

lines. The method of approximation which takes this distribution F_1 as typical of much of the distribution is not far in error.

The peaks in the other functions are less satisfactory. Function F_2 is along a line ending at an edge. For other lines ending at the same edge the same peaks are to be expected, but for lines ending away from the edge the peaks will be displaced. In the case of function F_3 the peaks are probably not justified at all, since the line $x=y=z$ ends at a corner, and the decrease in solid angle around the line will more than compensate the infinity in the function F_3 .

Most methods of approximation previously used have tended to obscure and smooth out the actually existing peaks. This method overemphasizes them and adds some extra ones, without, however, diminishing the accuracy of representation of the low frequencies. It must be further emphasized that the use of additional terms in the expansion will reduce the overemphasis and the spurious peaks, and will tend to approach the correct distribution.

The simple cubic lattice is particularly ill-adapted to this method because of the shape of the Brillouin zone. For a body-centered or a face-centered lattice the zones will have less acute

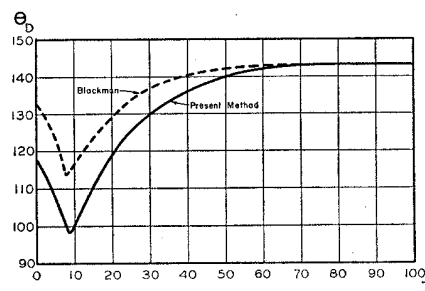


FIG. 4. The equivalent Debye characteristic temperature as a function of temperature for the distributions obtained by the present method and that of Blackman.

angles and corners, and the method will be correspondingly more rapidly convergent.

Figure 4 indicates the Debye characteristic temperature, as a function of temperature, derived from the frequency distribution of Fig. 3. The force constants are adjusted to make θ approach 142° at high temperature. The corresponding values obtained by Blackman are also shown in this curve, and the effect of the sharper peaks in making a deeper dip is evident.

It is proposed to apply this method to the model of Fine for a body-centered lattice and of Leighton for a face-centered lattice, as well as to investigate the effect of solving the secular equation along several other directions.

The Vibrational Spectrum and Specific Heat of a Face-Centered Cubic Crystal

ROBERT B. LEIGHTON

California Institute of Technology, Pasadena, California

The frequency spectrum of a face-centered cubic crystal lattice is found by actually modeling the constant-frequency surfaces of the secular determinant in plaster of Paris and measuring the volume enclosed between successive surfaces. The frequency spectrum so obtained is used in the evaluation of the specific heat of a general crystal of the type treated, and numerical values are presented for the element silver. The present theory (that of Born and v. Karman) is in much better agreement with experimental values for temperatures below 100°K than is the Debye theory. Certain anomalies in the specific heat curves of silver and potassium chloride at temperatures below 10°K are not explicable in terms of the atomic model that is used.

MANY of the thermal properties of solids can be explained semiquantitatively by interpretation in terms of thermal vibrations of the

atoms about their mean rest positions. Some of these properties can be treated satisfactorily by using only the qualitative features of the atomic

vibrations, but in certain cases the experimental data indicate that a more refined treatment is necessary. In particular, the latter is true of the specific heat; the measured specific heats of silver and of potassium chloride¹ disagree seriously (and in the same way) with the Debye theory² in the temperature range up to 50°K, and there is reason to believe that the agreement between theory and experiment can be improved by using the Born-von Karman theory³ of specific heats. The greatest deterrent to the use of the Born-von Karman theory has been the difficulty encountered in solving the secular determinant to obtain the frequency spectrum of the vibrating lattice. Blackman⁴ has discussed qualitatively the differences to be expected between the two theories in the low temperature range. He has treated the two-dimensional case and the sodium chloride lattice (assumed to be a monatomic, simple cubic lattice) numerically. No such calculation has been made for a crystal type actually occurring in nature, however. Fine⁵ obtained the frequency spectrum of the body-centered cubic element tungsten by numerical integration, but

no special application to specific heats at low temperatures was made. Montroll⁶ and his co-workers have obtained approximate analytical expressions for the frequency spectrum of a general monatomic, body-centered cubic lattice, but these expressions cannot be applied to the calculation of specific heat in the low temperature region because they do not behave properly in the low frequency range.

It is the purpose of this paper to determine the frequency spectrum of a monatomic, face-centered cubic crystal lattice, and to attempt to improve the agreement between theoretical and experimental values of specific heats.

1. THE SECULAR DETERMINANT FOR THE LATTICE

The secular determinant for the lattice being considered can be obtained from the equations of motion by a method that has been used so frequently in the literature³⁻⁶ and in textbooks⁷ for various one-, two-, and three-dimensional lattices that it need not be repeated here. The secular determinant is

$$\begin{vmatrix} 2+2(\gamma/\alpha) \sin^2x & \sin x \sin y & \sin x \sin z \\ -\cos x(\cos y + \cos z) - \lambda^2 & & \\ \sin x \sin y & 2+2(\gamma/\alpha) \sin^2y & \sin y \sin z \\ & -\cos y(\cos z + \cos x) - \lambda^2 & \\ \sin x \sin z & \sin y \sin z & 2+2(\gamma/\alpha) \sin^2z \\ & & -\cos z(\cos x + \cos y) - \lambda^2 \end{vmatrix} = 0. \quad (1)$$

The quantities appearing in this determinant have the following meanings:

The quantities α and γ are the force constants for central, Hooke's law forces which are assumed to act between an atom and its nearest and next nearest neighbors, respectively.

The quantity λ is a dimensionless parameter which is proportional to the frequency ν . Explicitly, $\lambda^2 = 2\pi^2 m \nu^2 / \alpha$, where m is the mass of each particle.

The quantities x , y , and z are dimensionless variables which take on discrete values defined

by

$$\begin{aligned} x &= \pi(-l/N_1 + m/N_2 + n/N_3), \\ y &= \pi(l/N_1 - m/N_2 + n/N_3), \\ z &= \pi(l/N_1 + m/N_2 - n/N_3). \end{aligned} \quad (2)$$

Here, (lmn) are integers, and the crystal is assumed to be a parallelepiped that contains N_1 , N_2 , and N_3 atoms along its three principal edges, respectively. The range of variation of the integers (lmn) is such that, if the quantities (x, y, z) are interpreted as being Cartesian coordinates, the points corresponding to the integers (lmn) all lie inside a region having the shape of the first Brillouin zone of the crystal lattice.

¹ W. H. Keesom and C. W. Clark, *Physica* **2**, 698 (1935).

² P. Debye, *Ann. d. Physik* **39**, 789 (1912).

³ M. Born and T. von Karman, *Physik. Zeits.* **13**, 297 (1912); **14**, 15 (1913).

⁴ M. Blackman, *Proc. Roy. Soc.* **148**, 384 (1935); **159**, 416 (1937); *Proc. Camb. Phil. Soc.* **33**, 94 (1937).

⁵ P. C. Fine, *Phys. Rev.* **55**, 355 (1939).

⁶ E. W. Montroll, *J. Chem. Phys.* **10**, 218 (1942); **11**, 481 (1943); **12**, 98 (1944).

⁷ L. Brillouin, *Wave Propagation in Periodic Structures* (McGraw-Hill Book Company, Inc., New York, 1946).

These points, which will henceforth be called the "permissible points" of the determinant, are uniformly distributed in (x, y, z) space. The total number of permissible points inside the zone is $N_1N_2N_3$ (i.e., the number of atoms in the crystal lattice).

The significance of the secular determinant itself may be stated as follows: a vector drawn from the origin to a permissible point (x, y, z) represents the propagation vector of a plane wave traveling through the crystal; its direction gives the direction of propagation, while its length is proportional to the wave number of the plane wave. The insertion of the quantities (x, y, z) into the secular determinant and the solution of the resulting cubic equation in λ^2 will yield three values of λ^2 , that is, three *frequencies* corresponding to such a wave. One can thus solve for the velocities of propagation of elastic waves through the crystal, as functions of the direction of propagation and frequency. In addition, the successive substitution of these three frequencies into the set of equations from which the determinant was derived, will yield the relative amplitudes of the coordinates of which each normal mode is composed. In short, the secular determinant, together with the transformation equations connecting the atomic displacements with the coordinates for which the determinant was written, constitute a complete solution of the dynamical problem.

For the purposes of this discussion the normal coordinates themselves need not be known; however, a knowledge of the distribution of frequencies of the various normal vibrations is required, since the statistical treatment leading to the specific heat depends upon the distribution function $G(\lambda)$, where

$$dn = N_1N_2N_3G(\lambda)d\lambda, \quad (3)$$

dn being the number of normal frequencies lying between the limits λ and $\lambda+d\lambda$. $G(\lambda)$ can be regarded as being a continuous function of λ if the above expression is always understood to apply to a range $d\lambda$ that contains a large number of frequencies.

2. THE SURFACES OF CONSTANT FREQUENCY

Rearrangement of Eq. (3) yields

$$G(\lambda) = (1/N_0)dn/d\lambda,$$

where $N_0 = N_1N_2N_3$, and since the permissible points are uniformly distributed in (x, y, z) space,

$$G(\lambda) = (1/N_0v_0)dV/d\lambda,$$

where v_0 is the volume of (x, y, z) space associated with one permissible point and V is the total volume of (x, y, z) space enclosed by a surface defined by a constant value of λ . Finally,

$$G(\lambda) = (1/V_0)dV/d\lambda, \quad (4)$$

where V_0 is the volume of (x, y, z) space associated with N_0 permissible points. It is clear from Eq. (4) that the function $G(\lambda)$ can be found by computing the volume enclosed by successive surfaces defined by $\lambda = \text{const.}$ and then differentiating the volume with respect to the parameter λ . This method was used to find the frequency spectrum of the face-centered cubic lattice.

Three constant-frequency surfaces pass through each permissible point in (x, y, z) space, one for each of the three roots of the secular determinant. That these surfaces possess the symmetry properties of a cubic lattice can easily be seen by observing that the secular determinant is invariant to all of the rotations and reflections of the cubic system. The surfaces need therefore be studied only inside a suitably defined solid angle amounting to $1/48$ of the total solid angle surrounding the origin. This region was taken to be that lying in the positive octant between the planes $y=0$, $x=y$, and $x=z$. The outer boundary of this region of interest was not taken to be the boundary of the Brillouin zone but was modified so as to have the same volume and to contain points defining the same frequencies. This was done to facilitate the construction of the surfaces and has no effect upon the final result. The outer boundary was taken to be the planes $z=\pi$ and $x=\pi/2$.

The secular determinant leads to a cubic equation in λ^2 for a general permissible point, but in the symmetry planes of the constant frequency surfaces the determinant can be factored into a quadratic and linear factor. The quadratic equation can then easily be solved. The three families of surfaces corresponding to the three roots of the secular determinant are commonly called the three *branches* of the solution, and are here identified by the arbitrary

labels I, II, and III. The solutions for the three branches in the symmetry planes are as follows:

Branch I

Plane $y=0$: $\lambda_1^2 = 2 - \frac{1}{2} \cos x - \frac{1}{2} \cos z$
 $-\cos x \cos z + (\gamma/\alpha) \sin^2 x + (\gamma/\alpha) \sin^2 z$
 $-\left[(\gamma/\alpha) \sin^2 x - (\gamma/\alpha) \sin^2 z - \frac{1}{2} \cos x \right. \\ \left. + \frac{1}{2} \cos z \right]^2 + \sin^2 x \sin^2 z \Big)^{\frac{1}{2}}, \quad (5)$

Plane $x=y$: $\lambda_1^2 = 1 - \cos x \cos z + 2(\gamma/\alpha) \sin^2 x$.

Branch II

Plane $y=0$: $\lambda_2^2 = 2 - \cos x - \cos z$,
 Plane $x=y$: $\lambda_2^2 = (3/2)(1 - \cos x \cos z)$
 $+ (1 + \gamma/\alpha) \sin^2 x + (\gamma/\alpha) \sin^2 z$
 $-\frac{1}{2} \left[1 - \cos x \cos z - (2 + 2\gamma/\alpha) \sin^2 x \right. \\ \left. + 2(\gamma/\alpha) \sin^2 z \right]^2 + 8 \sin^2 x \sin^2 z \Big)^{\frac{1}{2}}. \quad (6)$

Branch III

Plane $y=0$: $\lambda_3^2 = 2 - \frac{1}{2} \cos x - \frac{1}{2} \cos z$
 $-\cos x \cos z + (\gamma/\alpha) \sin^2 x + (\gamma/\alpha) \sin^2 z$
 $+\left[(\gamma/\alpha) \sin^2 x - (\gamma/\alpha) \sin^2 z - \frac{1}{2} \cos x \right. \\ \left. + \frac{1}{2} \cos z \right]^2 + \sin^2 x \sin^2 z \Big)^{\frac{1}{2}}, \quad (7)$

Plane $x=y$: $\lambda_3^2 = 3/2(1 - \cos x \cos z)$
 $+ (1 + \gamma/\alpha) \sin^2 x + (\gamma/\alpha) \sin^2 z$
 $+\frac{1}{2} \left[1 - \cos x \cos z - (2 + 2\gamma/\alpha) \sin^2 x \right. \\ \left. + 2(\gamma/\alpha) \sin^2 z \right]^2 + 8 \sin^2 x \sin^2 z \Big)^{\frac{1}{2}}.$

In obtaining the above expressions, the solutions in the various planes were matched along their common lines so as to obtain a consistent identification of the branches. The solutions for the plane $x=z$ are obtained by substituting z for y in the solutions for the plane $x=y$; and for the plane $x=\pi$ by substituting $\pi-x$ for x and $\pi-z$ for y in the expressions for the plane $y=0$.

The above identification of the branches is not unique, because the expressions for branches I and II coincide along the lines $x=y=z$ and $y=0, x=z$. The difficulty can be resolved by studying these two solutions in the neighborhood of the line $x=y=z$. The result is that it is necessary to interchange the above expressions for branches I and II in the plane $x=z$. Furthermore, in order to match the solutions in the

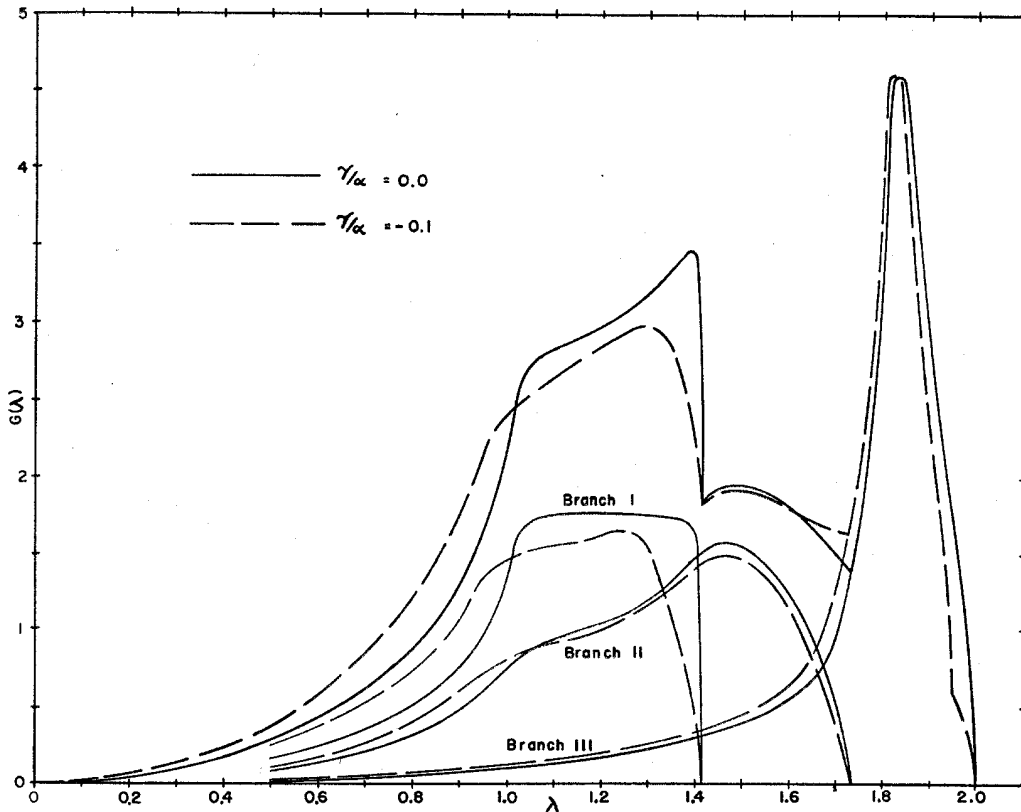


FIG. 1. The frequency spectrum of a face-centered cubic crystal lattice. The three branches extend from $\lambda=0$ to $\lambda=\sqrt{2}$, $\lambda=\sqrt{3}$, and $\lambda=2$, respectively.

various planes for branches II and III, it is necessary to interchange these two solutions in the plane $z=\pi$ for $\lambda^2 > 3$.

One more property of the constant-frequency surfaces, in addition to their cubic symmetry, can be derived from the secular determinant. By evaluating the first and second directional derivatives of λ with respect to coordinates at right angles to the symmetry planes, it can be shown that the curvature of each surface at a symmetry plane is finite, so that the surfaces intersect these symmetry planes at right angles. This fact greatly simplifies the construction of the surfaces.

The contours of constant frequency were evaluated numerically from the above expressions by inserting uniformly spaced points into these equations and interpolating graphically to find the points corresponding to prescribed values of λ .

3. THE FREQUENCY SPECTRUM

The volumes contained between successive surfaces were found by actually modeling the surfaces in plaster of Paris. A mold was constructed of sheet brass, and blocks of plaster were cast in the shape of the region enclosed by the planes $y=0$, $x=y$, $x=z$, $z=\pi$, and $x=\pi/2$. The contours of constant frequency were carefully plotted on coordinate paper to the same scale as the plaster blocks, and were transferred to the blocks by wrapping the paper around the blocks and pricking through the paper with a sharp pin along each contour. One set of contours was thus transferred to each block. The blocks were then sawed into a number of pieces between alternate pairs of contours, and the pieces were carved along each contour. The extrapolation of the contours into surfaces with the required accuracy was possible because of the known orthogonality of the surfaces with the symmetry planes and the small solid angle included between the symmetry planes. The intercepts of the surfaces with the line $x=y/2=z/4$ were also computed. This line passes through the origin and makes almost equal angles with the three symmetry planes. Errors were reduced further by carving each set of surfaces twice. The saw cuts for one such set were halfway between those for the other set, so that each surface was carved

TABLE I. Elastic constants,* atomic force constants, and cell dimensions of some face-centered metals. (c_{11} , c_{12} , and c_{44} in units of 10^{11} dynes/cm².)

Metal	$d(\text{Å})$	c_{11}	c_{12}	c_{44}	$c_{11}-c_{12}$	$\alpha \times 10^{-3}$	γ/α
Cu	3.61	17.0	12.3	7.5	4.7	27.1	-0.09
Ag	4.08	12.2	9.1	4.4	3.1	18.0	-0.08
Au	4.07	18.7	15.7	4.4	3.0	17.9	-0.08
Al	4.04	11.9	6.2	2.9	5.7	11.7	+0.25

* See reference 10.

once from the side farthest from the origin, and once from the side nearest the origin.

The alternate pieces of plaster of each set (those that were destroyed by the saw cuts) were obtained by placing the carved pieces in the brass mold and pouring a thin mixture of plaster between them. In this way, two complete sets of plaster models of the surfaces were obtained for each branch. The volumes of the various pieces were then measured by weighing each piece twice, once while submerged in water and once while suspended in air. The water absorbed by the plaster does not affect the measurements if the pieces are known to contain the same amount of water for both weighings.

The total volume occupied by each set, as calculated from the dimensions of the mold, should have been 486.0 cc. Inasmuch as the measurements agreed among themselves and with this value to within one or two percent, the method used to determine the volume of the plaster pieces is probably sufficiently accurate. It was found that the volumes of the pieces of a given set were generally alternately higher and then lower than the volumes of the corresponding pieces of the duplicate set. This reflects a tendency to carve away too little material in the modeling process. The differences were not large, and were furthermore quite regular, so that the mean of the two measured volumes for each piece is probably much closer to the true value than either of the measured values.

Figure 1 contains the (smoothed) results of these measurements for the case $\gamma/\alpha=0$, plotted for each branch, and the function $G(\lambda)$, which is the sum of the three curves. Plotted also are the results of a similar treatment of the case $\gamma/\alpha=-0.1$.

4. SERIES EXPANSION OF $G(\lambda)$ FOR LOW FREQUENCIES

In the neighborhood of the origin, where the approximations $\sin x = x$, $\cos x = 1 - x^2/2$, etc., are valid, the secular determinant has solutions of the form, $\lambda^2/r^2 = F(\theta, \phi)$, where r , θ , and ϕ are spherical polar coordinates. The volume enclosed by a surface in this region therefore is proportional to λ^3 so that $G(\lambda)$ is proportional to λ^2 .

For application to the specific heat of a face-centered lattice in the region of very low temperatures, it is desirable to possess a power series expansion of $G(\lambda)$ in ascending powers of λ , valid for small values of λ . This can be found approximately for two or three terms by studying the deviations of the function $G(\lambda)$ from the parabolic law that is valid for very small values of λ . This was done by evaluating the fractional volume enclosed by each constant-frequency surface in the form

$$V(\lambda)/V_0 = k(\lambda)\lambda^3,$$

where $k(\lambda) = k_0 + k_2\lambda^2 + k_4\lambda^4 + \dots$, and $V(\lambda)$ represents the sum of the volumes for the three branches. From Eq. (4) and the above expression, we see that

$$G(\lambda) = 3k_0\lambda^2 + 5k_2\lambda^4 + 7k_4\lambda^6 + \dots$$

The derivatives of k with respect to λ were obtained graphically. Evaluation of these derivatives at $\lambda=0$ yielded the following expression

TABLE II. The function

$$f(\beta\lambda/T) = (\beta\lambda/T)^2 e^{\beta\lambda/T} / (e^{\beta\lambda/T} - 1)^2.$$

λ	T/β								
	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.50	1.00
0.0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.1	0.922	0.964	0.980	0.987	0.990	0.993	0.998	0.998	1.000
0.2	0.723	0.864	0.922	0.950	0.964	0.974	0.980	0.987	0.998
0.3	0.495	0.723	0.831	0.889	0.922	0.942	0.955	0.972	0.993
0.4	0.304	0.569	0.723	0.812	0.864	0.898	0.922	0.950	0.987
0.5	0.171	0.423	0.607	0.723	0.798	0.843	0.878	0.922	0.980
0.6	0.090	0.304	0.495	0.629	0.723	0.786	0.832	0.889	0.972
0.7	0.045	0.207	0.392	0.539	0.648	0.723	0.779	0.852	0.961
0.8	0.021	0.137	0.304	0.454	0.569	0.657	0.723	0.812	0.950
0.9	0.010	0.090	0.228	0.374	0.495	0.590	0.666	0.769	0.935
1.0	0.004	0.056	0.171	0.304	0.423	0.525	0.608	0.723	0.922
1.1	0.002	0.035	0.125	0.242	0.357	0.463	0.550	0.677	0.904
1.2	0.001	0.021	0.090	0.193	0.304	0.405	0.495	0.629	0.889
1.3	0.000	0.013	0.064	0.150	0.250	0.350	0.442	0.585	0.871
1.4	0.000	0.006	0.045	0.118	0.207	0.302	0.392	0.539	0.852
1.5	0.000	0.004	0.031	0.089	0.171	0.259	0.346	0.495	0.831
1.6	0.000	0.003	0.021	0.067	0.137	0.222	0.304	0.454	0.812
1.7	0.000	0.002	0.015	0.050	0.110	0.186	0.263	0.413	0.790
1.8	0.000	0.001	0.010	0.037	0.090	0.155	0.228	0.374	0.769
1.9	0.000	0.000	0.008	0.028	0.070	0.130	0.196	0.338	0.746
2.0	0.000	0.000	0.004	0.020	0.056	0.108	0.171	0.304	0.723

for $G(\lambda)$:

$$G(\lambda) = 0.99\lambda^2 + 0.35\lambda^4 + 0.42\lambda^6 + \dots \quad (\gamma/\alpha = 0),$$

$$G(\lambda) = 1.32\lambda^2 + 0.40\lambda^4 + 0.36\lambda^6 + \dots \quad (\gamma/\alpha = -0.1).$$

5. ATOMIC FORCE CONSTANTS

The elastic constants of some typical monovalent, cubic metals were calculated by Fuchs,⁸ who obtained good agreement with experiment in all cases by regarding the conduction electrons as a gas of perfectly free, non-interacting Fermi particles. The energy of such a gas depends upon its volume, so that the conduction electrons contribute to the deformation energy if the volume of the crystal changes. By considering two types of deformation that leave the volume of the crystal unchanged, Fuchs found that the quantities $(c_{11} - c_{12})$ and c_{44} are independent of the presence of the Fermi gas. Fuchs' result was used in the evaluation of the atomic force constants α and γ , because the Born-von Karman boundary condition, which was used in the derivation of the secular determinant, requires that the volume of the crystal remain constant so that the conduction electrons have no effect upon the motion of the lattice.

When the potential energy of the lattice for an

TABLE III. Values of $G(\lambda)$ for $\gamma/\alpha=0.0$ and $\gamma/\alpha=-0.1$.

λ	$G(\lambda)$	
	$\gamma/\alpha=0.0$	$\gamma/\alpha=-0.1$
0.0	0.000	0.000
0.1	0.011	0.013
0.2	0.039	0.052
0.3	0.092	0.122
0.4	0.170	0.224
0.5	0.28	0.39
0.6	0.42	0.58
0.7	0.62	0.84
0.8	0.89	1.20
0.9	1.29	1.75
1.0	2.19	2.37
1.1	2.80	2.64
1.2	2.97	2.84
1.3	3.18	2.94
1.4	2.74	2.22
1.5	1.92	1.90
1.6	1.80	1.80
1.7	1.53	1.70
1.8	3.42	3.66
1.9	2.92	2.37
2.0	0.53	0.18

⁸ K. Fuchs, Proc. Roy. Soc. 153A, 622 (1936).

TABLE IV. C_v in cal./mole deg. for face-centered cubic elements.

T/β	C_v (Cal./mole deg.)	
	$\gamma/\alpha=0.0$	$\gamma/\alpha=-0.1$
0.10	0.0594	0.0792
0.15	0.236	0.294
0.20	0.585	0.681
0.25	1.050	1.170
0.30	1.565	1.692
0.35	2.075	2.200
0.40	2.548	2.670
0.50	2.335	3.438
1.00	5.07	5.11

 TABLE V. θ/β as a function of T/β for face-centered cubic elements.

T/β	θ/β	
	$\gamma/\alpha=0.0$	$\gamma/\alpha=-0.1$
0.10	1.985	1.805
0.15	1.875	1.741
0.20	1.824	1.722
0.25	1.812	1.728
0.30	1.810	1.741
0.35	1.813	1.750
0.40	1.812	1.751
0.50	1.814	1.760
1.00	1.825	1.780

homogeneous deformation, written in terms of the unit strains and the atomic force constants α and γ , is compared with the usual expression involving the elastic constants, the following correlations can be made:

$$c_{11}' = (2\alpha + 4\gamma)/d, \quad c_{12}' = \alpha/d, \quad c_{44}' = \alpha/d. \quad (9)$$

The primes indicate that these are the contributions of the lattice ions to the elastic constants, exclusive of the compressibility of the electron gas.

To evaluate α and γ , Fuchs' result is taken into account by writing

$$c_{11}' - c_{12}' = c_{11} - c_{12} = (\alpha + 4\gamma)/d, \quad (10)$$

and

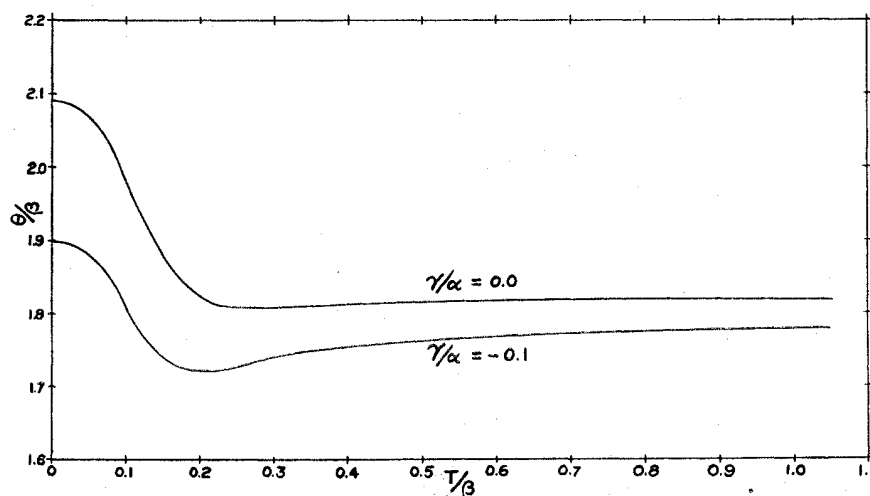
$$c_{44}' = c_{44} = \alpha/d,$$

where the actual values for the elastic constants of a face-centered cubic crystal may now be used.

In Table I are given the elastic constants at room temperature, together with the values of α and γ/α , computed from Eq. (10) for some typical face-centered elements.

The case of silver is treated numerically in the next section. It is in the region near absolute zero that the results of the theory are to be compared with experiment, so that the values of the atomic force constants near absolute zero must be used. Eucken⁹ in 1913 used a value for the shear modulus of silver at absolute zero that was derived from Grüneisen's theory. This value also agreed with the experimental data existing at that time. The ratio of the shear modulus at absolute zero to the same at room temperature (for a polycrystal) is assumed to be the same as the corresponding ratio of the values of c_{44} , upon which the basic constant α depends. Thus, at absolute zero the constant α for silver would

FIG. 2. The variation of Debye characteristic temperature, θ , with absolute temperature, T , for face-centered cubic crystals. The parameter β depends upon the elastic properties of the crystal, and must be evaluated for each individual case.



⁹ A. Eucken, Verh. deut. physik. Ges. 15, 571 (1913).

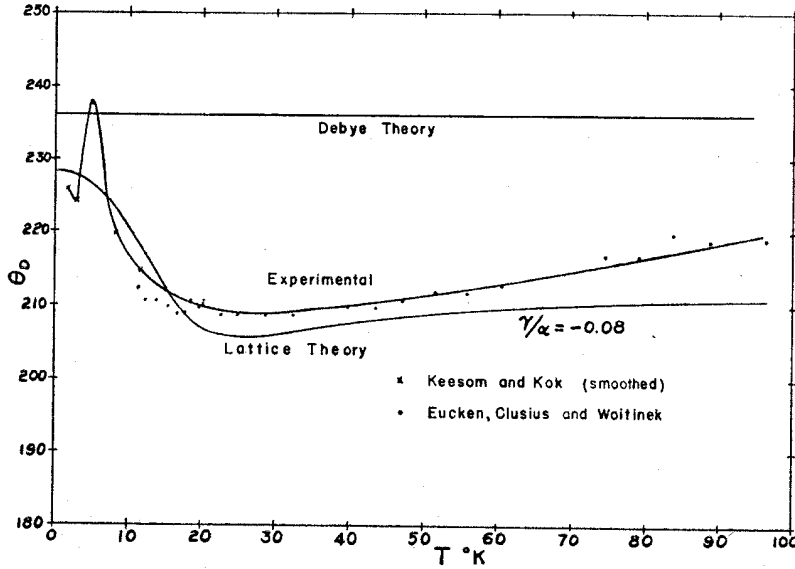


FIG. 3. The specific heat of silver, expressed in terms of the equivalent Debye temperature θ_D . The value of θ_D calculated from the Debye theory is also shown.

have the value

$$\alpha_0 = 21.3 \times 10^3. \quad (11)$$

The change in the cell dimension d due to thermal expansion is negligible over this temperature range.

6. SPECIFIC HEATS OF FACE-CENTERED CUBIC ELEMENTS

The frequency spectrum of a face-centered cubic crystal will now be applied to the computation of the specific heats of elements having this structure. It is possible to evaluate the specific heats without using the numerical data of the last paragraph, and this will be done. In order to compare these theoretical results with experimental observations, however, the numerical values of the force constants must be used.

The specific heat integral is usually written for a general solid body characterized by a frequency

distribution $N(\nu)$. This integral is

$$C_v = (h^2/kT^2) \int_0^{\nu_m} \frac{\nu^2 e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} N(\nu) d\nu. \quad (12)$$

The frequency distribution for a face-centered cubic lattice has been obtained in the form of a function of the dimensionless parameter λ . The above integral will therefore be in a more convenient form if it is rewritten in terms of the parameter λ .

According to the definition of λ in connection with the secular determinant (1),

$$\lambda = \pi\nu(2m/\alpha)^{1/2}, \quad (13)$$

and from (3)

$$dn = N(\nu)d\nu = N_0 G(\lambda)d\lambda, \quad (14)$$

where N_0 will now be taken as Avogadro's number.

Using (13) one may write

$$h\nu/kT = \beta\lambda/T, \quad (15)$$

where

$$\beta^2 = h^2\alpha/2\pi^2mk^2.$$

Thus (12) takes the form

$$\begin{aligned} C_v &= N_0 k \int_0^{\lambda_m} \frac{(\beta\lambda/T)^2 e^{\beta\lambda/T}}{(e^{\beta\lambda/T} - 1)^2} G(\lambda) d\lambda \\ &= R \int_0^2 \frac{(\beta\lambda/T)^2 e^{\beta\lambda/T}}{(e^{\beta\lambda/T} - 1)^2} G(\lambda) d\lambda, \end{aligned} \quad (16)$$

TABLE VI. Values of θ/β calculated from Eqs. (23) and (8).

T/β	$\gamma/\alpha=0.0$	θ/β	$\gamma/\alpha=-0.1$
0.00	2.090	1.898	
0.02	2.083	1.895	
0.04	2.076	1.888	
0.06	2.056	1.872	
0.08	2.025	1.850	
0.10	1.985	1.805	

since $N_0k = R$, the gas constant per mole, and $\lambda_m = 2.0$.

The expression (16) can now be used to evaluate the specific heats of face-centered cubic elements. The quantities appearing in the integrand must first be evaluated numerically.

Table II contains values of

$$(\beta\lambda/T)^2 e^{\beta\lambda/T} / (e^{\beta\lambda/T} - 1)^2$$

as a function T/β and λ .

The values given by Table II are to be multiplied by the corresponding average values of $G(\lambda)\Delta\lambda$ and summed over the range of λ . Values of $G(\lambda)$ obtained from Fig. 1 and Eq. (8) are given in Table III. These values do not correspond to the ordinates of the distribution function, but rather to averages over the intervals of width $\Delta\lambda = 0.1$ centered about the given values of λ . Multiplication of corresponding ordinates and summation over λ yielded the values of C_v given in Table IV.

The specific heats obtained by this process were then compared with a table of Debye specific heats.¹⁰ The values of the Debye parameter θ/T which yield specific heats equal to those in Table II were determined. These values of θ/T , when multiplied by T/β , yielded the values of θ/β that appear in Table V.

The integral (16) is not in a convenient form for the evaluation of specific heats and characteristic temperatures at very low temperatures. Inasmuch as the function of Table II decreases exponentially for large values of $\beta\lambda/T$, and is negligible outside the range of validity of the series expressions (8) when $T/\beta < 0.05$, no appreciable error will be made if the integral (16) is evaluated from $\lambda = 0$ to $\lambda = \infty$, using the series expressions for $G(\lambda)$ over the entire infinite range. Thus (16) would become, using a previous notation,

$$\begin{aligned} C_v &= R \int_0^\infty \frac{\beta^2 e^{\beta\lambda/T}}{T^2 (e^{\beta\lambda/T} - 1)^2} \\ &\quad \times (3k_0\lambda^4 + 5k_2\lambda^6 + 7k_4\lambda^8 + \dots) d\lambda \\ &= R [3k_0(T/\beta)^3 D(4) + 5k_2(T/\beta)^5 D(6) \\ &\quad + 7k_4(T/\beta)^7 D(8) + \dots], \quad (17) \end{aligned}$$

¹⁰ Landolt-Bornstein, *Physicalish—Chemische Tabellen* (Julius Springer, Verlag, Berlin, 1927), fifth edition.

where

$$D(n) = \int_0^\infty \frac{x^n e^x dx}{(e^x - 1)^2}. \quad (17a)$$

In this notation, the Debye specific heat, is

$$C_v = 9R(T/\theta)^3 D(4). \quad (18)$$

To find the Debye characteristic temperature θ as a function of T/β , the expressions (17) and (18) may be equated, with the result

$$\begin{aligned} 9R(T/\theta)^3 D(4) \\ &= R(T/\beta)^3 D(4) \left[3k_0 + 5k_2 \frac{D(6)}{D(4)} \left(\frac{T}{\beta}\right)^2 \right. \\ &\quad \left. + 7k_4 \frac{D(8)}{D(4)} \left(\frac{T}{\beta}\right)^4 + \dots \right]. \quad (19) \end{aligned}$$

This equation may now be solved for θ/β :

$$\theta/\beta = 9^{1/3} [3k_0 + 5k_2(T/\beta)^2 D(6)/D(4) + 7k_4(T/\beta)^4 D(8)/D(4) + \dots]^{-1/3}. \quad (20)$$

To evaluate the $D(n)$ function appearing in (20), integration of (17a) by parts and subsequent expansion of the denominator in a series yields

$$\begin{aligned} D(n) &= \int_0^\infty \frac{x^n e^x dx}{(e^x - 1)^2} = n \int_0^\infty \frac{x^{n-1} dx}{(e^x - 1)} \\ &= n \int_0^\infty \frac{x^{n-1} e^{-x} dx}{1 - e^{-x}} \\ &= n \sum_{r=0}^\infty \int_0^\infty x^{n-1} e^{-x} e^{-rx} dx = n \sum_{r=0}^\infty \frac{(n-1)!}{(r+1)^n} \\ &= n! \sum_{s=1}^\infty 1/S^n = (2\pi)^n / 2B_{n/2} \quad (n \text{ even}), \quad (21) \end{aligned}$$

where $B_{n/2}$ is the $n/2$ th Bernoulli number as tabulated by Dwight.¹¹ Dwight gives

$$B_2 = 1/30, \quad B_3 = 1/42, \quad B_4 = 1/30$$

so that

$$D(6)/D(4) = 20\pi^2/7 \quad \text{and} \quad D(8)/D(4) = 16\pi^4. \quad (22)$$

Insertion of (22) into (20) yields

$$\theta/\beta = 9^{1/3} [3k_0 + 100k_2\pi^2 T^2 / 7\beta^2 + 112k_4\pi^4 T^4 / \beta^4 + \dots]^{-1/3}. \quad (23)$$

¹¹ H. B. Dwight, *Tables of Integrals and Other Mathematical Data* (The Macmillan Company, New York, 1934).

Table VI contains values of θ/β calculated from Eqs. (23) and (8).

The data of Tables V and VI are shown in Fig. 2. For the basic case (central forces between nearest neighbors only) the characteristic temperature drops abruptly from its value at absolute zero to a value approximately fifteen percent below the initial value, where it remains sensibly constant over a large temperature range. In the case of weak coupling between next nearest neighbors of the type that is apparently characteristic of the noble metals, the characteristic temperature falls abruptly as for the basic case but instead of remaining nearly constant it passes through a definite minimum, and at the higher temperatures seems to be approaching the curve of the basic case. The difference between the maximum and minimum values of the characteristic temperature is in this case only about ten percent.

These results will now be compared numerically with the observed specific heat of silver. By use of the numerical value of α at absolute zero, as given by (11), β may be evaluated:

$$\beta^2 = h^2 \alpha_0 / 2\pi^2 m k^2 = 1.39 \times 10^4$$

or

$$\beta = 118 \text{ deg.}$$

The experimental values for the Debye characteristic temperature of silver were taken from the work of Keesom and Clark¹ and Eucken, Clusius, and Woitinek.¹²

Figure 3 shows the theoretical curve for $\gamma/\alpha = -0.08$ (obtained by linear interpolation between the two curves of Fig. 2) and the experimental values as given by the above authors. The values given by Keesom and Clark

¹² A. Eucken, K. Clusius, and H. Woitinek, *Zeits. f. anorg. Chem.* **203**, 47 (1931).

are smoothed values, whereas the others are not. There is fair agreement between the two curves with regard to the rise of the characteristic temperature with decreasing absolute temperature below $T/\beta = 0.2$, and the existence of a minimum characteristic temperature at about this value of T/β . It is also evident that there is a great difference in behavior between the two in the very low temperature range. Here, the theoretical curve attains a relatively smooth maximum at absolute zero, while the experimental curve shows a very sharp maximum at about 5°K, with a second minimum at about 3.5°K. This behavior is also shown by the characteristic temperature of potassium chloride. This matter has been discussed for both silver and potassium chloride by Keesom and Clark.¹

Blackman⁴ deduced that the frequency spectrum of the sodium-chloride lattice increased more rapidly than a Debye spectrum in the low frequency region, and hence concluded that the characteristic temperature of this lattice should decrease from a maximum at absolute zero. This conclusion can also be drawn for the face-centered lattice, both from the actual curves of Fig. 2 and from the positive values of the coefficients in the series expansions (8). For this reason, it seems quite clear that the very low temperature behavior of the characteristic temperature θ cannot be explained in terms of the differences between the frequency spectrum of a Debye continuum and that of an atomic lattice.

On the other hand, it seems reasonable to suppose that the agreement between the experimental and theoretical curves in the range from 7°K to 50°K is not purely fortuitous, especially as the theoretical results were obtained by direct calculation, without attempting to fit the experimental data as is often done in the Debye theory.