cubic crystal taking into account the elastic forces acting on a given atom due to its eighteen nearest neighbors. However, it was necessary to make simplifying assumptions about the five force constants involved in order to evaluate them in terms of the three measurable elastic constants. The secular equation for the frequency is a determinant of the third order in ν^2 and no useful explicit solution can be obtained in general. The frequency depends on the three phase angles, φ, ψ, and χ, which are related to the direction of the wave in the crystal, so that

$$dn = [3N(1/2\pi)^3 d\varphi\, d\psi\, d\chi]\, d\nu.$$

To compute the specific heat it is necessary to integrate a function of ν over a cube in the first octant of the $\varphi\psi\chi$ space. Due to the symmetry of the cubic crystal this integration can be carried out over one-third of the cube represented by a pyramid with its vertex at the origin and with one face of the cube as its base. The pyramid has square cross-sections parallel to the base and perpendicular to the φ axis and their area is φ^2. An average value of the frequency equal to the result found for the one dimensional case is assumed to be valid over each cross-section. This simplifying approximation merely takes the place of more accurate information about the spectrum. The formula for the internal energy then takes the form,

$$U = 3N[3/(2\pi)^3] \int_0^{2\pi} \{(h\nu_0 \sin \tfrac{1}{2}\varphi)/[e^{(h\nu_0 \sin \frac{1}{2}\varphi)/kT} - 1]\}\varphi^2 d\varphi.$$

If $\theta = h\nu_0/k$, the specific heat is (20)

$$C_v = [9R/(2\pi)^3](\theta/T)^2 \int_0^{2\pi} \{(\sin \tfrac{1}{2}\varphi)^2\, e^{(\theta/T)\sin\frac{1}{2}\varphi}/[e^{(\theta/T)\sin\frac{1}{2}\varphi} - 1]^2\}\varphi^2 d\varphi.$$

According to this relation the specific heat has the equipartition value at temperatures large compared with θ, while at absolute zero the specific heat vanishes. For a given θ, the curve is between the one of Einstein's and the one due to Nernst and Lindemann. The actual course of the specific heat is not greatly different from that given by Debye's theory. The only advantage is that the dispersion of the elastic waves has been approximately taken into account although the anisotropy of the crystal has been neglected. However, the Debye formula is always used instead of the Born-von Karman expression, partly because it is simpler and partly because it is better known.

Various attempts have been made to improve and extend the Born-von Karman method of treatment. Blackman[17] has discussed in detail the effect of dispersion and anisotropy on the variation of the Debye characteristic temperature. It has been suggested that three such parameters are required in general and Born has shown that terms of the Einstein type are also necessary when there is more than one atom in the lattice cell. The present treatment differs from those previously discussed in that an actual numerical evaluation of the secular equation and the frequency distribution is carried out for the special case of tungsten, a body-centered cubic crystal with elastic properties which happen to be isotropic. The results will then differ from the Debye theory in showing the effects of dispersion due to the atomic nature of the crystal. Also, the Cauchy relations will be utilized in a new way, already mentioned in connection with the Wigner-Seitz theory.

It must be realized that all these treatments disregard many complicated features of the solid state. For example, the assumption of the Hooke's law type of force is in some respects entirely inadequate. That hypothesis permits no thermal expansion of the solid since there is no reason for a change in the equilibrium position of the atoms under such a symmetrical force. It is necessary to go to the next approximation and consider third order terms in the potential energy as has been done by Adams[18] and Born and Brody[19]. The effect on the specific heat of these anharmonic terms is to cause a linear rise with temperature above the equipartition value at high temperatures. It is an experimental fact that specific heats do often considerably exceed the classical value, but there are discrepancies between the theory and the observations.

A different kind of complication has been discussed by Compton[20], who assumed that a degree of freedom due to the motion of one atom relative to another is not excited unless the energy exceeds a certain critical value $\mathcal{E}$, depending on the substance. The specific heat which then follows from purely classical considerations is

$$C_V = 3R\, e^{-(\theta/T)}\left[(\theta/T) + 1\right], \quad \text{where } \theta = \mathcal{E}/2k. \tag{21}$$

Although this is quite an improvement on the ordinary classical theory, it gives a specific heat which is much too small at low temperatures. Of course, the quantum theory changed the average energy per oscillator without altering the number of degrees of freedom.

A significant omission in the previous theories for the specific heats of metals was the neglect of a contribution from the "free" electrons. The thermal motion of the ions is certainly shared by the valence electrons and there must be a complicated interdependence which results in the observed phenomena. The simplest method of handling the situation is to arbitrarily separate the problem into two parts; first, a consideration of the lattice vibrations alone, and second, a treatment of actually free electrons as in the Fermi-Dirac model of an electron gas.

Sommerfeld[21] showed that an electron gas has a specific heat which is directly proportional to the temperature, the coefficient depending on the number of free electrons per atom. Recent experimental work by Kok and Keesom[22] exhibit the fact that at very low temperatures the specific heat of platinum and copper can be resolved into two parts, one varying as the third power of the temperature and the other as the first power. However, the specific heat assigned to the electrons is several times as large as that given by Sommerfeld's formula. As to the electronic contribution at higher temperatures the situation is even more obscure. This means that a computation based solely on the atomic lattice vibrations cannot be readily verified by means of experimental data which includes these extraneous effects.

Bound electrons may also affect the specific heat. Shottky has shown that a multiplet in the atomic or molecular energy levels may result in a hump in the specific heat curve at low temperatures[23]. A quantitative explanation of peculiarities in the behavior of gadolinium sulfate and orthohydrogen has been ascribed to this cause, which has also been suggested as a means of clearing up certain discrepancies in the specific heats of zinc, tin, and silicon. These questions tend to emphasize the fact that each substance presents a problem in itself and that the hope of obtaining a universal function to represent the specific heat of solids will probably not be realized.

SECTION 3, REFLECTION OF X-RAYS.

A somewhat simpler phenomenon involving atomic vibrations is the dependence of the intensity of reflection of x-rays on the temperature. In a crystal where the atoms in their equilibrium positions are situated in planes oriented in various ways there is constructive interference of the x-rays reflected by all the atoms in a given plane. However, due to the thermal motion, the atoms are displaced from their equilibrium positions and this has the effect of weakening the intensity of the x-rays reflected. The higher the temperature the greater the amplitude of the vibrations and the less the intensity of reflection.

Debye first developed these considerations into a complete mathematical theory[24] and more recently this has been put into a more concise form by Zener and Jauncey[25]. The problem is to compute a quantity H which is defined as the ratio of the amplitude of the x-rays reflected from a layer of atoms to the amplitude for a single atom. Let the z axis be located so that it bisects the angle between the incident and reflected rays and is therefore perpendicular to the reflecting plane. Suppose p(z) is the average number of atoms at a distance z from the reflecting plane because of the thermal motion. If φ is the grazing angle of incidence, then

$$(22) \qquad H = \int_{-\infty}^{\infty} p(z)\{\exp[(-2\pi i/\lambda)(2z \sin\varphi)]\}dz.$$

The basis for this equation is the fact that the resultant wave is the superposition of many waves reflected at various levels and differing in phase because of the difference in path length, $2z \sin\varphi$. Since p(z) is an even function, the integral can be written in the form

$$(23) \qquad H = 2\int_{0}^{\infty} p(z)\{\cos[(4\pi z \sin\varphi)/\lambda]\}dz.$$

Now, if the displacements from the equilibrium position are small and the potential energy is considered a quadratic function, normal modes of vibration can be found which combine to give the desired motion of the atoms. Since the normal vibrations are independent of each other, p(z) has exactly the same form as the probability function or the formula for Brownian motion. Einstein[26] found this to be

(24) $p(z) = [1/(2\pi\mu)^{\frac{1}{2}}]\, e^{-z^2/2\mu}$, where $\mu = \Sigma\, \mu_s$ and μ_s is the mean square of the z component of the displacement resulting from the sth normal mode of vibration. When this is substituted into the integral, it can be immediately evaluated as follows:

(25) $H = \exp[-(8\pi^2\mu \sin^2\varphi)/\lambda^2]$.

Let $M = (8\pi^2\mu \sin^2\varphi)/\lambda^2$, so that the temperature factor is e^{-M}.

The whole problem then is to find the value of μ. Now, $\mu_s = \frac{1}{2}\gamma_s^2 A_s^2$, where γ_s is the cosine of the angle between the amplitude vector $\bar{A}_s$ and the z axis. The energy due to the sth normal mode is (26)

$\varepsilon_s = \frac{1}{2} Nm(2\pi\nu_s)^2 A_s^2$, m being the mass of an atom and N the number of atoms. This is combined with the Planck formula, modified by the addition of the zero point energy which was later found necessary[27].

(27) $\varepsilon = [h\nu/(e^{h\nu/kT} - 1)] + \frac{1}{2} h\nu$.

Substituting for the amplitude in terms of the frequency results in the following equation:

(28) $\mu = (h/4\pi^2 Nm)\Sigma\, \gamma_s^2\, (1/\nu_s)\{[1/(e^{h\nu_s/kT} - 1)] + \frac{1}{2}\}$.

The value of this sum depends on the type of crystal. For an isotropic substance γ_s^2 may be given its average value of 1/3, since the frequency in that case does not depend on the direction of the wave. It so happens that the symmetry properties make this procedure valid for a cubic crystal also, as will be shown later. The summation can then be changed into an integration over ν by utilizing the frequency distribution, which specifies the number of vibrations in a given frequency range.

According to the Debye theory,

$$(29)\quad \mu = (h/12\pi^2Nm)\int_0^{\nu_m}(9N\nu^2/\nu_m^3)(1/\nu)\{[1/(e^{h\nu/kT}-1)]+\tfrac{1}{2}\}d\nu.$$

$$= (3h^2/4\pi^2mk\Theta)\{(T/\Theta)^2\int_0^{(\Theta/T)}[x/(e^x-1)]dx + \tfrac{1}{4}\}.$$

$$= (3h^2/4\pi^2mk\Theta)[(T/\Theta)D(\Theta/T)+\tfrac{1}{4}],$$

where the Debye function is $D(\Theta/T) = (T/\Theta)\int_0^{(\Theta/T)}[x/(e^x-1)]dx.$ This means that

$$(30)\quad M = (6h^2/mk\Theta)[(T/\Theta)D(\Theta/T)+\tfrac{1}{4}](\sin\varphi)^2/\lambda^2.$$

It should be noted that the result at high temperatures involves the frequency distribution in a particularly simple way. If the number of vibrations in the range from ν to $\nu+d\nu$ is denoted by $dn = f(\nu)d\nu$, then replacing the exponential by the first two terms in its series expansion leads to the equation,

$$(31)\quad M = (2h/3Nm)\{(kT/h)\int_0^{\nu_m}[f(\nu)/\nu^2]d\nu + \int_0^{\nu_m}[f(\nu)/2\nu]d\nu\}.$$

This means that the frequency distribution shows up very significantly in the coefficient of reflection of x-rays at high temperatures. Here we have an important difference from the specific heat theory which gives the equipartition value when the temperature is high regardless of the way the frequencies are distributed over the normal modes of vibration. Thus it seems that experimental data on the intensity of x-ray reflection would be valuable in distinguishing between various treatments of atomic vibrations.

Measurements have been made on zinc and cadmium, hexagonal crystals which require two characteristic temperatures because of the difference in properties along the axis and at right angles to it. The linear dependence of M on the temperature was verified but neither the Debye nor the Born-von Karman theory gave a satisfactory numerical agreement with the observations[28]. It was suggested that this might be due to a distortion of the atomic structure in the crystal. Very recent experiments have also indicated discrepancies for a face-centered cubic lattice[29]. Similar data for tungsten would provide an interesting check on the results of the present work.

This summary of a few elastic and thermal characteristics of the solid state was intended as the groundwork for the more detailed and specialized treatment which follows. As stated before, the theory used is essentially that developed by Born. However, it was felt that an actual numerical application would be of interest and for that purpose the body-centered cubic crystal tungsten was chosen because of its convenient elastic properties. Although the results thus obtained are strictly valid only for a single substance, the nature of the influence exerted by the atomicity of the crystal should prove more generally significant. Also several innovations in the method of handling the elastic constants will be introduced. The frequency distribution which results will be applied to the calculation of the specific heat and the temperature dependence of the intensity of x-ray reflection and the deviations from the Debye theory will be indicated.

PART II. VIBRATIONS OF AN ATOMIC LATTICE

It is the purpose of this work to discuss the thermal motions of the atoms in a single crystal. The model used consists of point masses so that all complexities of nuclear and extranuclear structure are entirely disregarded. Thus there is no allowance for any independent motion of valence or "free" electrons.

If a particular group of atoms known as the basic cell is selected as representative of the space lattice, the whole configuration in the crystal can be built up by displacing this cell through distances whose components along the j axis of the lattice are integral multiples of the constant a_j. The equilibrium position of an atom in such a lattice is denoted by the vector,

$$\bar{r} = (s + q, \bar{a}) = \sum_{j=1}^{3} (s_j + q_j)\bar{a}_j, \tag{1}$$

where q_j is an integer designating the cell under consideration and s_j is a fraction giving the position of the corresponding atom in the basic cell. The interatomic dimensions of the lattice are taken directly from experimental findings and no attempt is made to account for the particular type of crystal structure which proves stable for a given substance.

SECTION 1. NORMAL MODES

If each atom acts on every other atom in the crystal, the potential energy due to displacements from the equilibrium positions can be expanded in the form,

(2) $$V = V_0 + \sum_j \sum_r (\partial V/\partial u_r^j)_0 u_r^j + \frac{1}{2} \sum_j \sum_k \sum_r \sum_{r'} (\partial^2 V/\partial u_r^j \partial u_{r'}^k)_0 u_r^j u_{r'}^k + \cdots$$

The summation with respect to r and r' is taken over all the atoms in the crystal and the superscripts j and k refer to the three coordinate directions. The derivatives are to be evaluated when the displacements are all zero. The justification for this McLaurin power series rests on the supposition that V is an analytic function, being continuous and possessing continuous derivatives, mathematical conditions which are usually assumed to be satisfied on physical grounds.

The force in the j direction on the atom located at the position specified by r is $(\partial V/\partial u_r^j)_0$ when all other atoms are also in their lattice positions, and this force must vanish since the solid is then in equilibrium. If V_0 is taken as the zero reference value for the potential energy, then

(3) $$V = \frac{1}{2} \sum_j \sum_k \sum_r \sum_{r'} C_{jk}^{rr'} u_r^j u_{r'}^k,$$

where $C_{jk}^{rr'} = (\partial^2 V/\partial u_r^j \partial u_{r'}^k)_0$ and higher order terms are neglected for displacements small compared with the distances between atoms. By definition, $C_{jk}^{rr'} = C_{kj}^{r'r}$, because both constants are factors of the displacement product, $u_r^j u_{r'}^k$. Also, $C_{jk}^{rr'}$ depends on q and q' only through the difference, q' - q, since all the cells are presumed to be exactly alike, boundary effects at the surface of the crystal being neglected.

An additional relation between the force constants may result from considering the effect of displacing only two atoms in the crystal. In that case the potential energy is given by the expression, $\frac{1}{2}C^{rr}_{jj}(u^j_r)^2 + C^{rr'}_{jk}u^j_r u^k_{r'} + \frac{1}{2}C^{r'r'}_{kk}(u^k_{r'})^2$. The first or last term is also present when only one atom is displaced from its equilibrium position. Therefore, the remaining term is due to the interaction between the two atoms when both are simultaneously disturbed. But the relative motion of the two atoms is unaltered if their displacements are interchanged and then reversed in direction. When this is done, the potential energy for the new situation becomes $\frac{1}{2}C^{rr}_{kk}(u^k_r)^2 + C^{rr'}_{kj}u^k_r u^j_{r'} + \frac{1}{2}C^{r'r'}_{jj}(u^k_{r'})^2$. The displacement of the atom at the position r is to be equal to the negative of the previous displacement of the atom at the position r' and vice versa.

Now, this expression may be entirely different from the former one and even the interaction term may not be the same when the two atoms do not occupy equivalent positions in the crystal. However, if each atom in the lattice is situated in exactly the same way with respect to the other atoms, the two forms of the potential energy must be identical and therefore

(4) $$C^{rr'}_{jk} = C^{rr'}_{kj},$$

or the force constants are then symmetrical in their subscripts. Combining this result with the previous relation, $C^{rr'}_{jk} = C^{r'r}_{kj}$, shows that

(5) $$C^{rr'}_{jk} = C^{r'r}_{jk},$$

which indicates symmetry with respect to the superscripts also. These equations, which later will lead to the Cauchy relations, are not used in the treatment of a general lattice but will be assumed for monatomic cubic crystals where each atom is a symmetry center.

The kinetic energy of the crystal can be written as

$$(6) \qquad T = \frac{1}{2} \sum_j \sum_r m_s (\dot{u}_r^j)^2$$

where m_s refers to the mass of the atom in the position s in the basic cell and $\dot{u}_r^j$ is the time derivative of the displacement. The problem is to reduce the potential energy to a simpler form by introducing normal coordinates for a general lattice without thereby complicating the kinetic energy expression.

The displacement of each atom is regarded as resulting from the superposition of plane waves in the crystal, so that

$$(7) \qquad \bar{u}_r = \sum_j \sum_n \bar{w}_{s,n} \exp\left[(2\pi i) \sum_j (n_j r_j / N_j a_j)\right],$$

where n_j is an integer related to the direction of the wave and has values from $-\frac{1}{2}(N_j - 1)$ to $\frac{1}{2}(N_j - 1)$, N_j being the total number of cells along the j axis of the lattice. $w_{s,n}^j$ is the nth normal coordinate in the j direction, the label s being added for convenience in indicating that there are the same number of normal coordinates as degrees of freedom in the crystal. This equation thus provides an expansion of the displacement of a given atom as a linear function of the normal coordinates. In order for the right side to be real it is necessary that $w_{s,n}^j$ be complex and that $w_{s,-n}^j = w_{s,n}^{j*}$. The quantities $w_{s,n}^j$ are to be considered as independent variables while their complex conjugates are regarded as dependent, so that the correct number of variables is obtained. The absolute value of $w_{s,n}$ represents the amplitude of the vibration and the phase of $w_{s,n}$ is connected with the phase of the vibration.

When the change of variables is made in the potential energy, the result is

$$V = \frac{1}{2} \sum_j \sum_k \sum_n \sum_{n'} \sum_r \sum_{r'} C_{jk}^{rr'} \, w_{s,n}^j w_{s',n'}^k \exp\{(2\pi i/N)[(n,s+q)+(n',s'+q')]\},$$

where the sum over r and r' includes a sum over s, s', q, and q' and $(1/N)(n,s+q)$ stands for $\sum_j n_j(s_j+q_j)/N_j$. Let $q' = q + g$, g having components g_j which are integers. The expression then becomes

$$V = \frac{1}{2} \sum_j \sum_k \sum_s \sum_{s'} \sum_q \sum_g \sum_n \sum_{n'} C_{jk}^{s,s',g} \, w_{s,n}^j \, w_{s',n'}^k \, e^{(2\pi i/N)[(n+n',q)+(n,s) +(n',s'+\underset{g}{\cancel{q'}})]}$$

Sum over q first, noting that the force constant does not depend on q. Therefore, it is a question of the value of $\sum_j \sum_{q_j=1}^{N_j} \exp[(2\pi i/N)(n+n',q)]$. Now this sum represents a division of the unit circle in the Argand plane into N equal parts and since the "center of mass" of such points is at the origin the sum is zero unless $n + n' = 0$. In that case each term of the sum is equal to unity and the total is simply the number of terms, $N_1N_2N_3$.

The potential energy is then

$$V = \frac{1}{2} N_1N_2N_3 \sum_j \sum_k \sum_s \sum_{s'} \sum_g \sum_n C_{jk}^{s,s',g} \, e^{(2\pi i/N)(-n,s'-s+g)} \, w_{s,n}^j w_{s',-n}^k$$

and this may be put in the condensed form,

$$V = \frac{1}{2} N_1N_2N_3 \sum_j \sum_k \sum_s \sum_{s'} \sum_n C_{jk}^{s,s',n} \, w_{s,n}^j \, w_{s',-n}^k, \text{ where} \tag{8}$$

$$C_{jk}^{s,s',n} = \sum_g C_{jk}^{s,s',g} \exp[(2\pi i/N)(-n,s'-s+g)] \,. \tag{9}$$

Similarly, the kinetic energy can be expressed as

$$T = \frac{1}{2} \sum_j \sum_s \sum_q \sum_n \sum_{n'} m_s \dot{w}_{s,n}^j \, \dot{w}_{s,n'}^j \, e^{(2\pi i/N)(n+n',s+q)}$$

and the reduction gives

$$(10)\qquad T = \frac{1}{2} \sum_j \sum_s \sum_n N_1 N_2 N_3 m_s \dot{w}^j_{s,n} \dot{w}^j_{s,-n} .$$

The equations of motion are obtained by Lagrange's method.

$$\partial(T - V)/\partial w^k_{s',-n} = (d/dt)[\partial(T - V)/\partial \dot{w}^k_{s',-n}].$$

Therefore,

$$(11)\qquad \sum_s \sum_j C^{s,s',n}_{jk} w^j_{s,n} = - m_{s'} \ddot{w}^k_{s',n}.$$

This differential equation can be satisfied by assuming that each normal coordinate varies in a simple harmonic way with the time.

$$(12)\qquad w^j_{s,n} = A^j_{s,n} e^{i\omega_n t} .$$

$A^j_{s,n}$ is a constant amplitude and ω_n is 2π times the frequency of vibration for the nth normal coordinate. Substitution results in the following series of linear homogeneous equations in the unknown amplitudes:

$$(13)\qquad \sum_s \sum_j C^{s,s',n}_{jk} A^j_{s,n} - m_{s'} \omega^2_n A^k_{s',n} = 0.$$

These may be partially written out as follows:

$$\sum_s \left[C^{s,s',n}_{11} A^{(1)}_{s,n} - m_{s'} \omega^2_n A^{(1)}_{s',n} + C^{s,s',n}_{21} A^{(2)}_{s,n} + C^{s,s',n}_{31} A^{(3)}_{s,n}\right] = 0.$$

$$\sum_s \left[C^{s,s',n}_{12} A^{(1)}_{s,n} + C^{s,s',n}_{22} A^{(2)}_{s,n} - m_{s'} \omega^2_n A^{(2)}_{s',n} + C^{s,s',n}_{32} A^{(3)}_{s,n}\right] = 0.$$

$$\sum_s \left[C^{s,s',n}_{13} A^{(1)}_{s,n} + C^{s,s',n}_{23} A^{(2)}_{s,n} + C^{s,s',n}_{33} A^{(3)}_{s,n} - m_{s'} \omega^2_n A^{(3)}_{s',n}\right] = 0.$$

The condition for these equations to have a non-trivial solution is that the determinant of the coefficients of the $A^j_{s,n}$ vanish. This determinant is made up of blocks which are so constituted that the jth block horizontally and kth block vertically has the following form when $j \neq k$:

$$\begin{matrix} C_{jk}^{s_1,s_1,n} & \cdots & C_{jk}^{s_p,s_1,n} \\ \vdots & & \vdots \\ C_{jk}^{s_1,s_p,n} & \cdots & C_{jk}^{s_p,s_p,n} \end{matrix}$$

where the number of atoms in the basic cell is denoted by p. The diagonal blocks are represented as follows:

$$\begin{matrix} C_{jj}^{s_1,s_1,n} - m_{s_1}\omega_n^2 & \cdots & C_{jj}^{s_p,s_1,n} \\ \vdots & & \vdots \\ C_{jj}^{s_1,s_p,n} & \cdots & C_{jj}^{s_p,s_p,n} - m_{s_p}\omega_n^2 \end{matrix}$$

Now, $C_{jk}^{s,s',g} = C_{kj}^{s',s,-g}$, according to the definition mentioned on page 33. Therefore, from equation (9) it is seen that

$$C_{kj}^{s',s,n} = C_{jk}^{s,s',n*}, \tag{14}$$

The determinant is Hermitean and the values of ω_n^2 which are the roots of the equation are all real. Moreover, because of the stability of the lattice, V is a positive definite form, always greater than zero for any displacement of the atoms in the crystal. This means that all the roots of the secular equation are positive. That this must follow is clear from the fact that a negative root for ω_n^2 would mean a real exponential time factor indicating a motion of the atoms which would either be damped out as time went on or would increase with the time until the solid was disrupted.

The order of the secular equation is equal to three times the number of atoms in the basic cell and there is a set of solutions for each value of n so that the number of possible frequencies equals the total number of degrees of freedom. The main problem is to determine the frequency distribution, i.e., the number of normal modes of vibration in a given frequency range. There is one vibration for each point in the $n_1n_2n_3$ space having integral components, so that the volume between surfaces of constant frequency in that space corresponds to the number of oscillations in that frequency range. However, the constant frequency surfaces here are not simply spheres as in the Debye theory but have complicated equations involving sums of trigonometric functions. Evidently, it is not possible to find an explicit solution in general for the frequency distribution and it is necessary to resort to numerical methods.

In order to clarify the preceding theory an application will be made to the special cases of body-centered and face-centered cubic lattices. A discussion of the simple cubic lattice may be omitted since no monatomic substances are known which crystallize in such form.

A body-centered cubic lattic has an atom at each corner of the cube and one at its center. The basic cell consists of two atoms, one situated at the point 0,0,0 and the other at the point $\frac{1}{2}$ a, $\frac{1}{2}$ a, $\frac{1}{2}$ a, where a is the length of one edge of the cube. The position of any atom in the crystal is given either by $r = (q,a)$ or by $r = (q + \frac{1}{2}, a)$, with the $\frac{1}{2}$ to be added to each component of q. The potential energy may be written in the form:

$$V = \frac{1}{2} \sum_j \sum_k \sum_r \sum_{r'} C^{rr'}_{jk} u^j_r u^k_{r'}.$$

(15) $$u^j_r = w^j_{o,n} e^{(2\pi i/N)(n,q)} + w^j_{\frac{1}{2},n} e^{(2\pi i/N)(n,q + \frac{1}{2})}.$$

In a cubic monatomic lattice every atom is situated in exactly the same way with respect to its neighbors, so that the force constants can depend only on the difference in coordinates of the atoms concerned. Therefore,

(16) $$C^{rr'}_{jk} = C^{r'-r}_{jk} = C^{r-r'}_{jk},$$

and the symmetry relations given in equations (4) and (5) are satisfied. Let $q' - q = g$, as before. Then,

$$V = \frac{1}{2} \sum_j \sum_k \sum_g \sum_q \sum_{q'} \sum_n \sum_{n'} \Big\{ C^g_{jk} w^j_{o,n} w^k_{o,n'} e^{(2\pi i/N)[(n,q) + (n',q')]}$$
$$+ C^g_{jk} w^j_{\frac{1}{2},n} w^k_{\frac{1}{2},n'} e^{(2\pi i/N)[(n,q + \frac{1}{2}) + (n',q' + \frac{1}{2})]}$$
$$+ 2\, C^{g + \frac{1}{2}}_{jk} w^j_{o,n} w^k_{\frac{1}{2},n'} e^{(2\pi i/N)[(n,q) + (n',q' + \frac{1}{2})]} \Big\}$$

and this reduces to

(17) $$V = \sum_j \sum_k \sum_n \frac{1}{2} N_1 N_2 N_3 \Big[C^n_{jk} (w^j_{o,n} w^k_{o,-n} + w^j_{\frac{1}{2},n} w^k_{\frac{1}{2},-n})$$
$$+ 2\, C^{n'}_{jk} w^j_{o,n} w^k_{\frac{1}{2},-n} \Big],$$ where

(18) $$C^n_{jk} = \sum_g C^g_{jk} e^{(2\pi i/N)(-n,g)}$$ and

(19) $$C^{n'}_{jk} = \sum_g C^{g + \frac{1}{2}}_{jk} e^{(2\pi i/N)(-n,g + \frac{1}{2})}$$

The summation is from $g_j = -(N_j - 1)$ to $g_j = (N_j - 1)$ and the term in g_j is the complex conjugate of the one in $-g_j - 1$. If the last term, which equals $2\, C^{N - \frac{1}{2}}_{jk} e^{\pi i(-n/N)}$, is neglected because the force constant between such distant atoms is inappreciable, then C^n_{jk} and $C^{n'}_{jk}$ are real.

The kinetic energy has the form:

$$T = \frac{1}{2} m \sum_{j} \sum_{q} \sum_{n} \sum_{n'} \Big[\dot{w}^{j}_{0,n} \dot{w}^{k}_{0,n'} e^{(2\pi i/N)(n + n', q)} + \dot{w}^{j}_{\frac{1}{2},n} \dot{w}^{k}_{\frac{1}{2},n'} e^{(2\pi i/N)(n + n', q + \frac{1}{2})} \Big]$$

and the reduction gives

$$(20) \qquad T = \frac{1}{2} m N_1 N_2 N_3 \sum_{j} \sum_{n} \big(\dot{w}^{j}_{0,n} \dot{w}^{j}_{0,-n} + \dot{w}^{j}_{\frac{1}{2},n} \dot{w}^{j}_{\frac{1}{2},-n} \big).$$

The equations of motion are then

$$(21) \qquad \begin{aligned} &\sum_{j} \Big[C^{n}_{jk} w^{j}_{0,n} + C^{-n\,\prime}_{kj} w^{j}_{\frac{1}{2},n} \Big] = m \ddot{w}^{k}_{0,n} \\ &\sum_{j} \Big[C^{n\,\prime}_{jk} w^{j}_{0,n} + C^{n}_{jk} w^{j}_{\frac{1}{2},n} \Big] = m \ddot{w}^{k}_{\frac{1}{2},n} \end{aligned}$$

If now it is assumed that $w^{j}_{0,n} = A^{j}_{0,n} e^{i\omega_n t}$ and $w^{j}_{\frac{1}{2},n} = A^{j}_{\frac{1}{2},n} e^{i\omega_n t}$ the following equations for the unknown amplitudes result:

$$\sum_{j} \Big[(C^{n}_{jk} - m\omega^{2}_{n}) A^{j}_{0,n} + C^{-n\,\prime}_{kj} A^{j}_{\frac{1}{2},n} \Big] = 0.$$

$$\sum_{j} \Big[C^{n\,\prime}_{jk} A^{j}_{0,n} + (C^{n}_{jk} - m\omega^{2}_{n}) A^{j}_{\frac{1}{2},n} \Big] = 0.$$

Since $C^{n}_{jk} = C^{-n}_{jk} = C^{n}_{kj}$ and $C^{n\,\prime}_{jk} = C^{-n\,\prime}_{jk} = C^{n\,\prime}_{kj}$, the condition for a non-trivial solution is equation (22),

$$\begin{vmatrix} (C^{n}_{11} - m\omega^{2}_{n}) & C^{n}_{12} & C^{n}_{13} & C^{n\,\prime}_{11} & C^{n\,\prime}_{12} & C^{n\,\prime}_{13} \\ C^{n}_{12} & (C^{n}_{22} - m\omega^{2}_{n}) & C^{n}_{23} & C^{n\,\prime}_{12} & C^{n\,\prime}_{22} & C^{n\,\prime}_{23} \\ C^{n}_{13} & C^{n}_{23} & (C^{n}_{33} - m\omega^{2}_{n}) & C^{n\,\prime}_{13} & C^{n\,\prime}_{23} & C^{n\,\prime}_{33} \\ C^{n\,\prime}_{11} & C^{n\,\prime}_{12} & C^{n\,\prime}_{13} & (C^{n}_{11} - m\omega^{2}_{n}) & C^{n}_{12} & C^{n}_{13} \\ C^{n\,\prime}_{12} & C^{n\,\prime}_{22} & C^{n\,\prime}_{23} & C^{n}_{12} & (C^{n}_{22} - m\omega^{2}_{n}) & C^{n}_{23} \\ C^{n\,\prime}_{13} & C^{n\,\prime}_{23} & C^{n\,\prime}_{33} & C^{n}_{13} & C^{n}_{23} & (C^{n}_{33} - m\omega^{2}_{n}) \end{vmatrix} = 0.$$

This is what is known as a block determinant and may be written in the symbolic form $\begin{vmatrix} A & B \\ B & A \end{vmatrix} = 0,$ where A and B represent third order arrays. It has been shown that such a determinant can be expanded as if A and B were single elements[30]. The result is that the sixth order equation in ω_n^2 can be reduced to the product of two third order equations.

$$\begin{vmatrix} A & B \\ B & A \end{vmatrix} = |A - B|\,|A + B| = 0.$$

The two determinantal equations can be written together in the following way: (23).

$$\begin{vmatrix} (C^n_{11} \pm C^{n'}_{11} - m\,\omega^2_n) & (C^n_{12} \pm C^{n'}_{12}) & (C^n_{13} \pm C^{n'}_{13}) \\ (C^n_{12} \pm C^{n'}_{12}) & (C^n_{22} \pm C^{n'}_{22} - m\,\omega^2_n) & (C^n_{23} \pm C^{n'}_{23}) \\ (C^n_{13} \pm C^{n'}_{13}) & (C^n_{23} \pm C^{n'}_{23}) & (C^n_{33} \pm C^{n'}_{33} - m\,\omega^2_n) \end{vmatrix} = 0.$$

The positive sign results in one equation and the negative sign in another.

There is a frequency here for every value of n so that a whole spectrum is obtained. For certain special directions in the crystal the determinant can be reduced to linear or quadratic equations and explicit solutions immediately obtained, but in general numerical methods must be used in solving the cubic equation. This necessitates numerical information about the force constants involved and in the next section the matter of relating these constants to macroscopic elastic properties will be considered. Certain simplifications are possible because of the symmetry properties of a cubic lattice. Then, in the third section actual solutions for the atomic model selected to represent a tungsten single crystal will be presented.

The second case of a face-centered cubic crystal is somewhat more complicated. The basic cell is then composed of four atoms, one at the origin, 0,0,0, and the others at the points, $\frac{1}{2}a$, $\frac{1}{2}a$, 0; $\frac{1}{2}a$, 0, $\frac{1}{2}a$; 0, $\frac{1}{2}a$, $\frac{1}{2}a$. Here again a is the length of one edge of the cube. Any atom in the crystal can be located by means of the equations, $r = (q,a)$ or $r = (q + \frac{1}{2}, a)$, where the $\frac{1}{2}$ is to be added to only two components of q at a time.

Then, specialization of the general theory gives the following results:

$$V = \frac{1}{2} \sum_j \sum_k \sum_r \sum_{r'} \overset{C_{jk}^{rr'}}{\downarrow} u_r^j \, u_{r'}^k .$$

$$(24) \quad \begin{aligned} u_r^j = \sum_n \Big\{ & w^j_{0,0,0;n} \, e^{2\pi i(n_1 q_1/N_1 + n_2 q_2/N_2 + n_3 q_3/N_3)} \\ & + w^j_{\frac{1}{2},\frac{1}{2},0;n} \, e^{2\pi i[n_1(q_1 + \frac{1}{2})/N_1 + n_2(q_2 + \frac{1}{2})/N_2 + n_3 q_3/N_3]} \\ & + w^j_{\frac{1}{2},0,\frac{1}{2};n} \, e^{2\pi i[n_1(q_1 + \frac{1}{2})/N_1 + n_2 q_2/N_2 + n_3(q_3 + \frac{1}{2})/N_3]} \\ & + w^j_{0,\frac{1}{2},\frac{1}{2};n} \, e^{2\pi i[n_1 q_1/N_1 + n_2(q_2 + \frac{1}{2})/N_2 + n_3(q_3 + \frac{1}{2})/N_3]} \Big\} \end{aligned}$$

Then,

$$(25) \quad \begin{aligned} V = \frac{1}{2} N_1 N_2 N_3 \sum_j \sum_k \sum_n \Big[& C^n_{jk} (w^j_{0,0,0;n} \, w^k_{0,0,0;-n} + w^j_{\frac{1}{2},\frac{1}{2},0;n} \, w^k_{\frac{1}{2},\frac{1}{2},0;-n} \\ & \quad + w^j_{\frac{1}{2},0,\frac{1}{2};n} \, w^k_{\frac{1}{2},0,\frac{1}{2};-n} + w^j_{0,\frac{1}{2},\frac{1}{2},n} \, w^k_{0,\frac{1}{2},\frac{1}{2};-n}) \\ & + C^{n'}_{jk} (w^j_{0,0,0;n} \, w^k_{\frac{1}{2},\frac{1}{2},0;-n} + w^j_{\frac{1}{2},0,\frac{1}{2};n} \, w^k_{0,\frac{1}{2},\frac{1}{2};-n}) \\ & + C^{n''}_{jk} (w^j_{0,0,0;n} \, w^k_{\frac{1}{2},0,\frac{1}{2};-n} + w^j_{\frac{1}{2},\frac{1}{2},0;n} \, w^k_{0,\frac{1}{2},\frac{1}{2};-n}) \\ & + C^{n'''}_{jk} (w^j_{0,0,0,n} \, w^k_{0,\frac{1}{2},\frac{1}{2},-n} + w^j_{\frac{1}{2},\frac{1}{2},0,n} \, w^k_{\frac{1}{2},0,\frac{1}{2},-n}) \Big], \end{aligned}$$

where

$$C^{n}_{jk} = \sum_{g} C^{g}_{jk}\, e^{(2\pi i/N)(-n,g)} \quad \text{and} \tag{26}$$

$$C^{n\prime}_{jk} = 2\sum_{g} C^{g_1+\frac{1}{2},\,g_2+\frac{1}{2},\,g_3}_{jk}\, e^{2\pi i\,[n_1(g_1+\frac{1}{2})/N_1 \,+\, n_2(g_2+\frac{1}{2})/N_2 \,+\, n_3 g_3/N_3]},$$

with similar equations for $C^{n''}_{jk}$ and $C^{n'''}_{jk}$. These quantities are real if $C^{N-\frac{1}{2}}_{jk}$ is neglected.

In the same way, the kinetic energy can be expressed as

$$T = \tfrac{1}{2}\, m\, N_1 N_2 N_3 \sum_{j}\sum_{n} \big(\dot{w}^{j}_{0,0,0;n}\, \dot{w}^{j}_{0,0,0;-n} + \dot{w}^{j}_{\frac{1}{2},\frac{1}{2},0;n}\, \dot{w}^{j}_{\frac{1}{2},\frac{1}{2},0;-n} + \dot{w}^{j}_{\frac{1}{2},0,\frac{1}{2};n}\, \dot{w}^{j}_{\frac{1}{2},0,\frac{1}{2};-n} + \dot{w}^{j}_{0,\frac{1}{2},\frac{1}{2};n}\, \dot{w}^{j}_{0,\frac{1}{2},\frac{1}{2};-n}\big). \tag{27}$$

The resulting secular equation is

$$\begin{vmatrix} A & B & C & D \\ B & A & D & C \\ C & D & A & B \\ D & C & B & A \end{vmatrix} = 0, \tag{28}$$

where A, B, C, and D are third order arrays.

$$A = \begin{array}{ccc} C^{n}_{11} - m\,\omega^{2}_{n} & C^{n}_{12} & C^{n}_{13} \\ C^{n}_{12} & C^{n}_{22} - m\,\omega^{2}_{n} & C^{n}_{23} \\ C^{n}_{13} & C^{n}_{23} & C^{n}_{33} - m\,\omega^{2}_{n} \end{array},$$

$$B = \begin{array}{ccc} C^{n\prime}_{11} & C^{n\prime}_{12} & C^{n\prime}_{13} \\ C^{n\prime}_{12} & C^{n\prime}_{22} & C^{n\prime}_{23} \\ C^{n\prime}_{13} & C^{n\prime}_{23} & C^{n\prime}_{33} \end{array},$$

with similar equations for C and D. By the theory of block determinants the following simplifications can be made:

$$\begin{vmatrix} A & B & C & D \\ B & A & D & C \\ C & D & A & B \\ D & C & B & A \end{vmatrix} = \begin{vmatrix} A + C & B + D \\ B + D & A + C \end{vmatrix} \begin{vmatrix} A - C & B - D \\ B - D & A - C \end{vmatrix}$$

$$= |A + C + B + D|\,|A + C - B - D|\,|A - C + B - D|\,|A - C - B + D|.$$

These factors may be written together in the form:

$$\begin{vmatrix} (C^{n}_{11} \pm C^{n\prime}_{11} \pm C^{n\prime\prime}_{11} \pm C^{n\prime\prime\prime}_{11} - m\omega^{2}_{n}) & (C^{n}_{12} \pm C^{n\prime}_{12} \pm C^{n\prime\prime}_{12} \pm C^{n\prime\prime\prime}_{12}) & (C^{n}_{13} \pm C^{n\prime}_{13} \pm C^{n\prime\prime}_{13} \pm C^{n\prime\prime\prime}_{13}) \\ (C^{n}_{12} \pm C^{n\prime}_{12} \pm C^{n\prime\prime}_{12} \pm C^{n\prime\prime\prime}_{12}) & (C^{n}_{22} \pm C^{n\prime}_{22} \pm C^{n\prime\prime}_{22} \pm C^{n\prime\prime\prime}_{22} - m\omega^{2}_{n}) & (C^{n}_{23} \pm C^{n\prime}_{23} \pm C^{n\prime\prime}_{23} \pm C^{n\prime\prime\prime}_{23}) \\ (C^{n}_{13} + C^{n\prime}_{13} + C^{n\prime\prime}_{13} + C^{n\prime\prime\prime}_{13}) & (C^{n}_{23} + C^{n\prime}_{23} + C^{n\prime\prime}_{23} + C^{n\prime\prime\prime}_{23}) & (C^{n}_{33} + C^{n\prime}_{33} + C^{n\prime\prime}_{33} + C^{n\prime\prime\prime}_{33} - m\omega^{2}_{n}) \end{vmatrix}$$

$$(29) \qquad = 0.$$

The double signs are not all independent; either one of them must be chosen as positive and the other two negative or all three must be positive, and the choice must be the same in each term. Thus, there are really four separate equations represented here.

In the next section a discussion of the connection between the macroscopic elastic properties and the microscopic force constants for a face-centered cubic crystal will be given. However, no numerical solution of the secular equation for such a lattice has been carried out yet.

It must be pointed out that, although the problem might be considered as theoretically solved when the secular equation is presented, very little useful information is available at this point. Certainly, in order to say anything definite about the frequency distribution a complete set of numerical solutions is indispensable. Before that can be obtained actual numerical values for the force constants involved are necessary.

SECTION 2. FORCE CONSTANTS.

There are two parts to this section: first, a general derivation of the relation between observed elastic properties and atomic force constants and second, a specialization to cubic crystals with additional assumptions for simplification.

Suppose that the displacement of an atom in the lattice is given in a general way by the sum of a rigid body translation, an infinitesimal rotation of the crystal as a whole, and a pure strain. Then,

$$\begin{aligned} u^1_r &= u_1 + e_{11} r_1 + (\tfrac{1}{2} e_{12} - \theta_3) r_2 + (\tfrac{1}{2} e_{13} + \theta_2) r_3 \\ u^2_r &= u_2 + (\tfrac{1}{2} e_{12} + \theta_3) r_1 + e_{22} r_2 + (\tfrac{1}{2} e_{23} - \theta_1) r_3 \qquad (30) \\ u^3_r &= u_3 + (\tfrac{1}{2} e_{13} - \theta_2) r_1 + (\tfrac{1}{2} e_{23} + \theta_1) r_2 + e_{23} r_3 \end{aligned}$$

where u_j is the component of translation, the same for all atoms, θ_j is the infinitesimal rotation about the j axis, and e_{jk} is the component of strain. When this is substituted into the equation for the potential energy, $V = \frac{1}{2} \sum_j \sum_k \sum_r \sum_{r'} C^{rr'}_{jk} u^j_r u^k_{r'}$, the result must be equal to the energy of a strained crystal given on page 5, since rigid body translation and rotation can contribute nothing to the potential energy. As the various components of translation, rotation, and strain are to be considered as entirely independent of each other, the identity must give rise to the following relations corresponding to the coefficients of the terms indicated.

(31) $u_j\ u_k$: $\sum_r \sum_{r'} C^{rr'}_{jk} u_j\ u_k = 0$, or $\sum_r \sum_{r'} C^{rr'}_{jk} = 0$.

$u_i\ e_{jk}$: $\sum_r \sum_{r'} (C^{rr'}_{ji}\ r_k + C^{rr'}_{ik}\ r'_j) = 0$.

$u_i\ \theta_1$: $\sum_r \sum_{r'} (C^{rr'}_{ij}\ r'_k - C^{rr'}_{ik}\ r'_j) = 0$. $(j \neq k;\ j,k \neq 1)$

Since $\sum_r \sum_{r'} C^{rr'}_{ij} r'_k = \sum_r \sum_{r'} C^{r'r}_{ji}\ r'_k = \sum_r \sum_{r'} C^{rr'}_{ji} r_k$, a combination of the two preceding equations shows that

(32) $$\sum_r \sum_{r'} C^{rr'}_{ij} r'_k = 0,$$

for all values of i, j, and k. There are then two sets of equations resulting from coefficients of terms containing u_i.

Consider now terms which contain θ_i.

θ_i^2: $\sum_r \sum_{r'} (C^{rr'}_{jj} r_k r'_k - 2\ C^{rr'}_{jk} r_k r'_j + C^{rr'}_{kk} r_j r'_j) = 0$.

$\theta_i\ \theta_j$: $\sum_r \sum_{r'} (C^{rr'}_{ij} r_k r'_k + C^{rr'}_{kk} r_j r'_i - C^{rr'}_{ik} r_k r'_j - C^{rr'}_{jk} r_k r'_i) = 0$.

$\theta_i\ e_{11}$: $\sum_r \sum_{r'} (C^{rr'}_{1j} r_1 r'_k - C^{rr'}_{1k} r_1 r'_j) = 0$.

$\theta_i\ e_{ik}$: $\sum_r \sum_{r'} (C^{rr'}_{kk} r_i r'_j - C^{rr'}_{ij} r_k r'_k + C^{rr'}_{ik} r_k r'_j - C^{rr'}_{kj} r_i r'_k) = 0$.

$\theta_i\ e_{jk}$: $\sum_r \sum_{r'} (C^{rr'}_{jj} r_k r'_k - C^{rr'}_{kk} r_j r'_j) = 0$.

In all cases, $i \neq j$ and $i,j \neq k$. The third equation can be written in the form:

(33) $$\sum_r \sum_{r'} C^{rr'}_{1j} r_1 r'_k = \sum_r \sum_{r'} C^{rr'}_{1k} r_1 r'_j\ .$$

From the second and fourth equations it is seen that

$$\sum_r \sum_{r'} (C^{rr'}_{kk} r_i r'_j - C^{rr'}_{jk} r_k r'_i) = \pm \sum_r \sum_{r'} (C^{rr'}_{ij} r_k r'_k - C^{rr'}_{ik} r_k r'_j)$$

Therefore, both sides of the equation must equal zero and

$$(34)\qquad \sum_r \sum_{r'} C^{rr'}_{kk}\, r_i r'_j = \sum_r \sum_{r'} C^{rr'}_{jk}\, r_k r'_i \,.$$

$$(35)\qquad \sum_r \sum_{r'} C^{rr'}_{ij}\, r_k r'_k = \sum_r \sum_{r'} C^{rr'}_{ik}\, r_k r'_j \,.$$

Finally, consider the coefficients of terms involving products of the strains.

$$e_{ii}e_{jk}:\qquad \sum_r \sum_{r'} \tfrac{1}{2}\left(C^{rr'}_{ik}\, r_i r'_j + C^{rr'}_{ij}\, r_i r'_k\right) = \sum_r \sum_{r'} C^{rr'}_{ij}\, r_i r'_k$$

$$= c^{ik}_{ij} = c^{ij}_{ik}.$$

equation (33) has been used here after l is set equal to i. The elastic constants with four indices are related to those ordinarily given by the following equations:

$$(36)\qquad c^{i3}_{i2} = c_{i4},\ c^{i3}_{i1} = c_{i5},\ c^{i2}_{i1} = c_{i6},\ c^{ii}_{ii} = c_{ii}.$$

$$e_{ik}e_{jk}:\qquad \sum_r \sum_{r'} \tfrac{1}{4}\left(C^{rr'}_{ij}\, r_k r'_k + C^{rr'}_{kj}\, r_i r'_k + C^{rr'}_{ik}\, r_k r'_j + C^{rr'}_{kk}\, r_i r'_j\right)$$

$$= \sum_r \sum_{r'} C^{rr'}_{ij}\, r_k r'_k = c^{kk}_{ij} = c^{ik}_{kj} = c^{kj}_{ik} = c^{ij}_{kk},$$

where equations (34) and (35) have been used and

$$(37)\qquad c^{33}_{21} = c_{45},\ c^{32}_{21} = c_{46},\ c^{32}_{11} = c_{56},$$

$$c^{22}_{11} = c_{66},\ c^{33}_{11} = c_{55},\ c^{33}_{22} = c_{44}.$$

All these relations can be combined into a single equation connecting the atomic force constants with the macroscopic elastic properties of the substance.

$$(38)\qquad c^{kl}_{ij} = \sum_r \sum_{r'} C^{rr'}_{ij}\, r_k r'_l$$

Since $C^{rr'}_{ij} = C^{rr'}_{ji}$ for a cubic crystal, it follows that $c^{kl}_{ij} = c^{kl}_{ji}$.

But this equality is equivalent to the Cauchy relations which are usually written as follows:

$c_{12} = c_{66}$, $c_{13} = c_{55}$, $c_{23} = c_{44}$, $c_{14} = c_{56}$, $c_{25} = c_{46}$, $c_{36} = c_{45}$.
These conditions, which result from the symmetry property discussed on page 34, are a necessary consequence of the model used here, but are not at all verified experimentally. Because of this difficulty it will later be necessary to make a plausible choice of the empirical data to be used in obtaining suitable atomic force constants.

Now that the general connection between atomic forces and large scale elastic properties has been obtained, a specialization for the case of a cubic crystal will be made. For this purpose the symmetry properties of a cube must be utilized. In the crystal the vertex of the cube is a symmetry center, any edge of the cube is a four-fold symmetry axis, the body diagonal is a three-fold symmetry axis, and any face of the cube is a symmetry plane. This means that the form of the potential energy must remain unchanged when the signs of any of the coordinates are reversed or when the coordinates are interchanged in any way.

If the interaction of each atom with every other atom in the crystal is considered, then the number of atomic force constants would be enormous and they could not individually be determined from elastic data available. However, for a non-polar solid such as tungsten the forces between atoms would presumably fall off fairly rapidly as the distance is increased. At any rate, only the effect on a given atom of its fourteen nearest neighbors has been taken into account.

The symmetry relations for a body-centered cubic lattice are as follows:

$$(39)\qquad C_{11}^{0,0,0} = C_{22}^{0,0,0} = C_{33}^{0,0,0}.$$

$$(40)\qquad C_{12}^{0,0,0} = C_{13}^{0,0,0} = C_{23}^{0,0,0} = 0,$$

$$\text{since } C_{12}^{0,0,0}\, u_r^1\, u_r^2 = C_{12}^{0,0,0}\,(-u_r^1)u_r^2.$$

$$(41)\qquad C_{11}^{1,0,0} = C_{11}^{-1,0,0} = C_{22}^{0,1,0} = C_{22}^{0,-1,0} = C_{33}^{0,0,1} = C_{33}^{0,0,-1},$$

$$\text{since } C_{11}^{1,0,0}\, u_r^1\, u^1_{r_1+1,r_2,r_3} = C_{11}^{-1,0,0}\,(-u_r^1)(-u^1_{r_1+1,r_2,r_3}).$$

$$(42)\qquad C_{11}^{0,1,0} = C_{11}^{0,-1,0} = C_{11}^{0,0,1} = C_{11}^{0,0,-1}$$
$$= C_{22}^{1,0,0} = C_{22}^{-1,0,0} = C_{22}^{0,0,1} = C_{22}^{0,0,-1}$$
$$= C_{33}^{0,1,0} = C_{33}^{0,-1,0} = C_{33}^{1,0,0} = C_{33}^{-1,0,0}.$$

$$(43)\qquad C_{12}^{1,0,0} = -C_{12}^{-1,0,0} = C_{12}^{0,1,0} = -C_{12}^{0,-1,0}$$
$$= C_{13}^{1,0,0} = -C_{13}^{-1,0,0} = C_{13}^{0,0,1} = -C_{13}^{0,0,-1}$$
$$= C_{23}^{0,1,0} = -C_{23}^{0,-1,0} = C_{23}^{0,0,1} = -C_{23}^{0,0,-1} = 0.$$

$$(44)\qquad C_{12}^{0,0,1} = C_{12}^{0,0,-1} = C_{13}^{0,1,0} = C_{13}^{0,-1,0} = C_{23}^{1,0,0} = C_{23}^{-1,0,0} = 0.$$

$$(45)\qquad C_{11}^{\pm\frac{1}{2},\pm\frac{1}{2},\pm\frac{1}{2}} = C_{22}^{\pm\frac{1}{2},\pm\frac{1}{2},\pm\frac{1}{2}} = C_{33}^{\pm\frac{1}{2},\pm\frac{1}{2},\pm\frac{1}{2}}.$$

(Each term represents eight equal constants.)

$$(46)\qquad C_{12}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} = C_{12}^{\frac{1}{2},\frac{1}{2},-\frac{1}{2}} = -C_{12}^{\frac{1}{2},-\frac{1}{2},\frac{1}{2}} = -C_{12}^{-\frac{1}{2},\frac{1}{2},\frac{1}{2}}$$
$$= C_{13}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} = C_{13}^{\frac{1}{2},-\frac{1}{2},\frac{1}{2}} = -C_{13}^{\frac{1}{2},\frac{1}{2},-\frac{1}{2}} = -C_{13}^{-\frac{1}{2},\frac{1}{2},\frac{1}{2}}$$
$$= C_{23}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} = C_{23}^{-\frac{1}{2},\frac{1}{2},\frac{1}{2}} = -C_{23}^{\frac{1}{2},\frac{1}{2},-\frac{1}{2}} = -C_{23}^{\frac{1}{2},-\frac{1}{2},\frac{1}{2}}$$

$$= C_{12}^{-\frac{1}{2},-\frac{1}{2},\frac{1}{2}} = C_{12}^{-\frac{1}{2},-\frac{1}{2},-\frac{1}{2}} = -C_{12}^{-\frac{1}{2},\frac{1}{2},-\frac{1}{2}} = -C_{12}^{\frac{1}{2},-\frac{1}{2},-\frac{1}{2}}$$
$$= C_{13}^{-\frac{1}{2},\frac{1}{2},-\frac{1}{2}} = C_{13}^{-\frac{1}{2},-\frac{1}{2},-\frac{1}{2}} = -C_{13}^{-\frac{1}{2},-\frac{1}{2},\frac{1}{2}} = -C_{13}^{\frac{1}{2},-\frac{1}{2},-\frac{1}{2}}$$
$$= C_{23}^{\frac{1}{2},-\frac{1}{2},-\frac{1}{2}} = C_{23}^{-\frac{1}{2},-\frac{1}{2},-\frac{1}{2}} = -C_{23}^{-\frac{1}{2},\frac{1}{2},-\frac{1}{2}} = -C_{23}^{-\frac{1}{2},-\frac{1}{2},\frac{1}{2}} .$$

By means of these equations the number of constants is reduced from ninety to five. If now all the relations for the constants of a body-centered cubic crystal are collected, the question of their evaluation can be considered. Before this is done, it is convenient to throw some of the equations into a more useful form. This is possible because of the following relation:

$$\sum_r \sum_{r'} C_{ij}^{rr'} r_k r'_l = \sum_r \sum_{r'} (C_{ij}^{rr'} r_k r'_l - C_{ij}^{rr'} r_k r_l)$$
$$= \frac{1}{2} \sum_r \sum_{r'} C_{ij}^{rr'} (r_k r'_l + r_l r'_k - r_k r_l - r'_k r'_l)$$
$$(47) \qquad = -\frac{1}{2} \sum_r \sum_{r'} C_{ij}^{rr'} (r'_k - r_k)(r'_l - r_l) .$$

The first equation is based on the fact that $\sum_r \sum_{r'} C_{ij}^{rr'} r_k r_l = \sum_r (\sum_{r'} C_{ij}^{r'-r}) r_k r_l$ and the sum within the parenthesis is zero according to equation (31). The sum there over r and r' is simply equal to the product of the number of atoms in the crystal by the sum over r' alone, if boundary effects at the edge of the solid are neglected. This is equivalent to disregarding the square of the number of atoms in comparison with the cube of that quantity. Writing the sum in (47) in terms of differences of coordinates simplifies the evaluations.

Equation (32) is automatically satisfied for a cubic lattice, while equations (31) and (38) give the following results:

$$
\begin{aligned}
&C_{11}^{0,0,0} + 2\,C_{11}^{1,0,0} + 4\,C_{11}^{0,1,0} + 8\,C_{11}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} = 0. \\
&C_{11}^{1,0,0} + C_{11}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} = -\tfrac{1}{2}\,a\,c_{11}. \\
&C_{12}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} = -\tfrac{1}{2}\,a\,c_{12}. \\
&C_{11}^{0,1,0} + C_{11}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} = -\tfrac{1}{2}\,a\,c_{44}.
\end{aligned}
\tag{48}
$$

The terms on the left had a factor from the summation of 2 $N_1N_2N_3$, the number of atoms in the crystal, but then it was necessary to divide by $N_1N_2N_3a$, the volume of the solid, since the elastic constants on the right are for a unit volume.

There are four equations here in five unknowns so that a solution cannot be found unless an additional condition is imposed. Since the model used consists of point masses, it is natural to assume that they are acted upon by central forces. Then,

$$C_{11}^{0,1,0} = 0, \tag{49}$$

for the displacement in this case is at right angles to the line joining the atoms concerned and the resulting potential energy is a second order effect. This can be shown by considering the variation in the distance between the atoms at the positions, r_1, r_2, r_3 and r_1, r_2+1, r_3 when their respective displacements are $u^1_{r_1,r_2,r_3}$ and $u^1_{r_1,r_2+1,r_3}$ The change in the distance separating the atoms can be represented as

$$
\begin{aligned}
&[(u^1_{r_1,r_2+1,r_3} - u^1_{r_1,r_2,r_3})^2 + a^2]^{\frac{1}{2}} - a \\
&\qquad = \tfrac{1}{2}\,(u^1_{r_1,r_2+1,r_3} - u^1_{r_1,r_2,r_3})^2/a^2,
\end{aligned}
$$

the first two terms in a series expansion of the radical being retained. If the atoms had been displaced along the line connecting them, the force constant involved would be $C_{22}^{0,1,0}$ and the resulting change in distance would equal $u^2_{r_1,r_2+1,r_3} - u^2_{r_1,r_2,r_3}$, the superscript refers to the fact that the displacement is in the y direction. It is therefore clear that the previous case where the square of the difference in displacements enters gives a negligible contribution in a theory where only Hooke's law type of forces are considered.

It should be noted that the assumption of central forces need not be correct, a priori. Although in a monatomic cubic crystal each lattice point is a center of symmetry, the atoms are actually extended bodies with probability functions for the positions of extranuclear electrons that are not necessarily spherically symmetrical. Nevertheless, since the presence of electrons is disregarded here, it seems logical to extend the hypotheses to include central forces.

Only the question of the Cauchy relation remains before proceeding to the actual evaluation of the atomic force constants. This relation in the case of a cubic crystal is $c_{12} = c_{44}$. According to the explanation given in the introduction, the quantum mechanical considerations of Fuchs have indicated that it is the influence of the "free" electrons on the compressibility of the crystal which causes the deviation from the Cauchy theory. It was shown there that $c_{11} - c_{12}$ and c_{44} are not affected in this way by the electrons and so their experimental values may be used, while instead of the observed compressibility the Cauchy relation is utilized in this work. This means that an attempt is made to secure atomic force constants suitable for the simple model considered here.

Introduction of these additional assumptions leads to the following simplified conditions for a body-centered cubic crystal:

$$
\begin{aligned}
& C_{12}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} = C_{11}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} = -\tfrac{1}{2}\, a\, c_{44} \\
(50) \qquad & C_{11}^{1,0,0} = -\tfrac{1}{2}\, a(c_{11} - c_{12}). \\
& C_{11}^{0,0,0} = 4\, a\, c_{44} + a(c_{11} - c_{12}).
\end{aligned}
$$

Now, in the special case of tungsten, the condition for isotropy of elastic properties is also satisfied, so that $c_{44} = \frac{1}{2}(c_{11} - c_{12})$ Under these circumstances,

$$
\begin{aligned}
& C_{12}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} = C_{11}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} = -\tfrac{1}{2}\, a\, c_{44} \\
(51) \qquad & C_{11}^{1,0,0} = -\, a\, c_{44} \\
& C_{11}^{0,0,0} = 6\, a\, c_{44}
\end{aligned}
$$

The fact that only one constant remains will prove significant. It must be emphasized that, in spite of the apparently large number of assumptions made, the underlying hypothesis is simply the conception of a solid body as composed of point atoms acted on by central forces.

The situation is quite similar for a face-centered cubic lattice. Exactly the same types of symmetry apply and the relations which result when each atom is affected by its eighteen nearest neighbors are identical with those for a body-centered cubic crystal except for the following equations which replace (45) and (46):

$$C_{11}^{0,\pm\frac{1}{2},\pm\frac{1}{2}} = C_{22}^{\pm\frac{1}{2},0,\pm\frac{1}{2}} = C_{33}^{\pm\frac{1}{2},\pm\frac{1}{2},0}. \tag{52}$$

$$\begin{aligned} C_{11}^{\pm\frac{1}{2},0,\pm\frac{1}{2}} &= C_{22}^{0,\pm\frac{1}{2},\pm\frac{1}{2}} = C_{33}^{0,\pm\frac{1}{2},\pm\frac{1}{2}} \\ &= C_{11}^{\pm\frac{1}{2},\pm\frac{1}{2},0} = C_{22}^{\pm\frac{1}{2},\pm\frac{1}{2},0} = C_{33}^{\pm\frac{1}{2},0,\pm\frac{1}{2}}. \end{aligned} \tag{53}$$

$$\begin{aligned} C_{12}^{0,\pm\frac{1}{2},\pm\frac{1}{2}} &= C_{23}^{\pm\frac{1}{2},0,\pm\frac{1}{2}} = C_{13}^{0,\pm\frac{1}{2},\pm\frac{1}{2}} \\ &= C_{12}^{\pm\frac{1}{2},0,\pm\frac{1}{2}} = C_{23}^{\pm\frac{1}{2},\pm\frac{1}{2},0} = C_{13}^{\pm\frac{1}{2},\pm\frac{1}{2},0} = 0. \end{aligned} \tag{54}$$

$$\begin{aligned} C_{12}^{\frac{1}{2},\frac{1}{2},0} &= -C_{12}^{-\frac{1}{2},\frac{1}{2},0} = -C_{12}^{\frac{1}{2},-\frac{1}{2},0} = C_{12}^{-\frac{1}{2},-\frac{1}{2},0} \\ &= C_{13}^{\frac{1}{2},0,\frac{1}{2}} = -C_{13}^{-\frac{1}{2},0,\frac{1}{2}} = -C_{13}^{\frac{1}{2},0,-\frac{1}{2}} = C_{13}^{-\frac{1}{2},0,-\frac{1}{2}} \\ &= C_{23}^{0,\frac{1}{2},\frac{1}{2}} = -C_{23}^{0,-\frac{1}{2},\frac{1}{2}} = -C_{23}^{0,\frac{1}{2},-\frac{1}{2}} = C_{23}^{0,-\frac{1}{2},-\frac{1}{2}}. \end{aligned} \tag{55}$$

(In the first three equations each term represents four equal constants.)

The one hundred and fourteen constants for a face-centered cubic lattice are therefore reduced to six by these symmetry relations. Equations (31) and (38) then become

$$\begin{aligned} &C_{11}^{0,0,0} + 2\,C_{11}^{1,0,0} + 4\,C_{11}^{0,1,0} + 4\,C_{11}^{0,\frac{1}{2},\frac{1}{2}} + 8\,C_{11}^{\frac{1}{2},\frac{1}{2},0} = 0. \\ &C_{11}^{1,0,0} + C_{11}^{\frac{1}{2},\frac{1}{2},0} = -\tfrac{1}{4}\,a\,c_{11}. \\ &C_{12}^{\frac{1}{2},\frac{1}{2},0} = -\tfrac{1}{2}\,a\,c_{12}. \\ &C_{11}^{0,1,0} + \tfrac{1}{2}\left(C_{11}^{\frac{1}{2},\frac{1}{2},0} + C_{11}^{0,\frac{1}{2},\frac{1}{2}}\right) = -\tfrac{1}{4}\,a\,c_{44}. \end{aligned} \tag{56}$$

If again central forces are assumed, $C_{11}^{0,1,0}$ and $C_{11}^{0,\frac{1}{2},\frac{1}{2}}$ may be neglected since the displacements involved are at right angles to the line connecting the atoms. In that case there are just enough equations to determine the four remaining constants. The Cauchy relation may be used in the same way as for the body-centered cubic lattice, but no face-centered cubic crystals seems to have elastic constants which satisfy the isotropy condition. The final form for the atomic force constants is therefore

$$\begin{aligned} & C_{12}^{\frac{1}{2},\frac{1}{2},0} = C_{11}^{\frac{1}{2},\frac{1}{2},0} = -\frac{1}{2}\,a\,c_{44}. \\ (57) \qquad & C_{11}^{1,0,0} = \frac{1}{4}\,a\,c_{44} - \frac{1}{4}\,a(c_{11} - c_{12}). \\ & C_{11}^{0,0,0} = \frac{7}{2}\,a\,c_{44} + \frac{1}{2}a(c_{11} - c_{12}). \end{aligned}$$

The numerical calculations have not yet been carried out for a face-centered cubic crystal, so no further discussion will be given.

This completes the discussion of the atomic force constants for the particular type of model used in this work. The next section will deal with the way in which these constants enter the secular equation. It will be found that, even with the assumptions about central forces between point atoms, the solution of the determinantal equation for the frequency involves considerable numerical work. If these simplifying hypotheses had not been made, the numerical evaluations would have been much more difficult.

SECTION 3. SECULAR EQUATION

The general form of the secular equation for a body-centered cubic lattice is given in equation (23) on page 42. The constants appearing there may be written out explicitly as follows:

$$C^{n}_{jk} = \sum_{g} C^{g_1, g_2, g_3}_{jk} e^{2\pi i(n_1 g_1/N_1 + n_2 g_2/N_2 + n_3 g_3/N_3)}$$

$$C^{n'}_{jk} = \sum_{g} C^{g_1+\frac{1}{2},\, g_2+\frac{1}{2},\, g_3+\frac{1}{2}}_{jk} e^{2\pi i\left[n_1(g_1+\frac{1}{2})/N_1 + n_2(g_2+\frac{1}{2})/N_2 + n_3(g_3+\frac{1}{2})/N_3\right]}.$$

Let $\pi n_1/N_1 = x$, $\pi n_2/N_2 = y$, $\pi n_3/N_3 = z$. These quantities are proportional to direction cosines for waves propagated in various ways through the crystal.

Under certain conditions the secular equation can be factored, and these circumstances will now be investigated. From the preceding equations it is seen that when $x = y$, $C^{n}_{11} = C^{n}_{22}$, $C^{n'}_{11} = C^{n'}_{22}$, $C^{n}_{13} = C^{n}_{23}$, and $C^{n'}_{13} = C^{n'}_{23}$. Then, the determinant obviously vanishes when

$$(58) \qquad (C^{n}_{11} \pm C^{n'}_{11} - m\,\omega^2_n) = (C^{n}_{12} \pm C^{n'}_{12})$$

since the first two columns are then identical. This leaves the quadratic equation (59)

$$(C^{n}_{33} \pm C^{n'}_{33} - m\,\omega^2_n)(C^{n}_{11} \pm C^{n'}_{11} + C^{n}_{12} \pm C^{n'}_{12} - m\,\omega^2_n) = 2(C^{n}_{13} \pm C^{n'}_{13})^2$$

A similar reduction can be made when $x = z$ or $y = z$. This corresponds to waves whose directions of propagation are in a plane containing one edge of the cube and making an angle of 45 with the other two edges.

If $x = y = z$, the cubic equation can be broken up into linear equations, for then $C^{n}_{11} = C^{n}_{22} = C^{n}_{33}$, $C^{n'}_{11} = C^{n'}_{22} = C^{n'}_{33}$, $C^{n}_{12} = C^{n}_{13} = C^{n}_{23}$, $C^{n'}_{12} = C^{n'}_{13} = C^{n'}_{23}$. The determinant then vanishes when

$$(60) \qquad (C^{n}_{11} \pm C^{n'}_{11} - m\,\omega^2_n) = (C^{n}_{12} \pm C^{n'}_{12})$$

$$(61) \qquad (C^{n}_{11} \pm C^{n'}_{11} - m\,\omega^2_n) = -2(C^{n}_{12} \pm C^{n'}_{12})$$

These frequencies correspond to waves along the body diagonal of the cube.

When only the interaction between a given atom in the body-centered cubic crystal and its fourteen nearest neighbors is considered, the constants in the secular equation have the following form:

$$C^{n}_{11} = C^{0,0,0}_{11} + 2\,C^{1,0,0}_{11}\cos 2x + 2\,C^{0,1,0}_{11}(\cos 2y + \cos 2z) \tag{62}$$

$$C^{n}_{22} = C^{0,0,0}_{11} + 2\,C^{1,0,0}_{11}\cos 2y + 2\,C^{0,1,0}_{11}(\cos 2x + \cos 2z) \tag{63}$$

$$C^{n}_{33} = C^{0,0,0}_{11} + 2\,C^{1,0,0}_{11}\cos 2z + 2\,C^{0,1,0}_{11}(\cos 2x + \cos 2y) \tag{64}$$

$$C^{n}_{12} = C^{n}_{13} = C^{n}_{23} = 0. \tag{65}$$

$$\begin{aligned} C^{n'}_{11} = C^{n'}_{22} = C^{n'}_{33} &= 2\,C^{\frac{1}{2},\frac{1}{2},\frac{1}{2}}_{11}\left[\cos(x+y+z) + \cos(x-y+z)\right. \\ &\qquad \left. + \cos(x+y-z) + \cos(x-y-z)\right] \\ &= 4\,C^{\frac{1}{2},\frac{1}{2},\frac{1}{2}}_{11}\left[\cos x\cos(y+z) + \cos x\cos(y-z)\right] \\ &= 8\,C^{\frac{1}{2},\frac{1}{2},\frac{1}{2}}_{11}\cos x\cos y\cos z. \end{aligned} \tag{66}$$

$$\begin{aligned} C^{n'}_{12} &= 2\,C^{\frac{1}{2},\frac{1}{2},\frac{1}{2}}_{12}\left[\cos(x+y+z) - \cos(x-y+z)\right. \\ &\qquad \left. + \cos(x+y-z) - \cos(x-y-z)\right] \\ &= -8\,C^{\frac{1}{2},\frac{1}{2},\frac{1}{2}}_{12}\sin x\sin y\cos z. \end{aligned} \tag{67}$$

$$C^{n'}_{13} = -8\,C^{\frac{1}{2},\frac{1}{2},\frac{1}{2}}_{12}\sin x\cos y\sin z. \tag{68}$$

$$C^{n'}_{23} = -8\,C^{\frac{1}{2},\frac{1}{2},\frac{1}{2}}_{12}\cos x\sin y\sin z. \tag{69}$$

In the special case of the atomic model set up for tungsten, the constants in the secular equation have the following form:

$$C^{n}_{11} = 4\,a\,c_{44}(1+\sin^2 x)$$

$$C^{n}_{22} = 4\,a\,c_{44}(1+\sin^2 y)$$

$$C^{n}_{33} = 4\,a\,c_{44}(1+\sin^2 z)$$

$$C^{n\prime}_{11} = C^{n\prime}_{22} = C^{n\prime}_{33} = -\,4\,a\,c_{44}\cos x\cos y\cos z. \tag{70}$$

$$C^{n\prime}_{12} = 4\,a\,c_{44}\sin x\sin y\cos z.$$

$$C^{n\prime}_{13} = 4\,a\,c_{44}\sin x\cos y\sin z.$$

$$C^{n\prime}_{23} = 4\,a\,c_{44}\cos x\sin y\sin z.$$

The secular equation then becomes

$$\begin{vmatrix} (1+\sin^2 x \mp\cos x\cos y\cos z - f_n^2) & (\pm\sin x\sin y\cos z) & (\pm\sin x\cos y\sin z) \\ (\pm\sin x\sin y\cos z) & (1+\sin^2 y \mp\cos x\cos y\cos z - f_n^2) & (\pm\cos x\sin y\sin z) \\ (\pm\sin x\cos y\sin z) & (\pm\cos x\sin y\sin z) & (1+\sin^2 z \mp\cos x\cos y\cos z - f_n^2) \end{vmatrix} = 0. \tag{71}$$

Here, $f_n = (m\omega_n^2/4ac_{44})^{\frac{1}{2}}$, a quantity directly proportional to the frequency. The values of x, y, and z are supposed to run from $-\pi/2$ to $\pi/2$. It is clear from the form of the determinant that the negative values give the same roots as the positive ones, so that actually the number of separate and distinct frequencies is less than the number of degrees of freedom. It should also be noted that the double sign can be dispensed with if x is allowed to run from 0 to π, since the root for x in the equation with the minus sign is the same as the root for $\pi - x$ in the equation with the plus sign. Therefore, the range of values of x will be so extended and the minus sign omitted.

Now, the explicit solutions for certain special directions may be written as follows:

(72) $$z = 0$$

$f^2 = 1 - \cos x \cos y$. (Double root.)

$f^2 = 1 - \cos x \cos y + \sin^2 x + \sin^2 y$.

(73) $$x = y$$

$f^2 = 1 + \sin^2 y + \cos z$.

$$f^2 = \frac{1}{4}\left[6 - \cos z - \cos 2z - (1 + 3 \cos z)\cos 2y\right]$$
$$\pm\frac{1}{4}\left\{\left[\cos 2z + \cos z - (1+\cos z)\cos 2y\right]^2 + 2(1-\cos 2z)(1-\cos 4y)\right\}^{\frac{1}{2}}$$

(There are similar equations for $x = z$ and $y = z$.)

(74) $$x = \pi - y$$

$f^2 = 1 + \sin^2 y + \cos z$.

$$f^2 = \frac{1}{4}\left[6 + \cos z - \cos 2z - (1 - 3 \cos z)\cos 2y\right]$$
$$\pm\frac{1}{4}\left\{\left[\cos 2z - \cos z - (1-\cos z)\cos 2y\right]^2 + 2(1-\cos 2z)(1- \cos 4y)\right\}^{\frac{1}{2}}$$

(75) $$x = y = z$$

$f^2 = 1 + \sin^2 y + \cos y$. (Double root.)

$f^2 = 2 + 2 \cos y - \cos^2 y - 3 \cos^3 y$.

However, when such simplifications cannot be made, it is necessary to solve the cubic equations. Due to the cubic symmetry a solution in a plane perpendicular to the z axis for $x = x_1$ and $y = y_1$ is equal to the solution in the same plane for $x = y_1$ and $y = x_1$. Also a solution along the line $y = y_1$ in the z_1 plane can be used as the solution along the line $y = z_1$ in the $z = y_1$ plane. The solutions have been found for values of x, y, and z at 10° intervals. Thus, 49 cubic equations were solved in the $z = 10°$ plane, 36 in the 20° plane, 25 in the 30° plane, etc., making a total of 140.

The method of numerical caluclation employed consisted of assuming a value for the root from an estimation based on roots already determined, trying this guess in the cubic equation and at the same time obtaining a more accurate value for the root. let f^2 be the true root and $f^2 - \delta$ the value being tested. If δ is small it can be expressed in the following way: (76)

$$\delta = \left[C^n_{11}(C^n_{22}C^n_{33}) + 2C^n_{12}C^n_{13}C^n_{23} - C^n_{33}(C^n_{12})^2 - C^n_{22}(C^n_{13})^2 - C^n_{11}(C^n_{23})^2\right]$$
$$\div \left[\{C_{11}(C_{22} + C_{33}) + C_{22}C_{33} - (C_{12})^2 - (C_{13})^2 - (C_{23})^2\}(4ac_{44})\right]$$

Second and third powers of δ have been neglected. After the value of δ is obtained it is added to the assumed root and a better approximation is the result. This process is repeated until the roots are known to be accurate to three decimal places. The actual numerical work was facilitated by use of a calculating machine.

Since all the roots of the secular equation are real and positive in this problem, there are three values of f^2 for each value of n. When these three roots are close together, it is sometimes not obvious how to separate them and assign them to the proper branch of the many-valued function. The choice has been made so as to preserve the cubic symmetry properties for each branch separately. In particular, this means that in the case of the linear and quadratic reductions for special directions in the crystal it has been necessary sometimes to interchange the assignment of roots to various branches when the point where $x = y = z$ is reached.

The roots of the secular equation are given in the following tables. Because of the cubic symmetry of the lattice, the values may be reflected across the diagonals, x = y or x = π − y. The first set of roots is double in the plane, z = 0°, but in higher planes all three roots of the cubic equation appear.

$z = 0^0$

x y	0^0	10^0	20^0	30^0	40^0	50^0	60^0	70^0	80^0	90^0	100^0	110^0	120^0	130^0	140^0	150^0	160^0	170^0	180^0
0^0	0	0.015	0.060	0.134	0.234	0.357	0.500	0.658	0.826	1.000	1.174	1.342	1.500	1.643	1.766	1.866	1.940	1.985	2.000
10^0		0.030	0.075	0.147	0.246	0.367	0.508	0.663	0.829	1.000	1.171	1.337	1.492	1.633	1.754	1.853	1.925	1.970	
20^0			0.117	0.186	0.280	0.396	0.530	0.679	0.837	1.000	1.163	1.321	1.470	1.604	1.720	1.814	1.883		
30^0				0.250	0.337	0.443	0.567	0.704	0.850	1.000	1.150	1.296	1.433	1.557	1.663	1.750			
40^0					0.413	0.508	0.617	0.738	0.867	1.000	1.133	1.262	1.383	1.492	1.587				
50^0						0.587	0.679	0.780	0.888	1.000	1.112	1.220	1.321	1.413					
60^0							0.750	0.829	0.913	1.000	1.087	1.171	1.250						
70^0								0.883	0.941	1.000	1.059	1.117							
80^0									0.970	1.000	1.030								
90^0										1.000									

0^0	0	0.045	0.177	0.384	0.647	0.944	1.250	1.541	1.796	2.000	2.143	2.225	2.250	2.230	2.179	2.116	2.057	2.015	2.000
10^0		0.090	0.222	0.427	0.689	0.984	1.288	1.576	1.829	2.030	2.171	2.250	2.273	2.250	2.198	2.133	2.073	2.030	
20^0			0.351	0.553	0.810	1.100	1.397	1.679	1.924	2.117	2.250	2.321	2.337	2.308	2.250	2.181	2.117		
30^0				0.750	1.000	1.280	1.567	1.837	2.069	2.250	2.370	2.429	2.433	2.394	2.327	2.250			
40^0					1.240	1.508	1.780	2.034	2.250	2.413	2.516	2.558	2.546	2.492	2.413				
50^0						1.760	2.015	2.250	2.445	2.587	2.668	2.690	2.658	2.587					
60^0							2.250	2.462	2.633	2.750	2.807	2.804	2.750						
70^0								2.649	2.793	2.883	2.912	2.883							
80^0									2.910	2.970	2.970								
90^0										3.000									

z = 10^0

x y	0^0	10^0	20^0	30^0	40^0	50^0	60^0	70^0	80^0	90^0	100^0	110^0	120^0	130^0	140^0	150^0	160^0	170^0	180^0
0^0	0.015	0.030	0.075	0.147	0.246	0.367	0.508	0.663	0.829	1.000	1.171	1.337	1.492	1.633	1.754	1.853	1.925	1.970	1.985
10^0		0.045	0.089	0.158	0.252	0.368	0.503	0.651	0.810	0.973	1.137	1.295	1.450	1.580	1.697	1.794	1.870	1.926	
20^0			0.132	0.198	0.287	0.394	0.519	0.656	0.803	0.954	1.106	1.253	1.392	1.519	1.631	1.727	1.805		
30^0				0.265	0.347	0.444	0.555	0.678	0.809	0.944	1.080	1.212	1.338	1.454	1.558	1.648			
40^0					0.428	0.515	0.611	0.717	0.828	0.943	1.059	1.173	1.281	1.382	1.475				
50^0						0.602	0.683	0.768	0.858	0.950	1.043	1.134	1.222	1.305					
60^0							0.765	0.832	0.897	0.963	1.030	1.096	1.160						
70^0								0.898	0.941	0.980	1.019	1.058							
80^0									0.985	1.000	1.009								
90^0										1.015									

0^0	0.015	0.030	0.075	0.147	0.246	0.367	0.508	0.663	0.829	1.000	1.171	1.337	1.492	1.633	1.754	1.853	1.925	1.970	1.985
10^0		0.045	0.090	0.164	0.264	0.387	0.530	0.688	0.857	1.030	1.204	1.372	1.530	1.673	1.796	1.896	1.970	2.015	
20^0			0.133	0.206	0.304	0.425	0.566	0.721	0.887	1.058	1.228	1.394	1.549	1.689	1.809	1.904	1.966		
30^0				0.268	0.360	0.476	0.609	0.757	0.915	1.077	1.239	1.396	1.542	1.673	1.782	1.863			
40^0					0.434	0.537	0.659	0.794	0.938	1.087	1.234	1.377	1.508	1.624	1.718				
50^0						0.611	0.713	0.831	0.957	1.086	1.215	1.338	1.451	1.548					
60^0							0.776	0.868	0.971	1.078	1.187	1.283	1.374						
70^0								0.911	0.984	1.063	1.142	1.216							
80^0									1.000	1.045	1.095								
90^0										1.030									

0^0	0.045	0.090	0.222	0.427	0.689	0.984	1.288	1.576	1.829	2.030	2.171	2.250	2.273	2.250	2.198	2.133	2.073	2.030	2.015
10^0		0.134	0.264	0.468	0.728	1.021	1.323	1.609	1.859	2.057	2.195	2.271	2.290	2.265	2.209	2.139	2.072	2.015	
20^0			0.390	0.589	0.843	1.130	1.425	1.703	1.945	2.136	2.265	2.333	2.344	2.320	2.247	2.171	2.102		
30^0				0.781	1.026	1.303	1.586	1.853	2.082	2.259	2.375	2.430	2.429	2.385	2.314	2.235			
40^0					1.260	1.523	1.792	2.042	2.254	2.413	2.513	2.551	2.535	2.479	2.398				
50^0						1.771	2.021	2.251	2.442	2.581	2.659	2.677	2.644	2.572					
60^0							2.250	2.458	2.625	2.740	2.794	2.789	2.735						
70^0								2.641	2.782	2.870	2.898	2.868							
80^0									2.896	2.955	2.955								
90^0										2.985									

z = 20°

x y	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°	160°	170°	180°
0°	0.060	0.075	0.117	0.186	0.280	0.396	0.530	0.679	0.837	1.000	1.163	1.321	1.470	1.604	1.720	1.814	1.883	1.925	1.940
10°		0.089	0.132	0.198	0.287	0.394	0.519	0.656	0.803	0.954	1.106	1.253	1.392	1.519	1.631	1.727	1.805	1.870	
20°			0.177	0.242	0.324	0.422	0.534	0.657	0.789	0.925	1.061	1.195	1.322	1.440	1.547	1.642	1.727		
30°				0.310	0.389	0.477	0.576	0.683	0.796	0.913	1.031	1.148	1.259	1.365	1.464	1.555			
40°					0.473	0.556	0.640	0.729	0.822	0.918	1.015	1.110	1.203	1.293	1.380				
50°						0.647	0.723	0.793	0.864	0.936	1.008	1.081	1.152	1.223					
60°							0.810	0.870	0.918	0.965	1.011	1.057	1.104						
70°								0.943	0.979	1.000	1.018	1.036							
80°									1.030	1.037	1.028								
90°										1.060									

0°	0.060	0.075	0.117	0.186	0.280	0.396	0.530	0.679	0.837	1.000	1.163	1.321	1.470	1.604	1.720	1.814	1.883	1.925	1.940
10°		0.090	0.133	0.206	0.304	0.425	0.566	0.721	0.887	1.058	1.228	1.394	1.549	1.689	1.809	1.904	1.966	1.970	
20°			0.177	0.251	0.351	0.474	0.617	0.775	0.943	1.117	1.291	1.459	1.617	1.760	1.883	1.983	2.057		
30°				0.317	0.413	0.534	0.675	0.830	0.995	1.166	1.336	1.501	1.655	1.793	1.908	1.986			
40°					0.491	0.600	0.732	0.878	1.035	1.196	1.356	1.510	1.651	1.773	1.865				
50°						0.676	0.786	0.918	1.059	1.204	1.347	1.484	1.606	1.706					
60°							0.850	0.951	1.070	1.193	1.315	1.429	1.529						
70°								0.992	1.073	1.169	1.265	1.354							
80°									1.085	1.138	1.204								
90°										1.117									

0°	0.177	0.222	0.351	0.553	0.810	1.100	1.397	1.679	1.924	2.117	2.250	2.321	2.337	2.308	2.250	2.181	2.117	2.073	2.057
10°		0.264	0.390	0.589	0.843	1.130	1.425	1.703	1.945	2.136	2.265	2.333	2.344	2.320	2.247	2.171	2.102	2.072	
20°			0.507	0.697	0.943	1.222	1.509	1.779	2.011	2.192	2.312	2.369	2.370	2.324	2.247	2.153	2.057		
30°				0.875	1.108	1.373	1.646	1.902	2.121	2.288	2.404	2.436	2.423	2.365	2.279	2.190			
40°					1.325	1.573	1.829	2.067	2.268	2.416	2.505	2.532	2.505	2.439	2.353				
50°						1.803	2.038	2.256	2.436	2.564	2.632	2.642	2.602	2.527					
60°							2.252	2.447	2.604	2.709	2.756	2.747	2.690						
70°								2.618	2.750	2.831	2.854	2.823							
80°									2.857	2.911	2.910								
90°										2.940									

z = 30°

x y	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°	160°	170°	180°
0°	0.134	0.147	0.186	0.250	0.337	0.443	0.567	0.704	0.850	1.000	1.150	1.296	1.423	1.557	1.663	1.750	1.814	1.853	1.866
10°		0.158	0.198	0.265	0.347	0.444	0.555	0.678	0.809	0.944	1.080	1.212	1.338	1.454	1.558	1.648	1.727	1.794	
20°			0.242	0.310	0.389	0.477	0.576	1.683	0.796	0.913	1.031	1.148	1.259	1.365	1.464	1.555	1.642		
30°				0.384	0.459	0.539	0.625	0.716	0.810	0.907	1.005	1.102	1.197	1.289	1.379	1.467			
40°					0.547	0.626	0.700	0.773	0.847	0.922	0.997	1.073	1.148	1.223	1.299				
50°						0.721	0.793	0.850	0.903	0.954	1.005	1.056	1.109	1.164					
60°							0.884	0.939	0.973	1.000	1.024	1.049	1.077						
70°								1.017	1.048	1.053	1.051	1.049							
80°									1.104	1.106	1.081								
90°										1.134									

0°	0.134	0.147	0.186	0.250	0.337	0.443	0.567	0.704	0.850	1.000	1.150	1.296	1.433	1.557	1.663	1.750	1.814	1.853	1.866
10°		0.164	0.206	0.268	0.360	0.476	0.609	0.757	0.915	1.077	1.239	1.396	1.542	1.673	1.782	1.863	1.904	1.896	
20°			0.251	0.317	0.413	0.534	0.675	0.830	0.995	1.166	1.336	1.501	1.655	1.793	1.908	1.986	1.983		
30°				0.384	0.484	0.607	0.750	0.908	1.076	1.250	1.424	1.592	1.750	1.893	2.016	2.116			
40°					0.567	0.683	0.822	0.977	1.142	1.312	1.481	1.645	1.797	1.928	2.022				
50°						0.767	0.886	1.029	1.183	1.341	1.498	1.646	1.778	1.881					
60°							0.957	1.067	1.200	1.339	1.475	1.601	1.707						
70°								1.113	1.202	1.312	1.422	1.522							
80°									1.215	1.274	1.351								
90°										1.250									

0°	0.384	0.427	0.553	0.750	1.000	1.280	1.567	1.837	2.069	2.250	2.370	2.429	2.433	2.394	2.327	2.250	2.181	2.133	2.116
10°		0.468	0.589	0.781	1.026	1.303	1.586	1.853	2.082	2.259	2.375	2.430	2.429	2.385	2.314	2.236	2.171	2.139	
20°			0.697	0.876	1.108	1.373	1.646	1.902	2.121	2.288	2.404	2.436	2.423	2.365	2.279	2.190	2.153		
30°				1.033	1.247	1.494	1.750	1.990	2.193	2.343	2.432	2.459	2.428	2.351	2.242	2.116			
40°					1.437	1.662	1.896	2.115	2.298	2.429	2.500	2.509	2.464	2.378	2.279				
50°						1.862	2.073	2.269	2.431	2.541	2.594	2.588	2.535	2.453					
60°							2.259	2.433	2.571	2.661	2.696	2.677	2.616						
70°								2.582	2.699	2.768	2.783	2.749							
80°									2.793	2.840	2.836								
90°										2.866									

z = 40°

x y	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°	160°	170°	180°
0°	0.234	0.246	0.280	0.337	0.413	0.508	0.617	0.738	0.867	1.000	1.133	1.262	1.383	1.492	1.587	1.663	1.720	1.754	1.766
10°		0.252	0.287	0.347	0.428	0.515	0.611	0.717	0.828	0.943	1.059	1.173	1.281	1.382	1.475	1.558	1.631	1.697	
20°			0.324	0.389	0.473	0.556	0.640	0.729	0.822	0.918	1.015	1.110	1.203	1.293	1.380	1.464	1.547		
30°				0.459	0.547	0.626	0.700	0.773	0.847	0.922	0.997	1.073	1.148	1.223	1.299	1.379			
40°					0.647	0.720	0.785	0.843	0.898	0.951	1.003	1.056	1.110	1.168	1.230				
50°						0.821	0.888	0.934	0.970	1.000	1.028	1.056	1.087	1.123					
60°							0.984	1.034	1.055	1.064	1.066	1.069	1.075						
70°								1.117	1.143	1.134	1.113	1.090							
80°									1.204	1.201	1.162								
90°										1.234									

0°	0.234	0.246	0.280	0.337	0.413	0.508	0.617	0.738	0.867	1.000	1.133	1.262	1.383	1.492	1.587	1.663	1.720	1.754	1.766
10°		0.264	0.304	0.360	0.434	0.537	0.659	0.794	0.938	1.087	1.234	1.377	1.508	1.624	1.718	1.782	1.809	1.796	
20°			0.351	0.413	0.491	0.600	0.732	0.878	1.035	1.196	1.356	1.510	1.651	1.773	1.865	1.908	1.883		
30°				0.484	0.567	0.683	0.822	0.977	1.142	1.312	1.481	1.645	1.797	1.928	2.022	2.016			
40°					0.647	0.770	0.913	1.071	1.240	1.413	1.587	1.755	1.913	2.056	2.179				
50°						0.863	0.993	1.145	1.309	1.478	1.646	1.807	1.952	2.060					
60°							1.075	1.197	1.344	1.497	1.647	1.786	1.897						
70°								1.253	1.353	1.477	1.601	1.709							
80°									1.372	1.438	1.524								
90°										1.413									

0°	0.647	0.689	0.810	1.000	1.240	1.508	1.780	2.034	2.250	2.413	2.516	2.558	2.546	2.492	2.413	2.327	2.250	2.198	2.179
10°		0.728	0.843	1.026	1.260	1.523	1.792	2.042	2.254	2.413	2.513	2.551	2.535	2.479	2.398	2.314	2.247	2.209	
20°			0.943	1.108	1.325	1.573	1.829	2.067	2.268	2.416	2.505	2.532	2.505	2.439	2.353	2.279	2.247		
30°				1.247	1.437	1.662	1.896	2.115	2.298	2.429	2.500	2.509	2.464	2.378	2.279	2.242			
40°					1.597	1.791	1.998	2.193	2.353	2.462	2.512	2.500	2.433	2.321	2.179				
50°						1.954	2.131	2.299	2.435	2.522	2.552	2.525	2.450	2.353					
60°							2.279	2.421	2.535	2.603	2.619	2.584	2.516						
70°								2.540	2.633	2.685	2.688	2.649							
80°									2.708	2.744	2.736								
90°										2.766									

z = 50°

x y	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°	160°	170°	180°
0°	0.357	0.367	0.396	0.443	0.508	0.587	0.679	0.780	0.888	1.000	1.112	1.220	1.321	1.413	1.492	1.557	1.604	1.633	1.643
10°		0.368	0.394	0.444	0.515	0.602	0.683	0.768	0.858	0.950	1.043	1.134	1.222	1.305	1.382	1.454	1.519	1.580	
20°			0.422	0.477	0.556	0.647	0.723	0.793	0.864	0.936	1.008	1.081	1.152	1.223	1.293	1.365	1.440		
30°				0.539	0.626	0.721	0.793	0.850	0.903	0.954	1.005	1.056	1.109	1.164	1.223	1.289			
40°					0.720	0.821	0.888	0.934	0.970	1.000	1.028	1.056	1.087	1.123	1.168				
50°						0.944	1.002	1.038	1.057	1.067	1.072	1.076	1.083	1.098					
60°							1.107	1.151	1.159	1.149	1.130	1.110	1.093						
70°								1.240	1.261	1.238	1.198	1.153							
80°									1.327	1.319	1.265								
90°										1.357									

0°	0.357	0.367	0.396	0.443	0.508	0.587	0.679	0.780	0.888	1.000	1.112	1.220	1.321	1.413	1.492	1.557	1.604	1.633	1.643
10°		0.387	0.425	0.476	0.537	0.611	0.713	0.831	0.957	1.086	1.215	1.338	1.451	1.548	1.624	1.673	1.689	1.673	
20°			0.474	0.534	0.600	0.676	0.786	0.918	1.059	1.204	1.347	1.484	1.606	1.706	1.773	1.793	1.760		
30°				0.607	0.683	0.767	0.886	1.029	1.183	1.341	1.498	1.646	1.778	1.881	1.928	1.893			
40°					0.770	0.863	0.993	1.145	1.309	1.478	1.646	1.807	1.952	2.060	2.056				
50°						0.944	1.087	1.245	1.413	1.587	1.760	1.929	2.087	2.230					
60°							1.179	1.317	1.478	1.644	1.809	1.963	2.084						
70°								1.389	1.505	1.645	1.783	1.900							
80°									1.534	1.611	1.707								
90°										1.587									

0°	0.944	0.984	1.100	1.280	1.508	1.760	2.015	2.250	2.445	2.587	2.668	2.690	2.658	2.587	2.492	2.394	2.308	2.250	2.230
10°		1.021	1.130	1.303	1.523	1.771	2.021	2.251	2.442	2.581	2.659	2.677	2.644	2.572	2.479	2.385	2.320	2.265	
20°			1.222	1.373	1.573	1.803	2.038	2.256	2.436	2.564	2.632	2.642	2.602	2.527	2.439	2.365	2.324		
30°				1.494	1.662	1.862	2.073	2.269	2.431	2.541	2.594	2.588	2.535	2.453	2.378	2.351			
40°					1.791	1.954	2.131	2.299	2.435	2.522	2.552	2.525	2.450	2.353	2.321				
50°						2.076	2.215	2.350	2.458	2.520	2.527	2.476	2.373	2.230					
60°							2.318	2.421	2.503	2.544	2.535	2.477	2.393						
70°								2.498	2.559	2.587	2.573	2.526							
80°									2.607	2.627	2.613								
90°										2.643									

z = 60°

x	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°	160°	170°	180°
y																			
0°	0.500	0.508	0.530	0.567	0.617	0.679	0.750	0.829	0.913	1.000	1.087	1.171	1.250	1.321	1.383	1.433	1.470	1.492	1.500
10°		0.503	0.519	0.555	0.611	0.683	0.765	0.832	0.897	0.963	1.030	1.096	1.160	1.222	1.281	1.338	1.392	1.450	
20°			0.534	0.576	0.640	0.723	0.810	0.870	0.918	0.965	1.011	1.057	1.104	1.152	1.203	1.259	1.322		
30°				0.625	0.700	0.793	0.884	0.939	0.973	1.000	1.024	1.049	1.077	1.109	1.148	1.197			
40°					0.785	0.888	0.984	1.034	1.055	1.064	1.066	1.069	1.075	1.087	1.110				
50°						1.002	1.107	1.151	1.159	1.149	1.130	1.110	1.093	1.083					
60°							1.250	1.281	1.277	1.250	1.210	1.166	1.125						
70°								1.383	1.395	1.357	1.298	1.231							
80°									1.470	1.454	1.385								
90°										1.500									
0°	0.500	0.508	0.530	0.567	0.617	0.679	0.750	0.829	0.913	1.000	1.087	1.171	1.250	1.321	1.383	1.433	1.470	1.492	1.500
10°		0.530	0.566	0.609	0.659	0.713	0.776	0.868	0.971	1.078	1.187	1.283	1.374	1.451	1.508	1.542	1.549	1.530	
20°			0.617	0.675	0.732	0.786	0.850	0.951	1.070	1.193	1.315	1.429	1.529	1.606	1.651	1.655	1.617		
30°				0.750	0.822	0.886	0.957	1.067	1.200	1.339	1.475	1.601	1.707	1.778	1.797	1.750			
40°					0.913	0.993	1.075	1.197	1.344	1.497	1.647	1.786	1.897	1.952	1.913				
50°						1.087	1.179	1.317	1.478	1.644	1.809	1.963	2.084	2.087					
60°							1.250	1.408	1.576	1.750	1.924	2.092	2.250						
70°								1.491	1.631	1.790	1.948	2.077							
80°									1.677	1.773	1.880								
90°										1.750									
0°	1.250	1.288	1.397	1.567	1.780	2.015	2.250	2.462	2.633	2.750	2.807	2.804	2.750	2.658	2.546	2.433	2.337	2.273	2.250
10°		1.323	1.425	1.586	1.792	2.021	2.250	2.458	2.625	2.740	2.794	2.789	2.735	2.644	2.535	2.429	2.344	2.290	
20°			1.509	1.646	1.829	2.038	2.252	2.447	2.604	2.709	2.756	2.747	2.690	2.602	2.505	2.423	2.370		
30°				1.750	1.896	2.073	2.259	2.433	2.571	2.661	2.696	2.677	2.616	2.535	2.464	2.428			
40°					1.998	2.131	2.279	2.421	2.535	2.603	2.619	2.584	2.516	2.450	2.433				
50°						2.215	2.318	2.421	2.503	2.544	2.535	2.477	2.393	2.373					
60°							2.375	2.438	2.486	2.500	2.466	2.381	2.250						
70°								2.466	2.489	2.486	2.446	2.383							
80°									2.497	2.493	2.470								
90°										2.500									

z = 70°

x y	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°	160°	170°	180°
0°	0.658	0.663	0.679	0.704	0.738	0.780	0.829	0.883	0.941	1.000	1.059	1.117	1.171	1.220	1.262	1.296	1.321	1.337	1.342
10°		0.651	0.656	0.678	0.717	0.768	0.832	0.898	0.941	0.980	1.019	1.058	1.096	1.134	1.173	1.212	1.253	1.295	
20°			0.657	0.683	0.729	0.793	0.870	0.943	0.979	1.000	1.018	1.036	1.057	1.081	1.110	1.148	1.195		
30°				0.716	0.773	0.850	0.939	1.017	1.048	1.053	1.051	1.049	1.049	1.056	1.073	1.102			
40°					0.843	0.934	1.034	1.117	1.143	1.134	1.113	1.090	1.069	1.056	1.056				
50°						1.038	1.151	1.240	1.261	1.238	1.198	1.153	1.110	1.076					
60°							1.281	1.383	1.395	1.357	1.298	1.231	1.166						
70°								1.541	1.534	1.483	1.407	1.319							
80°									1.628	1.600	1.513								
90°										1.658									

0°	0.658	0.663	0.679	0.704	0.738	0.780	0.829	0.883	0.941	1.000	1.059	1.117	1.171	1.220	1.262	1.296	1.321	1.337	1.342
10°		0.688	0.721	0.757	0.794	0.831	0.868	0.911	0.984	1.063	1.142	1.216	1.283	1.338	1.377	1.396	1.394	1.372	
20°			0.775	0.830	0.878	0.918	0.951	0.992	1.073	1.169	1.265	1.354	1.429	1.484	1.510	1.501	1.459		
30°				0.908	0.977	1.029	1.067	1.113	1.202	1.312	1.422	1.522	1.601	1.646	1.645	1.592			
40°					1.071	1.145	1.197	1.253	1.353	1.477	1.601	1.709	1.786	1.807	1.755				
50°						1.245	1.317	1.389	1.505	1.645	1.783	1.900	1.963	1.929					
60°							1.408	1.491	1.631	1.790	1.948	2.077	2.092						
70°								1.541	1.709	1.883	2.057	2.225							
80°									1.773	1.900	2.029								
90°										1.883									

0°	1.541	1.576	1.679	1.837	2.034	2.250	2.462	2.649	2.793	2.883	2.912	2.883	2.804	2.690	2.558	2.429	2.321	2.250	2.225
10°		1.609	1.703	1.853	2.042	2.251	2.458	2.641	2.782	2.870	2.898	2.868	2.789	2.677	2.551	2.430	2.333	2.271	
20°			1.779	1.902	2.067	2.256	2.447	2.618	2.750	2.831	2.854	2.823	2.747	2.642	2.532	2.436	2.369		
30°				1.990	2.115	2.269	2.433	2.582	2.699	2.768	2.783	2.749	2.677	2.588	2.509	2.459			
40°					2.193	2.299	2.421	2.540	2.633	2.685	2.688	2.649	2.584	2.525	2.500				
50°						2.350	2.421	2.498	2.559	2.587	2.573	2.526	2.477	2.476					
60°							2.438	2.466	2.489	2.486	2.446	2.383	2.381						
70°								2.447	2.432	2.400	2.334	2.225							
80°									2.391	2.353	2.312								
90°										2.342									

z = 80°

x y°	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°	160°	170°	180°
0°	0.826	0.829	0.837	0.850	0.867	0.888	0.913	0.941	0.970	1.000	1.030	1.059	1.087	1.112	1.133	1.150	1.163	1.171	1.174
10°		0.810	0.803	0.809	0.828	0.858	0.897	0.941	0.985	1.000	1.009	1.019	1.030	1.043	1.059	1.080	1.106	1.137	
20°			0.789	0.796	0.822	0.864	0.918	0.979	1.030	1.037	1.028	1.018	1.011	1.008	1.015	1.031	1.061		
30°				0.810	0.847	0.903	0.973	1.048	1.104	1.106	1.081	1.051	1.024	1.005	0.997	1.005			
40°					0.898	0.970	1.055	1.143	1.204	1.201	1.162	1.113	1.066	1.028	1.003				
50°						1.057	1.159	1.261	1.327	1.319	1.265	1.198	1.130	1.072					
60°							1.277	1.395	1.470	1.454	1.385	1.298	1.210						
70°								1.534	1.628	1.600	1.513	1.407							
80°									1.796	1.743	1.638								
90°										1.826									

0°	0.826	0.829	0.837	0.850	0.867	0.888	0.913	0.941	0.970	1.000	1.030	1.059	1.087	1.112	1.133	1.150	1.163	1.171	1.174
10°		0.857	0.887	0.915	0.938	0.957	0.971	0.984	1.000	1.045	1.095	1.142	1.187	1.215	1.234	1.239	1.228	1.204	
20°			0.943	0.995	1.035	1.059	1.070	1.073	1.085	1.138	1.204	1.265	1.315	1.347	1.356	1.336	1.291		
30°				1.076	1.142	1.183	1.200	1.202	1.215	1.274	1.351	1.422	1.475	1.498	1.481	1.424			
40°					1.240	1.309	1.344	1.353	1.372	1.438	1.524	1.601	1.647	1.646	1.587				
50°						1.413	1.478	1.505	1.534	1.611	1.707	1.783	1.809	1.760					
60°							1.576	1.631	1.677	1.773	1.880	1.948	1.924						
70°								1.709	1.773	1.900	2.029	2.057							
80°									1.796	1.970	2.143								
90°										1.970									

0°	1.796	1.829	1.924	2.069	2.250	2.445	2.633	2.793	2.910	2.970	2.970	2.912	2.807	2.668	2.516	2.370	2.250	2.171	2.143
10°		1.859	1.945	2.082	2.254	2.442	2.625	2.782	2.896	2.955	2.955	2.898	2.794	2.659	2.513	2.375	2.265	2.195	
20°			2.011	2.121	2.268	2.436	2.604	2.750	2.857	2.911	2.910	2.854	2.756	2.632	2.505	2.404	2.312		
30°				2.193	2.298	2.431	2.571	2.699	2.793	2.840	2.836	2.783	2.696	2.594	2.500	2.432			
40°					2.353	2.435	2.535	2.633	2.708	2.744	2.736	2.688	2.619	2.552	2.512				
50°						2.458	2.503	2.559	2.607	2.627	2.613	2.573	2.535	2.527					
60°							2.486	2.489	2.497	2.493	2.470	2.446	2.466						
70°								2.432	2.391	2.353	2.312	2.334							
80°									2.301	2.227	2.143								
90°										2.174									

z = 90°

x y	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°	160°	170°	180°
0°	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10°		0.973	0.954	0.944	0.943	0.950	0.963	0.980	1.000	1.015	1.000	0.980	0.963	0.950	0.943	0.944	0.954	0.973	
20°			0.925	0.913	0.918	0.936	0.965	1.000	1.037	1.060	1.037	1.000	0.965	0.936	0.918	0.913	0.925		
30°				0.907	0.922	0.954	1.000	1.053	1.106	1.134	1.106	1.053	1.000	0.954	0.922	0.907			
40°					0.951	1.000	1.064	1.134	1.201	1.234	1.201	1.134	1.064	1.000	0.951				
50°						1.067	1.149	1.238	1.319	1.357	1.319	1.238	1.149	1.067					
60°							1.250	1.357	1.454	1.500	1.454	1.357	1.250						
70°								1.483	1.600	1.658	1.600	1.483							
80°									1.743	1.826	1.743								
90°										2.000									
0°	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10°		1.030	1.058	1.077	1.087	1.086	1.078	1.063	1.045	1.030	1.045	1.063	1.078	1.086	1.087	1.077	1.058	1.030	
20°			1.117	1.166	1.196	1.204	1.193	1.169	1.138	1.117	1.138	1.169	1.193	1.204	1.196	1.166	1.117		
30°				1.250	1.312	1.341	1.339	1.312	1.274	1.250	1.274	1.312	1.339	1.341	1.312	1.250			
40°					1.413	1.478	1.497	1.477	1.438	1.413	1.438	1.477	1.497	1.478	1.413				
50°						1.587	1.644	1.645	1.611	1.587	1.611	1.645	1.644	1.587					
60°							1.750	1.790	1.773	1.750	1.773	1.790	1.750						
70°								1.883	1.900	1.883	1.900	1.883							
80°									1.970	1.970	1.970								
90°										2.000									
0°	2.000	2.030	2.117	2.250	2.413	2.587	2.750	2.883	2.970	3.000	2.970	2.883	2.750	2.587	2.413	2.250	2.117	2.030	2.000
10°		2.057	2.136	2.259	2.413	2.581	2.740	2.870	2.955	2.985	2.955	2.870	2.740	2.581	2.413	2.259	2.136	2.057	
20°			2.192	2.288	2.416	2.564	2.709	2.831	2.911	2.940	2.911	2.831	2.709	2.564	2.416	2.288	2.192		
30°				2.343	2.429	2.541	2.661	2.768	2.840	2.866	2.840	2.768	2.661	2.541	2.429	2.343			
40°					2.462	2.522	2.603	2.685	2.744	2.766	2.744	2.685	2.603	2.522	2.462				
50°						2.520	2.544	2.587	2.627	2.643	2.627	2.587	2.544	2.520					
60°							2.500	2.486	2.493	2.500	2.493	2.486	2.500						
70°								2.400	2.353	2.342	2.353	2.400							
80°									2.227	2.174	2.227								
90°										2.000									

By means of these solutions of the secular equation the question of dispersion of elastic waves in the crystal lattice may be investigated. In order to do this it is necessary to know the wave length as well as the frequency of the waves. According to the definition of normal modes of vibration given on page 36,

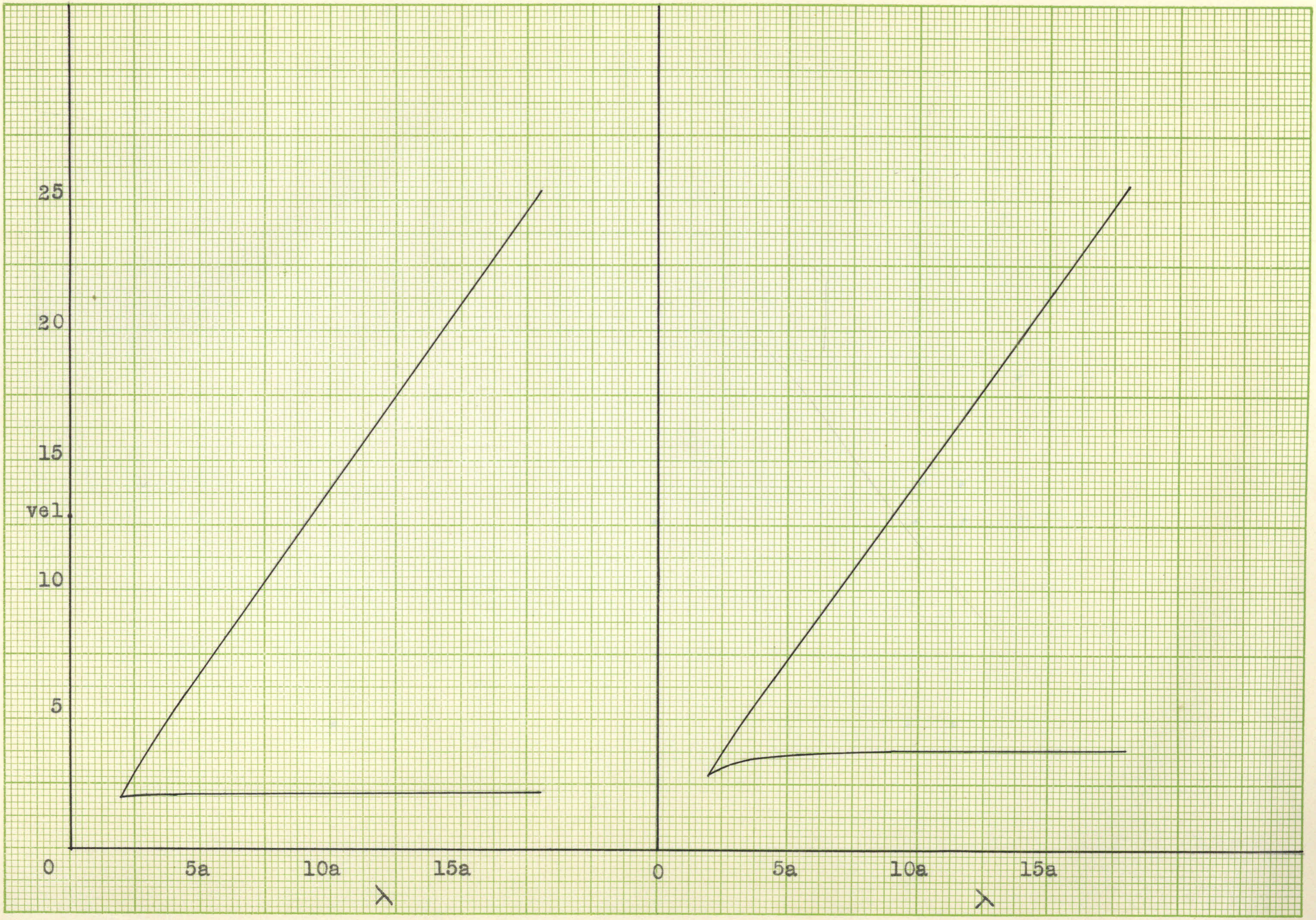
$$u_r = \sum_n w_{s,n} \exp[(2\pi i) \sum_j (n_j r_j / N_j a_j)],$$

so that the displacement of an atom is represented by the superposition of plane waves. The three quantities, $n_j/N_j a_j$, are proportional to the direction cosines of the propagation vector of the wave, the actual cosines being found by dividing by the square root of the sum of the squares of these quantities. When this is done, the usual expression for a plane wave can be exhibited and the wave length for a cubic lattice written in the form:

$$\lambda = (\pi a)/(x^2 + y^2 + z^2)^{\frac{1}{2}}, \qquad (77)$$

where $x = \pi n_1/N_1$, $y = \pi n_2/N_2$, and $z = \pi n_3/N_3$. The wave length is thus inversely proportional to the length of the radius vector from the origin in the xyz space.

On the next page are shown dispersion curves for waves in a direction parallel to one edge of the body-centered cube. The ordinate is the velocity of the wave obtained by multiplying the frequency by the wave length, and the four curves correspond to the four distinct roots of the original sixth degree secular equation. According to the Debye theory, the velocity should remain constant; this seems to be valid for two of the roots but is not at all correct for the other two.



Dispersion curves.

PART III. FREQUENCY DISTRIBUTION

The primary purpose of this work is to find out how many normal modes of vibration are present in a given frequency range. From such information specific heats and the temperature dependence of the intensity of x-ray reflection can be computed. To go from the roots of the cubic secular equation to the frequency distribution again requires numerical methods, since the complicated nature of the constant frequency surfaces makes an exact, explicit solution impossible.

SECTION 1. NUMERICAL EVALUATION

The problem is to calculate the number of normal modes of vibration with frequencies between ν and $\nu + d\nu$. Each mode of vibration is characterized by the set of numbers, x, y, z, which determine the direction of an elastic wave in the solid. There are so many normal coordinates for a crystal lattice that the xyz space may be considered as continuous. The number of vibrations in a given frequency range must then be equal to the volume between surfaces of constant frequency. The equation of these surfaces in the form of the determinant on page 60 is not susceptible to methods of exact integration, so that some scheme of approximate evaluation must be devised.

The general plan of procedure has been to trace out certain curves of constant frequency in planes parallel to the x-y plane at 10° intervals, to find the areas between these curves and the x and y axes, and then to combine these areas in such a way that the volumes bounded by the constant frequency surfaces and the coordinate planes are obtained. Now the roots which are given in Part II are located for convenience at 10° intervals in planes perpendicular to the z axis. In order to trace out constant frequency curves in these planes it is necessary to interpolate between the frequencies found by actual solution of the cubic equation. It was found by experience based on the plane, $z = 0$, where explicit solutions are known, that a linear interpolation is generally not sufficient but that a quadratic formula is often required. This means that three known points along a given line must be used to find the unknown point where the curve for a certain frequency crosses the line. The middle point is chosen as the one with a root most nearly equal to the given frequency.

Suppose that the line under consideration is parallel to the x axis and that the three points where the frequencies are known are separated by 10° intervals. It is assumed that the quantity f^2 which is proportional to the square of the frequency can be represented in the neighborhood of the second point by the first three terms in a power series expansion. Let x be measured from the center point. Then,

$$f^2 = f_2^2 + ax + bx^2.$$

$$f_1^2 = f_2^2 - 10a + 100b.$$

$$f_3^2 = f_2^2 + 10a + 100b.$$

$$a = (f_3^2 - f_1^2)/20.$$

$$b = [(f_3^2 - f_2^2) - (f_2^2 - f_1^2)]/200$$

$$\text{(1)} \quad x = [5/(f_3^2 + f_1^2 - 2\,f_2^2)]\{-(f_3^2 - f_1^2) + [(f_3^2 - f_1^2) + 8(f^2 - f_2^2)(f_3^2 + f_1^2 - 2\,f_2^2)]^{\frac{1}{2}}\}.$$

The positive sign is chosen here for the square root in order to obtain the interpolation desired, the other root of the quadratic equation being extraneous for the problem considered.

Such interpolations have been made at points where the constant frequency curves cross the network of lines at 10° intervals parallel to the x and y axes, and also where there is an intersection with the diagonal lines, $x = y$ or $x = \pi - y$. For each plane perpendicular to the z axis there are three sets of curves corresponding to the three roots of the cubic equations. An exception occurs in the $z = 0^\circ$ plane where two of the roots are everywhere equal.

As an example, the following points are given for the curves belonging to $f^2 = 0.800$ in the plane, $z = 10^\circ$:

y°	x	y°	x	y°	x
0°	78.3	0°	78.3	0°	43.85
10	79.4	10	76.6	10	42.6
20	79.8	20	74.8	20	38.4
30	79.3	30	72.8	30	30.9
40	77.5	40	70.4	30.4	30.4
50	73.5	50	67.4		
60	65.1	60	63.3		
62.4	62.4	61.6	61.6		

The termination of the table at these points is due to the fact that further values can be obtained by simply interchanging x and y because of the symmetry of the cubic lattice.

In some cases there are two or three branches of the same curve. For instance, in the plane, $z = 60^\circ$, there are three separate parts to the curve corresponding to $f^2 = 2.400$. Only one root, however, gives such large values of the frequencies in this plane. The three branches are shown in the following table:

y	x	y'	x'	y"	x"
0°	66.9°	0°	153.16°	46.7°	133.3°
10	67.0	10	153.15	46.4	130
20	67.4	13.76	153.76	49.5	120
30	67.9	20	153.7	50	118.75
40	68.4	24.7	155.3	60	108.2
50	67.8			70	106.2
60	64.1			71.6	108.4
62.1	62.1				

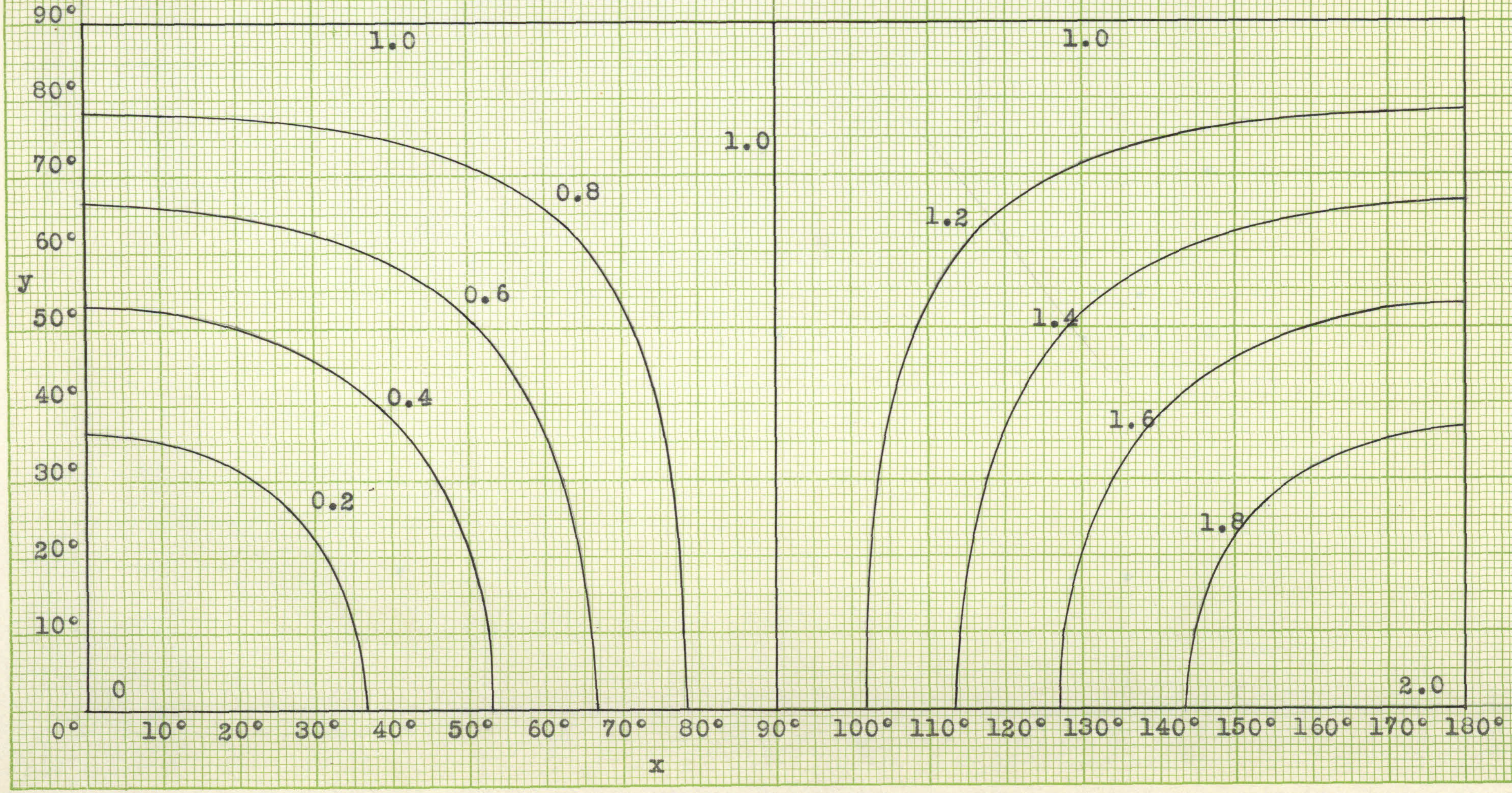
In certain cases it is more convenient to take equal intervals along the x axis rather than along the y axis. An example occurs in the plane, $z = 90^\circ$, for $f^2 = 1.600$.

y	x
74.6°	74.6°
70	80
66.5	90
70	100
74.6	105.4

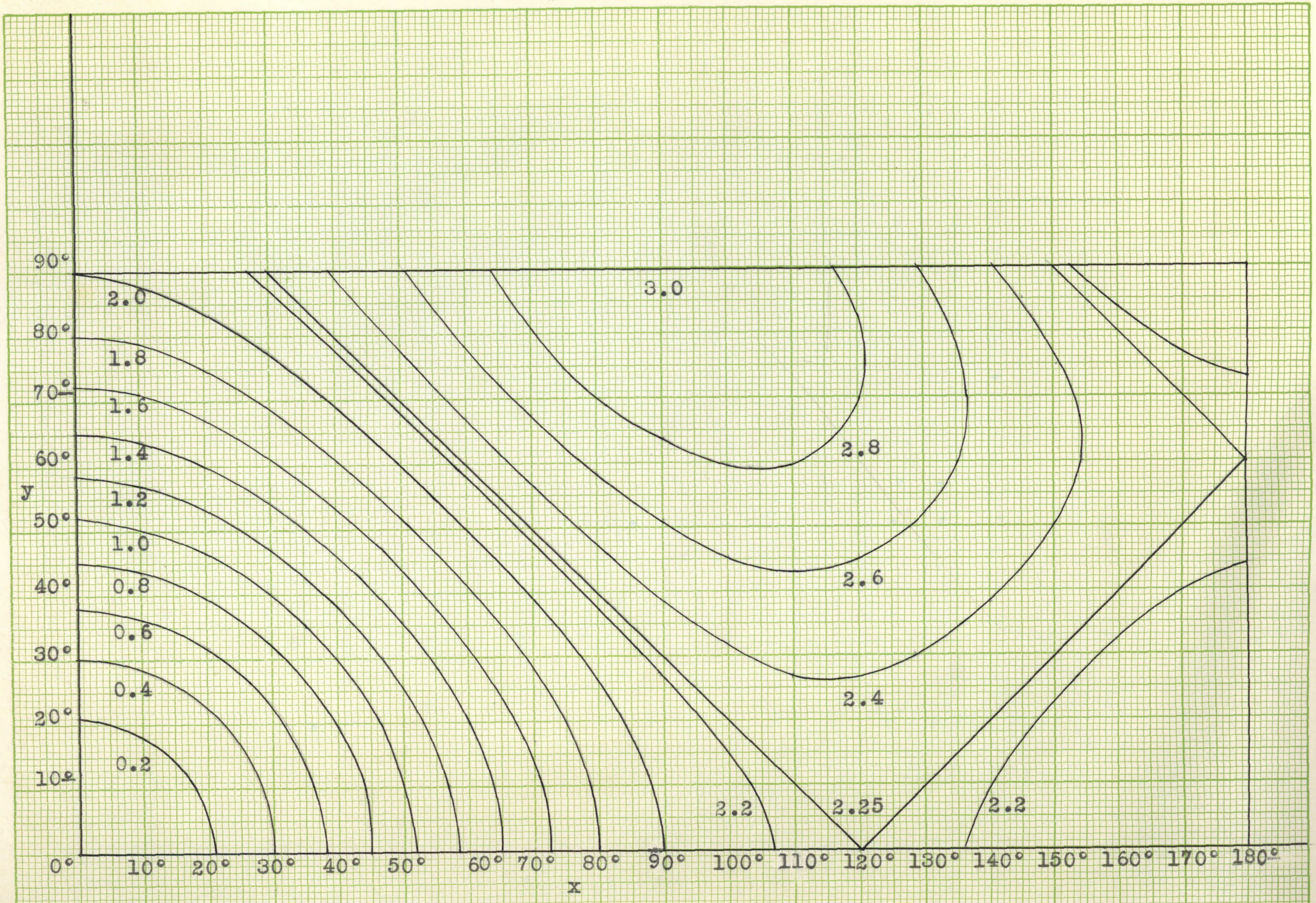
(The other two roots do not give such a value of f^2 in this plane.)

On the next two pages appear the curves of constant frequency for the basic plane, $z = 0^\circ$. The first of these is for the double root of the cubic in this plane. The values of f^2 for consecutive curves differ by 0.2. According to the Debye theory these curves should be arcs of circles centered at the origin. Although this seems to be true at low frequencies, deviations are soon apparent. In fact, one constant frequency curve turns out to be made of straight lines for each root in this particular plane. This results from the assumptions made about the elastic constants in the atomic model used.

The values of the frequency for x between 90° and 180° really correspond to a separate root of the original sixth degree equation as discussed on page 59. It is seen that the curves again tend to become circular around the point $y = 0^\circ$, $x = 180^\circ$, where the frequency does not have a zero value. In the case of the



Constant frequency curves.



Constant frequency curves.

second graph the curves seem to form ellipses around the point, $x = 90^\circ$, $y = 90^\circ$. There are other peculiarities in higher planes.

The problem now is to find the areas corresponding to values of the frequency less than a certain assigned frequency. Usually this means the areas bounded by the curves of constant frequency and the x and y axes, but sometimes the $x = \pi$ and $y = \pi/2$ lines are also parts of the boundary. In any case the area in planes perpendicular to the x axis has been determined by the approximate method embodied in Simpson's rules. The simplest of these is called the one-third rule and is the result of fitting a parabola to three points spaced at equal intervals. The area between that part of the curve passing through the three points and the x axis can be expressed in terms of the coordinates of the points in the following way:

$$A = \frac{1}{3} (\Delta x)(y_1 + 4\, y_2 + y_3) \tag{2}$$

where $\Delta x = (x_3 - x_2) = (x_2 - x_1)$. This formula can be extended to $2n + 1$ points by repetition.

A more accurate expression for the area is the three-eighths rule obtained by fitting a third degree curve to four points which are also spaced at equal intervals. In this case,

$$A = \frac{3}{8} (\Delta x)(y_1 + 3\, y_2 + 3\, y_3 + y_4). \tag{3}$$

An extension is easily made to $3n + 1$ points. This rule is used wherever possible, the one-fourth rule being employed where necessary.

However, it is often desirable to have an expression for unequal intervals to be applied near the intersections of the curves with the diagonal lines. If the assumption is made that

$$y = a + bx + cx^2,$$

the three constants can be evaluated in terms of the coordinates of three points and, when the integration is carried out to get the area, the result is Simpson's rule for unequal intervals:

$$(4)\qquad A = \frac{1}{3}(x_3 - x_1)(y_1 + y_3) + \left[(x_3 - x_1)/6(x_3 - x_2)(x_2 - x_1)\right]\left[- y_1(x_3 - x_2)^2 + y_2(x_3 - x_1)^2 - y_3(x_2 - x_1)^2\right].$$

By means of these three formulae the areas were found in the ten planes for curves of constant frequency corresponding to values of f^2 from 0 to 3 at intervals of 0.2. In all, about 230 curves were investigated, and it is believed that little systematic error was introduced by the approximations made. However, these areas must be combined to give the volume inclosed by a surface of constant frequency. Here again, Simpson's rule is used to build up the volume out of the traces in the ten parallel planes. The result for each of the three roots is given below.

f	$n'/3N$	$n''/3N$	$n'''/3N$
0	0	0	0
0.2	0.00629	0.00601	0.00114
0.4	0.0198	0.0183	0.00338
0.6	0.0416	0.0357	0.00631
0.8	0.0761	0.0617	0.0106
1.0	0.144	0.0990	0.0156
1.2	0.251	0.150	0.0218
1.4	0.294	0.202	0.0291
1.6	0.317	0.249	0.0387
1.8	0.329	0.291	0.0504
2.0	0.333	0.324	0.0657
2.2			0.0970
2.25		0.333	
2.4			0.169
2.6			0.259
2.8			0.312
3.0			0.333

In each case n is the number of vibrations having a frequency less than the value represented by f and N is the total number of atoms in the crystal. A normalization has been made at this point by dividing by the total volume in the xyz space, so that the total number of vibrations is equal to the number of degrees of freedom in the crystal.

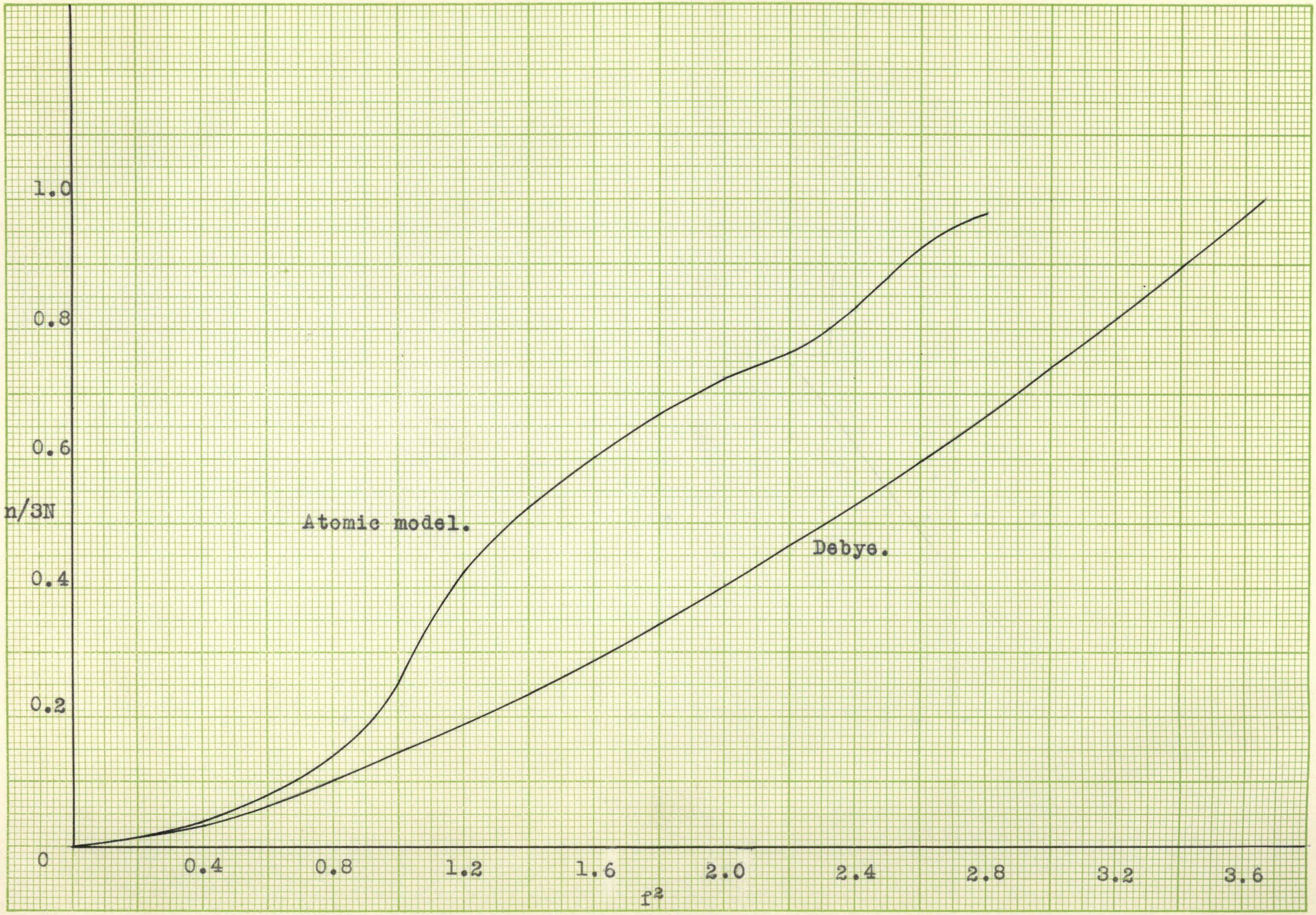
The figures for the three roots may be added together to obtain the total number of modes of vibration having frequencies less than a certain value. This may then be compared with the values that are given by the Debye formula. It may be noticed by reference to the roots of the cubic on pages 61 and 62 that in the planes, $z = 0^\circ$ and $z = 10^\circ$, near the origin the frequency is directly proportional to the distance from the origin. As a result, in this region the surfaces of constant frequency are spheres and the number of modes of vibration varies with the cube of the frequency in agreement with the Debye theory. However, it is clear from the following table that the Debye assumption is not at all valid for high frequencies and, in fact, that the discrepancies become large at relatively low frequencies.

f^2	n/3N	n/3N (Debye)
0	0	0
0.015	0.000262	0.000262
0.2	0.0134	0.0128
0.4	0.0416	0.0361
0.6	0.0836	0.0664
0.8	0.148	0.102
1.0	0.259	0.143
1.2	0.423	0.188
1.4	0.525	0.237
1.6	0.604	0.289
1.8	0.670	0.345
2.0	0.723	0.404
2.2	0.762	0.466
2.4	0.835	0.531

f^2	n/3N	n/3N (Debye)
2.6	0.926	0.599
2.8	0.978	0.670
3.0	1	0.743
3.2		0.818
3.4		0.896
3.6		0.976
3.66		1

If n/3N is plotted against f^2 as on the next page, it is seen that the curve based on the atomic model is always above the Debye curve and has several inflection points indicating a maximum slope. Moreover, in order to obtain the correct number of vibrations in the Debye case it is necessary to go to higher frequencies than are allowed by the atomic model discussed here. Since two of the roots are identical in the plane, $z = 0°$, while the third is quite different, two separate Debye functions might be used. In the neighborhood of the origin the two values of f^2 are in the ratio of three to one, so that there would be a maximum frequency corresponding to a value of f^2 equal to ~~3.66~~ 2.97 in one case and ~~$3.66\sqrt{3}$ or 6.34~~ 8.91 in the other. The last value greatly exceeds the upper limit set by the present theory. This difficulty could be removed by taking the two Debye frequencies equal to the two most probable frequencies which will be exhibited later and thus sacrificing agreement at low frequencies.

In order to determine the frequency distribution the derivative of n with respect to f must be evaluated. Also, for certain purposes the derivative with respect to f^2 is useful. Since the function to be differentiated is here represented by only sixteen points a method of approximation is required. The procedure has been to tabulate successive differences by first subtracting consecutive values of n, repeating the process with the differences


1.0
0.8
0.6
n/3N
0.4
0.2
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
f^2
Atomic model.
Debye.

thus obtained, and continuing as far as the number of points allows. Then, the derivative of Stirling's formula for the interpolation in the neighborhood of a known point was used. This formula may be written as follows:

$$(5)\qquad (dn/df^2)_0 = (1/2)(d^1_{-1} + d^1_{1}) + \left[(-1)(+1)/2(3!)\right](d^3_{-1} + d^3_{1}) + \left[(-1)(+1)(-2)(+2)/2(5!)\right](d^5_{-1} + d^5_{1}) + \cdots$$

where the derivative is to be evaluated at a known point f^2_0 and the d's are differences whose order is denoted by the superscript and whose subscripts indicate that the differences are taken on either side of f^2_0.

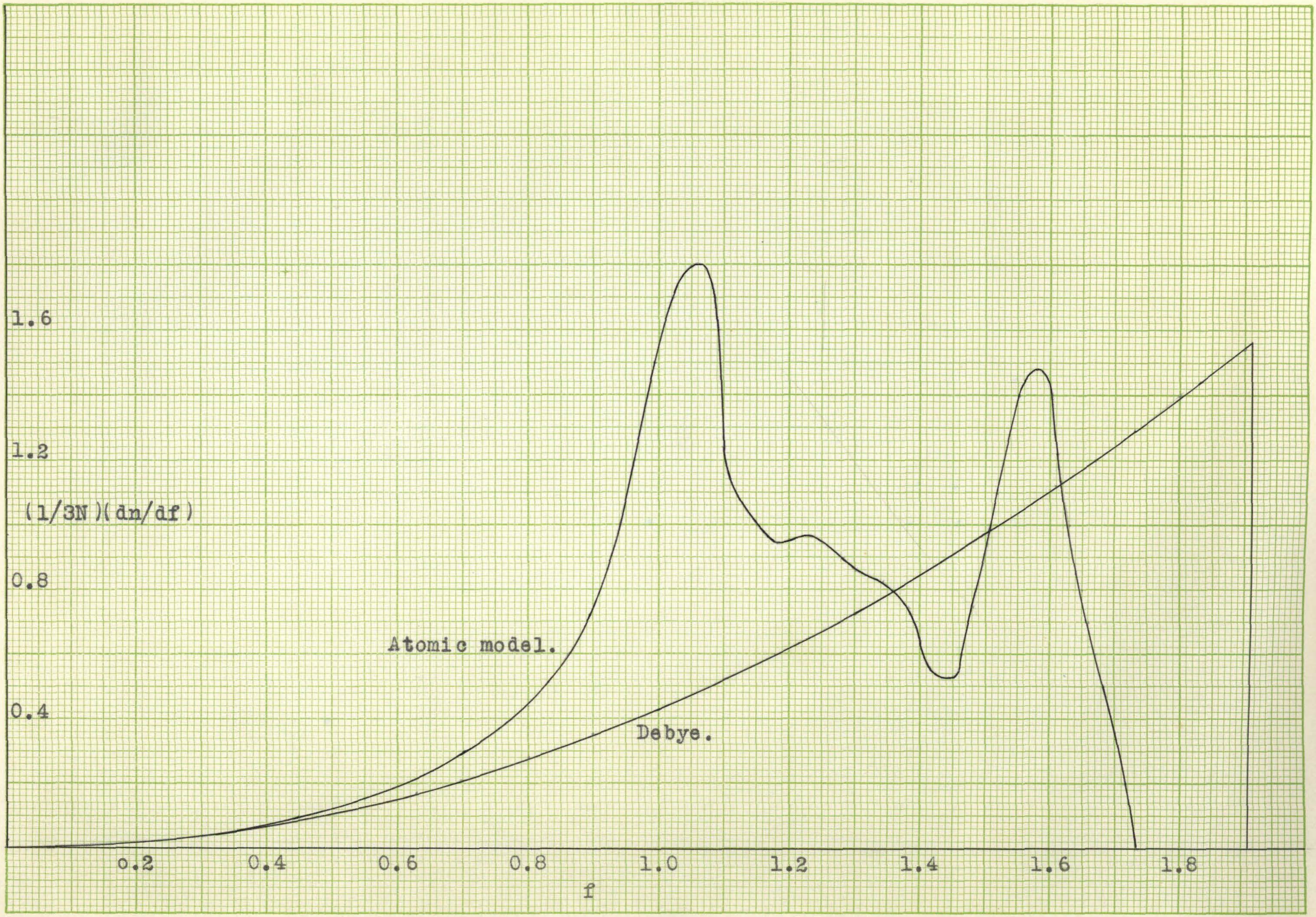
A similar relation known as Bessel's formula can be used for an interpolation halfway between two known points. After differentiation this can be expressed in the following form:

$$(6)\qquad (dn/df^2)_0 = d^1_0 + \left[(\tfrac{1}{2})(-\tfrac{1}{2})/3!\right]d^3_0 + \left[(\tfrac{1}{2})(-\tfrac{1}{2})(\tfrac{3}{2})(-\tfrac{3}{2})/5!\right]d^5_0 + \cdots$$

where the d_0's represent differences between the values at the known points on either side of f^2_0. Both Stirling's and Bessel's formulae are based on a polynomial approximation to the function and in this form apply only to cases where the known values are equally spaced with respect to the independent variable, and for that reason f^2 is used in the derivative instead of f. However, $(dn/df) = 2f(dn/df^2)$, so that the number of vibrations per unit frequency range can easily be found. In the following table, values are given for both derivatives.

f^2	$(1/3N)(dn/df^2)$	$(1/3N)(dn/df)$
0	0	0
0.1	0.0672	0.0425
0.2	0.104	0.0929
0.3	0.141	0.154
0.4	0.172	0.218
0.5	0.209	0.295
0.6	0.251	0.390
0.7	0.318	0.532
0.8	0.406	0.726
0.9	0.546	1.09
1.0	0.759	1.52
1.1	0.859	1.80
1.2	0.710	1.56
1.3	0.488	1.11
1.4	0.399	0.945
1.5	0.398	0.976
1.6	0.369	0.934
1.7	0.326	0.851
1.8	0.307	0.825
1.9	0.272	0.750
2.0	0.204	0.577
2.1	0.178	0.516
2.2	0.254	0.755
2.3	0.372	1.13
2.4	0.452	1.40
2.5	0.468	1.48
2.6	0.377	1.22
2.7	0.259	0.851
2.8	0.185	0.618
2.9	0.109	0.371
3.0	0	0

The graph on the next page shows a comparison between the Debye function and the one tabulated here. There are several essential differences to be noted. In the first place there is the point already mentioned that the Debye theory requires higher frequencies in order to include the same number of vibrations, if agreement with the atomic model is required at low frequencies. The appearance of two pronounced maxima in the curve instead of one is also significant. In this connection the discussion in the introduction with reference to the Nernst-Lindemann specific heat formula is pertinent. It was assumed there that an atom in



Frequency distribution.

a solid possessed two characteristic frequencies instead of the one suggested by Einstein. These frequencies were supposed to be in the ratio of two to one as far as magnitude was concerned but were presumed to be equally probable. According to the present model there are actually two frequencies which are more probable than any others, although their ratio is 1.5 instead of 2.0. Nevertheless, this result does throw some light on the advantage which the Nernst-Lindemann formula has over the Einstein relation as far as agreeing with observations is concerned.

It should be noticed that the deviation from the Debye function begins at relatively low frequencies and that the parabolic curve can be considered as a good approximation to the curve found in this work only over an insignificant part of the complete spectrum. Since the computations have been made with the elastic constants of tungsten, which happen to satisfy the isotropy conditions, the fundamental difference between the present theory and that of Debye's is that here an atomic model has been treated while Debye considered a continuous medium. Although various simplifying assumptions have been made in carrying out the calculations, at least it may be said that the present results indicate the type of deviations from the Debye theory that may be expected when the atomicity of the crystal is taken into account. The effect of anisotropy on the frequency distribution is equally important but has not been investigated here. However, the present work does show that elastic waves can have different properties in different directions in spite of the fact that the macroscopic elastic constants obey the isotropy law.

The sharpness of the maxima in the curves is apparent, and, although the Debye theory has been criticized because of the abrupt termination of the frequency distribution, that feature at least is confirmed to some extent by this work. The approximations that have been necessary are naturally not as good near these sharp peaks as might be desired. In fact, a lack of convergence of the successive differences obtained in evaluating the derivatives seems to indicate that the curve cannot be exactly represented by a polynomial equation. Some sort of exponential function is probably required, but in the applications which follow it was thought better to use the actual values found at the thirty-one points in a numerical integration rather than an empirical function which might represent these values approximately.

SECTION 2. APPLICATION TO SPECIFIC HEATS.

Now that the frequency distribution has been determined for a model based on the tungsten crystal, the results may be applied to several types of physical phenomena. The degree of accordance between the calculations and the observed data should indicate to what extent the present method and assumptions are valid.

One of the first questions to be asked in regard to a theory of the solid state is how the specific heat varies with the temperature. In the introduction there is presented in detail a discussion of the various attempts to find a satisfactory theoretical description for the empirical specific heat curves. It was pointed out that the hope of obtaining a single formula for the specific heats of all solids may not be realized. At least the method used here is greatly dependent on the particular elastic properties assumed and leads to no general expression.

According to the theories mentioned in the introduction, the specific heat at constant volume can be written in the form:

$$(7) \qquad C_v = \int_0^{\nu_m} \left[(h^2\nu^2/kT^2) e^{h\nu/kT} / (e^{h\nu/kT} - 1)^2 \right] dn.$$

where dn is the number of vibrations with frequencies between ν and $\nu + d\nu$. For the atomic model considered here,

$$(8) \qquad h\nu/k = \theta f,$$

where f is a dimensionless quantity proportional to the frequency and θ is a constant characteristic temperature defined in the following way:

$$(9) \qquad \theta = (h/2\pi k)(4ac_{44}/m)^{\frac{1}{2}}$$

m is the mass of the atom, a is the interatomic distance equal to the length of one edge of the cubic lattice cell, and c_{44} is one of the elastic constants.

Now, $dn = (dn/df^2)df^2$, in the notation used here. Also,

$$e^{h\nu/kT}/(e^{h\nu/kT} - 1)^2 = 1/(e^{h\nu/2kT} - e^{-h\nu/2kT})^2$$

$$= 1/[4\sinh^2(h\nu/2kT)] = (\tfrac{1}{2})/[\cosh(h\nu/kT) - 1].$$

Therefore,

$$(10) \quad C_v = \tfrac{3}{2} Nk(\theta/T)^2 \int_0^3 \{ f^2(1/3N)(dn/df^2)/[\cosh(f\theta/T) - 1] \} df^2.$$

In the case of tungsten, the following experimental values for the constants involved in θ are used:

$$
\begin{aligned}
&m = 3.03 \times 10^{-22} \text{ grams.}\\
(11)\qquad &a = 3.155 \times 10^{-8} \text{ cm.}\\
&c_{44} = 15.3 \times 10^{11} \text{ dynes/cm}^2.
\end{aligned}
$$

The resulting value of Θ for tungsten is 192°.

The integration is taken with respect to f^2 so that Simpson's rule for equal intervals can be used in the numerical evaluation. The integrand is indeterminate when $f = 0$ but the limit as found by l'Hospital's rule is zero since (dn/df^2) is of the order of f at low frequencies. However, since in the numerical integration the difference between the function at $f^2 = 0$ and $f^2 = 0.1$ is comparatively large at low temperatures, Simpson's rule was not applied to this one interval but a special treatment was devised. This was based on the assumption that at such low frequencies and temperatures the Debye function could be used. It has already been shown that a very limited region exists where this is true if the maximum Debye frequency corresponding to $f^2 = 3.66$ is assumed. Since the number of vibrations having a frequency less than a given value is proportional to the cube of the frequency in the Debye theory, the Debye function was evaluated for a maximum frequency corresponding to $f^2 = 0.1$ and then multiplied by $(0.1/3.66)^{\frac{3}{2}}$ in order to get the correct number of degrees of freedom for the small part of the curve considered. The complete formula used at low temperatures for tungsten can then be written as:

$$
\begin{aligned}
(12)\quad C_V &= 0.00448\ D(60.6/T)\\
&+ (3/2)R\int_{0.1}^{3}\left\{(192\ f/T)\ (1/3N)(dn/df^2)/\left[\cosh(192\ f/T) - 1\right]\right\}df^2
\end{aligned}
$$

From the nature of the derivation of the frequency distribution it is clear that at low temperatures this formula will give the Debye T^3 law and that at high temperatures the equipartition value for the specific heat will result. For intermediate temperatures, however, the characteristics of the distribution peculiar to tungsten should show up. It must be emphasized that the present work, like Debye's, gives a specific heat formula containing a single parameter. The possibility of representing the results in terms of a single constant of course originates in the various assumptions made in connecting the atomic force constants with the macroscopic elastic properties of the tungsten crystal.

In tabulating the values of the specific heats for tungsten it is desirable to show at the same time the values given by the Debye theory and those found by experiment. In the following table two sets of values based on two separate characteristic temperatures are given for the Debye results. The one for $\Theta = 367^\circ$ gives a frequency distribution which agrees with the one found in the present work at low frequencies, where presumably both should be valid. It is thus represented by the parabolic curve on the graph following page 83 and corresponds to a maximum f^2 of 3.66. It is natural to suppose that any choice between the results found here and the Debye theory should be based on this particular Debye parameter, since in neither case has any attempt been made to fit observed specific heat curves.

On the other hand, the results of the Debye theory for a characteristic temperature of 310° are based on an attempt to choose this constant so that the best possible agreement with empirical data can be obtained. This procedure is commonly employed in comparing experimental specific heats with those calculated by Debye and is perhaps a cause of undue confidence in the theory. The actual theoretical formula that Debye gave for determining his parameter is discussed on pages 18 and 19 and involves the two elastic constants for an isotropic continuum.

The observed values of the specific heat of tungsten given below are taken from the Landolt-Börnstein tables; the measurements for absolute temperatures from 26.01° to 91.1° were made by Lange.[31] The units are calories per mole per degree.

T	C_v (Atomic model)	C_v (Obs.)	C_v (Debye, $\theta = 367°$)	C_v (Debye, $\theta = 310°$)
26.01	0.242	0.213	0.165	0.272
32.3	0.495	0.434	0.310	0.506
38.8	0.842	0.750	0.528	0.826
46.7	1.34	1.21	0.861	1.28
54.7	1.84	1.80	1.25	1.77
74.4	2.94	2.87	2.25	2.85
78.3	3.12	3.07	2.42	3.03
84.2	3.37	3.33	2.69	3.29
91.1	3.63	3.60	2.97	3.55
100	3.92	3.77	3.30	3.85
150	4.90		4.50	4.86
200	5.32	5.30	5.06	5.30
250	5.52		5.36	5.52
300	5.66	5.87	5.54	5.65

The specific heat curve resulting from the atomic model treated in the present work is shown on the next page. The agreement between the values obtained here and those found experimentally is rather good at intermediate temperatures, but is not satisfactory at high or low temperatures. The specific heat continues to rise far above the equipartition value of 5.96 at temperatures higher than those given in the table, a fact that cannot be accounted for by a theory based on a quadratic potential function. It should be pointed out here that the discrepancy at low temperatures would be considerably greater if the frequency distribution had been approximated by two Debye functions with maximum frequencies corresponding to the position of the peaks in the curve shown after page 83.

It might be expected that the present work would give values that were too small at low temperatures, instead of the opposite situation that appears here, for the experimental data includes any contribution from the electrons, which have not been considered here. It is possible that the explanation of this discrepancy is the fact that the elastic constants measured at room temperature have been used in the computations, since no data seems to be available at lower temperatures.

It will be recalled that the formula derived here for the specific heat depends on the temperature in combination with the elastic constant, c , and the interatomic distance, a, in the form, $(ac_{44})^{\frac{1}{2}}/T$, so that an increase in a or c is equivalent to a decrease in T or a decrease in the specific heat. Now, it is known that a decreases and c_{44} increases as the temperature falls for certain crystals of the same type as tungsten. For example, recent determinations of the elastic properties of sodium, also a body-centered cubic crystal, show a marked increase for the elastic constants as the temperature is lowered. The change in the lattice spacing is not as significant. Thus, although the model used here gives no information about these changes, still it is felt that the discrepancies at low temperatures are due to the use of elastic constants which are too low for that region.

If the thermal variation of the elastic constants is known, it can be easily taken into account if the supposition is made that at each temperature a new atomic model is constructed to have the elastic properties and lattice spacing which is then appropriate, without inquiring as to why these changes come about. Let $h\nu/kT = (\theta/T)f$, where $\theta = (h/\pi k)(c_{44}a/m)^{\frac{1}{2}}$, as before. This characteristic temperature is, of course, not the same as Debye's. However, the same method will apply to the Debye function. The internal energy of the crystal is then

$$(13)\quad U = (3R/k)\int_0^{\nu_m}\left[h\nu/(e^{h\nu/kT} - 1)\right]dn = 3R\theta\int_0^{x_m}\left[f/(e^{f\theta/T} - 1)\right]dn.$$

$$(14)\quad C_v = (\partial U/\partial T)_v$$

$$= 3R(\theta/T)^2\int_0^{x_m}\left[f^2e^{f\theta/T}/(e^{f\theta/T} - 1)^2\right]dn$$

$$+ 3R\left\{\int_0^{x_m}\left[f/(e^{f\theta/T} - 1)\right]dn - (\theta/T)\int_0^{x_m}\left[f^2e^{f\theta/T}/(e^{\theta f/T} - 1)^2\right]dn\right\}(d\theta/dT)$$

$$= C_v' + (U - T\,C_v')(1/\theta)(d\theta/dT),$$

where C_v is the correct specific heat, C_v' is the specific heat calculated from the correct value of θ but neglecting the variation of θ with temperature.

If the first derivative of θ were known, C_v could be found. On the other hand, this expression might be utilized to find the thermal dependence of θ, for it could be written as

$$(15) \qquad (1/\theta)(d\theta/dT) = (C_v' - C_v)/(TC_v' - U).$$

By means of the observed values for C_v and the known value of θ at room temperature, $(d\theta/dT)$ could be computed and thus the value of θ determined at a slightly different temperature, the process being continued as far as desired. This procedure is of course based on the assumption that the discrepancy between C_v' and C_v is entirely due to the variation in θ, a premise which is probably not true.

The great difficulty in testing the validity of any such atomic model as is considered here arises from the uncertainty as to the electronic contribution to the experimental data. Even the separation of the problem into atomic and electronic phases is probably not correct, since there may be significant effects on the specific heats due to just the interaction between electrons and ions. There are then three contributing factors and a treatment of any one of them cannot pretend to the conclusive.

SECTION 3. APPLICATION TO REFLECTION OF X-RAYS

A somewhat simpler use of the frequency distribution for the normal modes of vibration of an atomic lattice is in calculating the intensity of reflection of x-rays as a function of the temperature. The reasons for a decrease in intensity as the amplitude of the vibrations increases have been discussed in the introduction, where the Debye theory has been presented. Here again there will be an opportunity to compare the results of the Debye distribution law with those given by the present atomic model.

Mention has been made of the fact that a cubic crystal behaves like an isotropic substance as far as the reflection of x-rays from differently oriented planes is concerned. On page 30 it was stated that the average value of the square of the cosine of the angle between the direction of the vibration vector and the z axis taken over a constant frequency surface had a value of one-third. This will now be proved from the symmetry properties of the cubic crystal.

Let S refer to the constant frequency surface in the $n_1 n_2 n_3$ space where the roots of the secular equation were found. The space required for each root just fills up a cube. If the body diagonal of the cube is drawn in, the surface S is divided into three similar parts, each of which is bounded by the intersections of S with the three planes determined by two of the coordinate axes and the diagonal. Now, each point on the constant frequency surface corresponds to a particular direction of propagation of one of the plane waves which, when superimposed, make up the displacement of the atom. The actual displacement vector, however, is not in general in the direction of the wave or at right angles to it, since the waves are neither strictly transverse nor longitudinal for all directions in the crystal. Nevertheless, if the actual vibration vectors are pictured as sticking out of the constant frequency surface, a simplifying result can be obtained.

Due to the cubic symmetry which this field of vectors must possess, the angle between the z axis and a vibration vector situated at a particular point on one of the three similar parts of S is equal to the angle between the y axis and the corresponding vector at the symmetrical point on a second part of S, and this in turn is equal to the angle between the x axis and the symmetrically located vector on the third part of S. Therefore, in carrying out the average desired over the whole surface, it is sufficient to consider one of these sections only. For,

$$(16) \qquad \overline{\cos^2\gamma} = \int \cos^2\gamma \, dS / \int dS = \tfrac{1}{3}\int (\cos^2\alpha + \cos^2\beta + \cos^2\gamma) dS / \int dS$$

$$= \tfrac{1}{3}, \quad \text{since } \cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1.$$

The same result holds for components of the vibration vectors in any direction in the crystal.

The formula for the mean square displacement of the atoms from any lattice plane in the crystal is then

$$(17) \quad \mu = (h/12\pi^2 Nm) \int_0^{\nu_m} (1/\nu) \left\{ \left[1/(e^{h\nu/kT} - 1) \right] + \tfrac{1}{2} \right\} dn$$

$$= (h/4\pi^2 mk\Theta) \int_0^3 (1/f)(1/3N)(dn/df^2) \left\{ \left[1/(e^{f\Theta/T} - 1) \right] + \tfrac{1}{2} \right\} df^2,$$

where Θ has the value 192° for tungsten just as in the case of the specific heat treatment. Due to the zero point energy, there is still a mean square displacement at absolute zero, which has the value

$$(18)\quad \mu_0 = (h^2/8\pi^2 mk\Theta)\int_0^3 (1/f)(1/3N)(dn/df^2)\,df^2 = 6.28 \times 10^{-20}\,\text{cm}^2.$$

The integrals are again evaluated by Simpson's three-eighths rule except for the interval from 0 to 0.1. The integrand becomes infinite as f approaches zero, so that a special treatment is necessary in that region. It has been assumed that for such low frequencies the Debye distribution is valid and $n = (f/f_m)^3$, where f_m is proportional to the maximum Debye frequency and has a value equal to $\sqrt{3.66}$ for tungsten. The equation for this single interval is

$$(19)\quad \mu = \mu_0 + (3/2)(1/f_m)^3 \int_0^{0.1} \left[1/(e^{f\Theta/T} - 1)\right] df^2$$

$$= \mu_0 + 3(T/\Theta)^2 (1/f_m)^3 \int_0^{\sqrt{0.1}(\Theta/T)} \left[x/(e^x - 1)\right] dx$$

The last integral is the one considered by Debye and tabulated for various values of the upper limit. The quantity Θ however has a different value here from the one given by Debye.

No experimental values for the intensity of reflection of x-rays from a single tungsten crystal are known, so a choice between the various theories is not possible. However, the influence of the temperature on the intensity is given by the factor e^{-M}, where $M = (8\pi^2\mu\sin^2\varphi)/\lambda^2$, φ being the grazing angle of incidence and λ the wave length of the x-rays. In the following table there is an indication of the magnitudes involved for the root mean square displacement of any atom in the crystal according to the present work and according to the two separate Debye representations, the first based on a distribution which agrees with the one calculated here at low frequencies and the other based on experimental specific heat data. $\sqrt{\mu}$ is in Ångstroms.

T	$\sqrt{\mu}$ (Atomic model)	$\sqrt{\mu}$ (Debye, 0 = 367°)	$\sqrt{\mu}$ (Debye, 0 = 310°)
0°K	0.0251	0.0231	0.0251
100	0.0307	0.0279	0.0319
200	0.0401	0.0356	0.0417
300	0.0480	0.0426	0.0502
400	0.0550	0.0488	0.0576
500	0.0613	0.0544	0.0642

It is clear that the second set of Debye values is in much better agreement with the results of the present work than the values which should logically form a basis of comparison.

At very much higher temperatures the theoretical formula for μ has a particularly simple and significant form. If the exponential function which appears in the denominator of the integrand is expanded in a power series in $f\theta/T$ and only the first two terms retained, the result is

$$(20) \qquad \mu = \mu_0 + (h^2/4\pi^2 mk\theta^2)T\int_0^3 (1/f^2)(1/3N)(dn/df^2)df^2.$$

Now the integral does not depend on the temperature so that μ is simply a linear function of the temperature. The coefficient of T is just the average value of the reciprocal of the square of the frequency with respect to the frequency distribution. This is a quantity which therefore depends directly on the distribution alone. The numerical factors are given in the following equations: (21)

Atomic model: $\mu = (6.28 + 0.0742\ T) \times 10^{-20}\ \text{cm}^2.$

Debye ($\theta = 367°$): $\mu = (5.34 + 0.0583\ T) \times 10^{-20}\ \text{cm}^2.$

Debye ($\theta = 310°$): $\mu = (6.32 + 0.0815\ T) \times 10^{-20}\ \text{cm}^2.$

These results indicate that a simple and direct te$\overset{s}{x}$t of the various theories would be afforded by information about the decrease of intensity of reflection of x-rays at high temperatures. An objection that might be raised is that the theoretical formulae do not apply when the amplitude of the thermal vibrations becomes so large that the assumption of a quadratic potential energy function is no longer valid. The increase of the specific heat above the equipartition value for temperatures exceeding 300°K in the case of many metals tends to show that such a breakdown in the theoretical postulates is soon reached. On the other hand, the results above indicate that the root mean square displacement of the atoms is still small in comparison with the interatomic distances at moderate temperatures. The conclusion that can be drawn is that either the continued rise in the specific heat is due to some other cause or that the above theories do not themselves correctly designate the point at which their validity may be questioned.

In conclusion, a few words may be said about possible extensions of the methods presented here and about additional experimental data which would prove valuable in verifying the results of the theory. The next immediate step in extending the theoretical treatment would be an investigation of other body-centered cubic crystals besides tungsten. The solution of the cubic secular equation would be more difficult because a removal of the isotropy condition so conveniently satisfied by the elastic constants of tungsten introduces numerical complications. However, in principle, the procedure could be carried out in an identical fashion to that discussed here.

In the case of a face-centered cubic crystal the secular equation which has been set up is more complicated than the one for the body-centered cubic lattice, but could presumably be solved in much the same way. As the structure of the lattice becomes more complex, the difficulty in carrying out numerical computations naturally increases also. Since considerable labor is involved in solving the simplest case even after several assumptions are made about the force constants, a point may soon be reached where further use of these methods is no longer profitable. What will then be needed is a way of shortening the calculations without sacrificing their accuracy, a goal that may not be possible of attainment.

It would also be valuable to investigate more completely the conditions which have been imposed on the force constants with a view to using additional experimental properties of the crystal. The difficulty is that the atomic model set up here does not even admit the existence of some of the physical characteristics of real crystals, such as the thermal coefficient of expansion. This indicates that eventually a thoroughgoing revision of the whole theory must be made by the introduction of higher order terms in the potential energy, as has been done to some extent by Born. However, then the normal coordinate treatment is not applicable in the form used here and must be modified.

Perhaps additional experimental investigations will throw some light on these matters. As far as the present case of tungsten is concerned, information about the variation of the elastic constants with temperature would certainly be valuable. Also, measurements of the specific heat of tungsten at lower temperatures might prove significant. It is at very low temperatures that a separation of the observed specific heat into electronic and atomic contributions can be attempted.

The question of the intensity of x-ray reflection from tungsten seems to have been neglected in experimental work on the subject. Due to the cubic symmetry properties, single crystals would not be necessary in such an investigation. Also, an absolute measurement of intensity would not be required; relative values at different temperatures would be sufficient to check certain aspects of the theory.

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