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Vibration Spectra and Specific Heats of Cubic Metals. I. Theory and Application to Sodium

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A model for monovalent metals is proposed, on the basis of which the secular equations determining the frequencies of the normal modes of vibration are derived for body-centered and face-centered cubic metals. In contrast to the two force constants occurring in the usual treatments based on the Born-von Kármán model, each of these equations—one for each type of lattice—contains three force constants which may be identified with the three independent elastic constants of a cubic metal. The limitations of the model are discussed.

The frequency spectrum of sodium, and hence its specific heat C_v at constant volume, are calculated. It is found that the agreement between the observed and calculated values of C_v is more satisfactory in the entire relevant temperature range, and especially at low temperatures, than that obtained by Bauer using the customary two force-constant model.

I. INTRODUCTION

ALTHOUGH a proper theory for calculating the frequencies ω of the normal modes of vibration of an ionic or homovalent crystal exists and has been applied by several authors,[1] the corresponding situation with regard to metals is not so satisfactory. This is because, whereas in the former types of crystals the forces on the ions (atoms) can be described in terms of an interaction potential function between the ions (atoms), in the latter the interaction between the ions and the valence electrons is of decisive importance. Hence, in general, the forces on ions in a metal are not describable in terms of an interaction potential function between the ions alone, and this makes any rigorous treatment of the problem difficult. It is customary, therefore, to calculate the frequencies of normal modes of vibration for metals on the basis of the Born-von Kármán[2] model. One considers the interactions to be significant only between the nearest and the next nearest neighbors and assumes Hooke's law of forces. The classical equations of motion for the ions are then set up and solved with the aid of Born's cyclic boundary conditions. These equations of motion naturally contain two Hooke's constants, usually denoted in literature by α and γ, which respectively correspond to nearest neighbor and next nearest neighbor interactions. The force constants α and γ are determined from the elastic constants by comparing expressions (in terms of α and γ) for the velocities of long elastic waves with the corresponding expressions of the elasticity theory. Now for cubic crystals there are three elastic constants c_{11}, c_{12}, and c_{44} from which α and γ have to be determined. This is possible only if there is a relation between the three elastic constants. One relation between them exists either if the crystal is elastically isotropic $\epsilon=c_{11}-c_{12}-2c_{44}=0$, or if the *entire* interactions are central when $c_{12}=c_{44}$ (Cauchy's relation). For the alkali and nobel metals with which we shall be primarily concerned in the present work, the isotropy condition is far from satisfied; the quantity $2c_{44}(c_{11}-c_{12})^{-1}$, which is unity for an elastically isotropic crystal, is of the order 8 and 3 for the alkali and noble metals respectively.

The Cauchy relation ($c_{12}=c_{44}$) also does not hold for metals. This is because certain energies—like the energy E_0 of the ground state of the valence electron and the Fermi, exchange, and correlation energies E_1 of the conduction electrons—depend on the atomic volume alone,[3] so that the forces on the displaced ions arising from these energies cannot be regarded as due to a central interaction potential between the ions. In addition to the forces arising from E_0 and E_1, there are contributions also from the exchange repulsion, van der Waals forces, ion-ion (screened) Coulomb interaction, etc.[4]; to a first approximation, all these latter may be described by a central interaction between the ions. We denote the corresponding potential function by $W(r)$, where r is the distance between the ions. If we distinguish the contributions to elastic constants from $W(r)$ and Es' by superscripts W and E respectively, we may show, following Fuchs,[3] that the contributions to combinations of elastic constants corresponding to shearing strains (no change in volume) come only from W (and not from E_0 and E_1). Thus

$$c_{11}{}^W-c_{12}{}^W=c_{11}-c_{12},\quad c_{44}{}^W=c_{44},$$

and

$$c_{44}{}^E=c_{11}{}^E-c_{12}{}^E=0. \tag{1}$$

The Born-von Kármán model has been applied to metals by Fine,[5] Leighton,[6] and Bauer.[7] Fine calculated

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[1] For an excellent account see M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, England, 1954).

[2] M. Born and T. von Kármán, Physik. Z. **13**, 297 (1912); **14**, 15 (1913).

[3] K. Fuchs, Proc. Roy. Soc. (London) **A153**, 622 (1935); **A157**, 444 (1936).

[4] See, for example, N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, England, 1936), p. 148.

[5] P. C. Fine, Phys. Rev. **56**, 355 (1939).

[6] R. B. Leighton, Revs. Modern Phys. **20**, 165 (1948).

[7] E. Bauer, Phys. Rev. **92**, 58 (1953).

the frequency spectrum for tungsten which is elastically isotropic so that, in this case, there are only two independent elastic constants. On the other hand, Leighton and Bauer, whose calculations refer to silver and sodium respectively, essentially assume that c_{11}^E and c_{12}^E do not contribute to the motion of the ions and that $c_{44}^W = c_{12}^W$, thus having only two independent elastic constants c_{11}^W and $c_{12}^W = c_{44}^W$ in their models. It should be noted that even though c_{12}^W and c_{44}^W arise wholly from a central interaction, these two constants need not necessarily be equal since the Cauchy relation $c_{12} = c_{44}$ holds only if the entire interactions under which the cubic crystal is in equilibrium are central. We should mention that both these authors were aware of the limitations of their models.

From the foregoing it is clear that for cubic metals, which are neither isotropic nor satisfy the Cauchy relation, one should set up equations of motion for the ions which contain three force constants and which, for the limiting case of infinitely long waves, reduce to the corresponding equations of the elasticity theory. In this paper we consider a *model* for a metal which enables one to set up such equations.[8] It is assumed[8a] that the forces on an ion may be regarded as arising from (a) a central interaction $W(r)$ between the ions which is significant between the nearest neighbors only and (b) from certain energies E which depend on the *atomic volume* only and which are due to the presence of the free electrons and their interactions with the ions. In order to calculate the effect of (b) on ionic vibrations it is assumed, following the Sommerfeld model, that in the absence of thermal motion the ionic charge it uniformly smeared out over the entire metal. The electrostatic potential φ of the system is then a constant ($=\varphi_0$, say). The change in φ due to a given displacement of the ions is calculated by the Thomas-Fermi-Dirac method. The force on an ion is then just $-e\,\mathrm{grad}\varphi$. Next the classical equations of motion are set up and solved for the body-centered and face-centered cubic lattices. Each of the resulting secular equations in ω^2—one for each type of lattice—contains three force constants which are identified with the three elastic constants of a cubic crystal. In each case, the secular equation for the limiting case of infinitely long waves then reduces to the well-known Christoffel equations of the elasticity theory.

Clearly, the assumptions and the consequent limitations underlying the procedure adopted here need some discussion. For convenience, this is deferred until the secular equations have been derived.

In Sec. III, the frequency spectrum of sodium, and hence its specific heat C_v at constant volume as a function of temperature, are calculated. It is found that the agreement between the calculated and observed values of C_v is more satisfactory than that obtained by Bauer[7] using the customary two force-constant model.

Similar calculations for silver which has face-centered cubic structure will be given in Part II of this work.

II. THE SECULAR EQUATION

CALCULATION OF φ FOR A GIVEN DISPLACEMENT OF THE IONS

As mentioned in the introduction, it will be assumed for the purposes of this calculation that the ionic charge is smeared out over the metal. Then in the absence of thermal motion, the ionic and the electronic charge densities are equal and constant at every point of the metal and the electrostatic potential φ of the system is also a constant, equal to φ_0, say. When an elastic wave passes through a metal, the ionic charge density and hence the electronic charge density will vary from point to point. This will result in a change in φ which will depend now on space and time coordinates. Let $\varphi = \varphi_0 + \varphi_1(\mathbf{r})$. For small amplitudes of the elastic wave, we may take $\varphi_1(\mathbf{r}) \ll \varphi_0$. One then also has the result that the changes in φ are small over regions of linear dimensions of the order of the de Broglie wavelength of the Fermi electrons. This condition is necessary for the validity of the Thomas-Fermi method. Hence we may calculate φ_1 for a given ionic displacement either by the Thomas-Fermi method (without exchange) or by the Thomas-Fermi-Dirac method (with exchange). For convenience, the calculations will be first made by the former method.

Let E_m denote the energy of the highest level occupied by a conduction electron. We may take E_m to be unchanged when the metal is disturbed by the passage of an elastic wave since it will not change the *over-all* volume of the metal. Then in the Thomas-Fermi method the electronic number density $n(\mathbf{r})$ and the potential $\varphi(\mathbf{r})$ are related by the equation[9] (choosing the zero for $\varphi(\mathbf{r})$ such that $E_m = 0$):

$$n(\mathbf{r}) = (8\pi/3h^3)(2me)^{\frac{3}{2}}[\varphi(\mathbf{r})]^{\frac{3}{2}}, \tag{2}$$

where $-e$ and m are the electronic charge and mass respectively, and other symbols have their usual meaning. The average density n_0 of the electrons is obtained from (2) by putting $\varphi = \varphi_0$ in it. Then remembering that $\varphi_1 \ll \varphi_0$, we have

$$\Delta n(\mathbf{r}) = n(\mathbf{r}) - n_0 = \eta' \varphi_1(\mathbf{r}), \tag{3}$$

where

$$\eta' = (4\pi me/h^2)(3/\pi)^{\frac{1}{3}} \times n_0^{\frac{1}{3}}. \tag{4}$$

Now let $\mathbf{u}(\mathbf{r})$ denote the magnitude and direction of the displacement of the ion at $\mathbf{r}$ from its normal position;

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[8] In the present work the discussion will be confined to the alkali and the noble metals which have body- and face-centered cubic structures respectively. To a good approximation, one may regard all the valence electrons to be free in both these groups of metals.

[8a] If one assumes a noncentral interaction and considers nearest and next nearest neighbour interactions only, one has five force constants in the scheme of Born and von Kármán. These can be determined in terms of the elastic constants only if there are two relations between the five force constants; thus it seems necessary to introduce explicit assumptions about the nature of interactions in a metal (see reference 5).

[9] See, for example, reference 4, pp. 48–49.

the change $\Delta N(\mathbf{r})$ in the ionic number density (average number$=N_0\equiv n_0$) is given by

$$\Delta N=N-N_0=-N_0 \operatorname{div} \mathbf{u}(\mathbf{r}). \tag{5}$$

Using (3) and (5) and applying Poisson's equation, we have

$$\nabla^2(\varphi_0+\varphi_1)=\nabla^2\varphi_1=-4\pi\rho=4\pi e[\eta'\varphi_1-\Delta N(\mathbf{r})]. \tag{6}$$

Since $\varphi_1(\mathbf{r})\equiv 0$ when $\Delta N(\mathbf{r})=0$, only the particular integral of (6) is of interest. Hence, formally,

$$\varphi_1(\mathbf{r})=-4\pi e\Delta N(\mathbf{r})/(\nabla^2-4\pi e\eta'). \tag{7}$$

The force on an ion at $\mathbf{r}$ (charge$+e$) due to $\varphi(=\varphi_0+\varphi_1)$ is given by

$$\mathbf{F}(\mathbf{r})=-e\operatorname{grad}\varphi=-e\operatorname{grad}\varphi_1(\mathbf{r}). \tag{8}$$

Let $\mathbf{u}(\mathbf{r})$ be of the form

$$\mathbf{u}(\mathbf{r})=\mathbf{e}Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}, \tag{9}$$

where A is the amplitude, $\mathbf{e}$ the unit vector in the direction of the displacements, $\mathbf{k}$ the wave-vector $(|k|=2\pi/\lambda)$, and ω is the angular frequency. Then $\mathbf{F}(\mathbf{r})$ is given by

$$\mathbf{F}(\mathbf{r})=-\mathbf{k}\frac{4\pi e^2N_0(\mathbf{e}\cdot\mathbf{k})}{4\pi e\eta'+k^2}A\exp[i(\mathbf{k}\cdot\mathbf{r}-\omega t)]. \tag{10}$$

The effect of exchange interaction between the electrons is easily included in the above calculation by Dirac's[10] modification of the Thomas-Fermi method, since one has only to replace (2) by the equation[11]

$$n(\mathbf{r})=(8\pi/3h^3)(2me)^{\frac{3}{2}}[(\varphi+\tau_0{}^2)^{\frac{1}{2}}+\tau_0]^3 \tag{2a}$$

with $\tau_0=(2me^3/h^2)^{\frac{1}{2}}$. The average electronic number density n_0 is now obtained by putting $\varphi=\varphi_0$ in (2a). Writing again $\varphi=\varphi_0+\varphi_1$ and remembering that $\varphi_1\ll\varphi_0$, it may be seen that, to include the exchange effects, one has to replace in (3) and all subsequent equations the constant η' by η, where

$$\begin{aligned}(\eta)^{-1}&=(\eta')^{-1}-\tfrac{1}{3}(3/\pi)^{\frac{1}{3}}en_0{}^{-\frac{2}{3}}\\&=(\eta')^{-1}-0.33en_0{}^{-\frac{2}{3}}.\end{aligned} \tag{11}$$

Derivation of the Secular Equation

Next we have to calculate the force on an ion due to the interaction potential $W(r)$ assumed to be effective only between the nearest neighbor ions in a lattice. Let the ion under consideration be situated on the lattice point at the origin of a Cartesian coordinate system and let the coordinates of the neighboring lattice points be $\mathbf{r}_{lmn}{}^{(0)}(la, ma, na)$. Here a is the distance between the nearest neighbors and (l, m, n) the direction cosines of the line joining the origin and a nearest neighbor. By making a suitable choice for the coordinate system, we may take (l, n, m) to be $|\sqrt{3}|^{-1}\times(\pm1, \pm1, \pm1)$ for body-centered cubic (b.c.c.) lattice which has eight nearest neighbors; similarly, for a face-centered cubic (f.c.c.) lattice which has twelve nearest neighbors, (l, m, n) may be taken as $|\sqrt{2}|^{-1}(\pm1, \pm1, 0)$, $|\sqrt{2}|^{-1}(\pm1, 0, \pm1)$ and $|\sqrt{2}|^{-1}(0, \pm1, \pm1)$. Denoting the displacements of the central and nearest neighbor ions from their normal positions by $\mathbf{u}_0$ and $\mathbf{u}_{lmn}$ respectively and denoting by V the contribution to the potential energy (due to W) of the crystal from the terms which involve the coordinates of the ion at the origin, we have

$$V=\sum_{l,m,n}W(|\mathbf{r}_{lmn}{}^{(0)}+\mathbf{u}_{lmn}-\mathbf{u}_0|).$$

Expanding the right-hand side by Taylor's theorem, we obtain

$$\begin{aligned}V=\sum_{l,m,n}\Bigg[\left\{\frac{1}{r}\frac{dW}{dr}\right\}_{r=a}&[\mathbf{r}_{lmn}{}^{(0)}\cdot(\mathbf{u}_{lmn}-\mathbf{u}_0)\\&+\tfrac{1}{2}|\mathbf{u}_{lmn}-\mathbf{u}_0|^2]+\frac{1}{2}\left\{\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{dW}{dr}\right)\right\}_{r=a}\\&\times[\mathbf{r}_{lmn}{}^{(0)}\cdot(\mathbf{u}_{lmn}-\mathbf{u}_0)]^2\Bigg]+O(u^3),\end{aligned} \tag{12}$$

where the summation is over all the nearest neighbors of the central ion. It should be noticed that $(dW/dr)_{r=a}$ is not zero in our case since $W(r)$ is not the entire potential which determines the equilibrium distance a. The force on a particle at the origin due to (12) is just $-\operatorname{grad}_{\mathbf{u}_0}V$.

Combining this last result with (10) we may write the equation of motion for the ion at the origin in the form

$$M(\partial^2/\partial t^2)\mathbf{u}_0=-\operatorname{grad}_{\mathbf{u}_0}V+\mathbf{F}(0), \tag{13}$$

where M is the mass of an ion. Similarly, one may write down the equations of motion for other ions in the lattice.

Now let us assume that the solution of (13) is of the form (9) and let the direction cosines of the vectors $\mathbf{e}$ and $\mathbf{k}$ be denoted by (λ, μ, ν) and (L, M, N) respectively. Then substituting[12] (9) into (13) and making use of (10) and (11), we get

$$\begin{aligned}\lambda\rho\omega^2=\sum_{l,m,n}&[4a^{-2}\{\sin^2\tfrac{1}{2}ka(Ll+Mm+Nn)\}\\&\times\{\delta l(l\lambda+m\mu+n\nu)+\beta\lambda\}]\\&+\frac{\kappa L(\lambda L+\mu M+\nu N)k^2}{1+k^2/(4\pi e\eta)},\end{aligned} \tag{14a}$$

and two similar equations obtained from (14a) by

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[10] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).

[11] See P. Gombas, *Die Statistische Theorie des Atoms und ihre Anwendung* (Springer, Berlin, 1949), p. 78, Eq. (9.5).

[12] As may be seen from symmetry considerations, one would obtain the same equations, namely (14), if one substituted (9) into the equation of motion for an ion whose equilibrium position is at a lattice point not located at the origin of our coordinate system.

TABLE I. Expressions for ρv^2 for long elastic waves propagating along (100), (110), and (111) directions in b.c.c. and f.c.c. crystals.

		ρv^2 from (14)		ρv^2 in terms of the elastic constants
(LMN)	(λ,μ,ν)	body-centered cubic	face-centered cubic	
(100)	$100(L)$[a]	$(8/3)\beta+(8/9)\delta+\kappa$	$4\beta+2\delta+\kappa$	c_{11}
	$010(T)$[b]	$(8/3)\beta+(8/9)\delta$	$4\beta+\delta$	c_{44}
	$001(T)$	$(8/3)\beta+(8/9)\delta$	$4\beta+\delta$	c_{44}
(110)	$110(L)$	$(8/3)\beta+(16/9)\delta+\kappa$	$4\beta+(5/2)\delta+\kappa$	$c_{11}-\frac{1}{2}\epsilon$
	$001(T)$	$(8/3)\beta+(8/9)\delta$	$4\beta+\delta$	c_{44}
	$1\text{-}10(T)$	$(8/3)\beta$	$4\beta+\frac{1}{2}\delta$	$c_{44}+\frac{1}{2}\epsilon$
(111)	$111(L)$	$(8/3)\beta+(56/27)\delta+\kappa$	$4\beta+(8/3)\delta+\kappa$	$c_{11}-\frac{2}{3}\epsilon$
	$1\text{-}10(T)$	$(8/3)\beta+(8/27)\delta$	$4\beta+\frac{2}{3}\delta$	$c_{44}+\frac{1}{3}\epsilon$
	$11\text{-}2(T)$	$(8/3)\beta+(8/27)\delta$	$4\beta+\frac{2}{3}\delta$	$c_{44}+\frac{1}{3}\epsilon$

[a] L: Longitudinal wave.
[b] T: Transverse wave.

interchanging (l, m, n), (λ, μ, ν), and (L, M, N) as follows:

$$l \rightleftarrows m, \quad \lambda \rightleftarrows \mu, \quad \text{and} \quad L \rightleftarrows M, \tag{14b}$$

and

$$l \rightleftarrows n, \quad \lambda \rightleftarrows \nu, \quad \text{and} \quad L \rightleftarrows N. \tag{14c}$$

Here $\rho(=n_0M)$ is the density of the metal and β, δ and κ are given by

$$\beta=\frac{\rho a^2}{2M}\left(\frac{1}{r}\frac{dW}{dr}\right)_{r=a}, \quad \delta=\frac{\rho a^3}{2M}\left[\frac{d}{dr}\left(\frac{1}{r}\frac{dW}{dr}\right)\right]_{r=a}$$

and

$$\kappa=en_0^2(\eta)^{-1}=en_0^2\left[\frac{h^2}{4\pi me}\left(\frac{\pi}{3}\right)^{\frac{1}{3}}\times n_0^{-\frac{1}{3}}-0.33en_0^{-\frac{2}{3}}\right]. \tag{15}$$

In deriving (14), use has also been made of the fact that in a cubic crystal corresponding to a nearest neighbor ion at (la, ma, na), there is a nearest neighbor ion at $(-la, -ma, -na)$. The summation in (14), however, is over all the nearest neighbors.

In order that a nontrivial solution ($\mathbf{e}\neq 0$) of (14) exist, the determinant formed from the coefficients of λ, μ, ν must vanish. This gives the secular equation in ω^2 in the form of a 3×3 determinantal equation which will not be written here explicitly. The secular equation is cubic in ω^2 and, therefore, has three solutions (three values of ω^2) for each $\mathbf{k}$. The direction cosines (λ, μ, ν) of the polarization vector $\mathbf{e}$ of the acoustic wave of wave-vector $\mathbf{k}$ and frequency $\omega(\mathbf{k})$ may be determined by substituting these particular values of $\mathbf{k}$ and $\omega^2(\mathbf{k})$ in (14) and then solving the latter for λ, μ, ν.

Identification of the Force Constants β, δ, and κ with the Elastic Constants

For this purpose, we shall solve Eqs. (14) for the velocities $v(=\omega/k)$ of the acoustic waves of infinitely long wavelengths ($k\rightarrow 0$). The solution of (14) is particularly simple for waves propagating along any of the three principal directions in a cubic crystal, *viz.*, (100), (110), and (111), since for these three directions of propagation the waves are either wholly longitudinal ($\mathbf{e}\|\mathbf{k}$) or wholly transverse ($\mathbf{e}\perp\mathbf{k}$). In Table I we give expressions for ρv^2 as obtained from (14) for these directions of propagation for both b.c.c. and f.c.c. crystals; corresponding expressions in terms of the elastic constants are given in the last column of Table I ($\epsilon=c_{11}-c_{12}-2c_{44}$).

For each type of lattice structure, we have from Table I nine relations between the three force constants β, δ, and κ and the three elastic constants. However, they are not all independent of each other and, as may be readily verified, they are identically satisfied if we put

$$\left.\begin{aligned}\beta&=\tfrac{3}{8}(c_{44}+\tfrac{1}{2}\epsilon)\\ \delta&=-(9/16)\epsilon\\ \kappa&=c_{11}-c_{44}\end{aligned}\right\}\text{for b.c.c.,} \tag{16a}$$

and

$$\left.\begin{aligned}\beta&=\tfrac{1}{4}(c_{44}+\epsilon)\\ \delta&=-\epsilon\\ \kappa&=c_{11}-c_{44}+\epsilon\end{aligned}\right\}\text{for f.c.c.} \tag{16b}$$

Moreover, by substituting (16a) or (16b) in (14) and remembering that the body-centered and face-centered cubic lattices have eight and twelve nearest neighbors respectively, one may verify that for the limiting case of infinitely long waves ($k\rightarrow 0$), Eqs. (14) reduce to the Christoffel equations of the elasticity theory.[13]

From (16), we also have

$$\left.\begin{aligned}c_{11}-c_{12}&=(16/3)\beta\\ c_{44}&=(8/3)\beta+(8/9)\delta\end{aligned}\right\}\text{for b.c.c.,} \tag{17a}$$

and

$$\left.\begin{aligned}c_{11}-c_{12}&=8\beta+\delta\\ c_{44}&=4\beta+\delta\end{aligned}\right\}\text{for f.c.c.} \tag{17b}$$

Thus c_{44} and $c_{11}-c_{12}$ are independent of κ, and are completely determined by the interaction potential[14] $W(r)$, a result which is in agreement with (1).

By substituting (16a) or (16b) in (14) and inserting the observed elastic constants for any particular metal, one may solve the latter for ω^2 for any $\mathbf{k}$. Further, if one defines a frequency distribution function $G(\omega)$ such that $G(\omega)d\omega$ denotes the number of frequencies lying between ω and $\omega+d\omega$, one may calculate $G(\omega)$ by solving (14) for sufficiently large number of points in k-space. The distribution function $G(\omega)$ for sodium, and hence its specific heat, will be calculated in Sec. III. We shall, however, first discuss some of the distinctive features of Eqs. (14) and the limitations inherent in the model on whose basis they have been derived.

Discussion

First, it will be noticed from (16) that in the present treatment one linear combination of the elastic constants—$\kappa=c_{11}-c_{44}$ and $\kappa=c_{11}-c_{44}+\epsilon$ for body- and face-centered cubic lattices respectively—depends es-

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[13] A. E. H. Love, *Mathematical Theory of Elasticity* (Dover Publications, New York, 1944), fourth edition, p. 299.

[14] It may be verified that expressions (17) for $c_{11}-c_{12}$ and c_{44} are the same as those obtained by considering changes in the potential energy $\Sigma W(\mathbf{r})$ of a crystal due to appropriate *static* homogeneous strains; this provides a check on our calculations.

sentially only on the number of free electrons per atom in the metal. Taking this number to be 1 per atom, the calculated values of κ for Na (b.c.c.) and Ag (f.c.c.) are 0.3×10^{11} and 1.7×10^{11} dynes/cm^2 respectively as compared with the corresponding experimental values 0.39×10^{11} and 2×10^{11} dynes/cm^2. The agreement between the two values for other monovalent metals is not so satisfactory, the worst examples being Li and Cu for which κ_{cal} is 0.99×10^{11} and 3.5×10^{11} dynes/cm^2 as compared with the experimental values 0.23×10^{11} and 0.2×10^{11} dynes/cm^2 respectively. Of course, in view of the crudeness of the model adopted here, and, in particular, since the use of the Sommerfeld model for a metal implies that the effect of the energy E_0 (E_0 depends on the atomic volume only) of the ground state of the valence electron on the ionic motion, and hence on the bulk modulus $\frac{1}{3}(c_{11}+2c_{12})$ of the crystal, is negligible, one can hardly expect more than a qualitative agreement between the experimental and calculated values of κ. Indeed, if in the expression (15) for κ, the second term, which arises from the exchange interaction between the electrons, is neglected, κ becomes

$$\kappa=(h^2/4\pi m)(\pi/3)^{\frac{1}{3}}\times n_0{}^{5/3}; \tag{18}$$

the right-hand side of (18) may be immediately recognized as the bulk modulus K of the electron gas if one remembers that $K=-V(\partial p/\partial V)$ and that the pressure p of an electron gas enclosed in a volume V is given by the expression[15] ($n=n_0V$)

$$p=(3h^2/20\pi m)(\pi/3)^{\frac{1}{3}}(n/V)^{5/3}. \tag{19}$$

Secondly, since the metal is treated here partly as a continuous system, the secular equation (14), and hence the frequencies ω obtained from it, will generally not be periodic functions of $\mathbf{k}$. We have, therefore, to restrict $\mathbf{k}$ values in some suitable way so that the total number of normal modes of vibration exactly equal the number of degrees of freedom, *viz.*, three per atom. Now, had the periodicity of the ionic lattice not been ignored, (14) and ω would have been distinct only for $\mathbf{k}$ values lying inside the first Brillouin zone in k-space, and the solutions corresponding to a $\mathbf{k}$ lying outside this zone would have given no new normal modes of vibration. Since the first Brillouin zone has just one $\mathbf{k}$-point per atom, one obtains the correct total number of normal modes of vibration by restricting the k values to the first Brillouin zone.[16] Therefore, it would seem reasonable to restrict the k values to the first Brillouin zone while calculating the frequency spectrum from (14) also. It may be mentioned that since the forces arising from the energies E do not contribute to the motion of the *wholly* transverse waves, the frequencies corresponding to these waves will be periodic functions of $\mathbf{k}$ [see Eqs. (28)].

Lastly, the application of the Thomas-Fermi method to calculate changes in φ due to *time-dependent* ionic displacements contains the implicit assumption that the electrons follow the motion of the ions "adiabatically" in the sense of the Thomas-Fermi method—namely, that the electrons occupy the lowest energy state of the instantaneous lattice potential. This seems to be reasonable for low frequencies. For higher frequencies, the validity of this assumption may be doubted. However, it does not appear easy to make a decision on this point from a comparison of the theoretical and observed specific heats since, first, the high frequency end of the spectrum affects the specific heats at comparatively high temperatures only and that not very sensitively, and secondly, the accuracy of the theoretical values is limited by the approximations involved in the calculation of frequency spectrum and by the accuracy of the available observed elastic constants which have to be inserted in the secular equation (14).

Although the foregoing discussion makes it clear that a more refined treatment than given here of the problem of determining the frequencies of the normal modes of vibration of a metal would be desirable, the present approach is likely to be an improvement over the customary two force-constant model. This is because, unlike the latter, it is able to incorporate all the three independent elastic constants of a cubic metal in the secular equation. The uncertainties mainly arise at the high frequency end of the spectrum, and these do not affect the results on specific heats very sensitively. Thus one may expect that, provided one uses the actually observed elastic constants in the secular equation (14), the calculations of frequency spectrum, and hence of specific heats, based on (14) would be an improvement over those based on a two force-constant model. This, of course, would be all the more so for the low-frequency end of the spectrum and hence for the specific heats at low temperatures.

II. FREQUENCY SPECTRUM AND SPECIFIC HEAT OF SODIUM

In this section, the frequency spectrum of sodium, and hence its specific heat C_v at constant volume, will be calculated from the solutions of the secular equation (14).

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[15] See, for example, reference 11, p. 6.

It should be mentioned here that recently Jules de Lunay [J. Chem. Phys. **29**, 1975 (1953)] has made an attempt to make a three force-constant model for a metal. Lunay superimposes the free electron gas on the Born-Kármán model, but appears to assume that the ionic lattice is in equilibrium under the central forces alone. He thus obtains the result that the deviation $c_{12}-c_{44}$ from Cauchy's relation is just equal to the bulk modulus of the free electron gas. No calculations of frequency spectrum have been made on this model. The author is indebted to Dr. E. Bauer for drawing his attention to this paper.

[16] For a periodic lattice, these results are obtained by the use of Born's cyclic boundary conditions. It should be mentioned that in general there exist several equivalent portions of reciprocal space to which $\mathbf{k}$ vectors may be confined. Of these, the Brillouin zones have the maximum possible geometrical symmetry consistent with that of the lattice. We choose one of these zones (namely, the *first* for obvious reasons) because the approximate method of Houston, by which the frequency spectrum is calculated in Sec. III, is the more reliable the more symmetrical is the k-space to which $\mathbf{k}$ vectors are confined.

Houston's Method of Calculating Frequency Spectrum

For cubic crystals, Houston's[17] method of calculating the frequency spectrum is, by far, the most convenient one. There exist for a cubic crystal certain directions (θ_n,ϕ_n) in k-space along which the secular equation in ω^2 can be solved analytically. Corresponding to each $\mathbf{k}$ there are, of course, three frequencies corresponding to the three branches. In the following, these will be distinguished by the subscript i $(i=1, 2, 3)$. The number $g(\omega)d\omega d\Omega$ of normal modes (frequencies) which lie between ω and $\omega+d\omega$ and whose wave vectors $\mathbf{k}$ lie in a solid angle $d\Omega$ around $\mathbf{k}(\theta,\phi)$ may be written as

$$g(\omega,\theta,\phi)d\omega d\Omega=\sum\nolimits_i g_i(\omega,\theta,\phi)d\omega d\Omega$$
$$=\frac{V}{(2\pi)^3}\sum\nolimits_i k^2\frac{dk}{d\omega_i(\theta,\varphi)}d\omega d\Omega, \tag{20}$$

where V is the volume of the crystal under consideration. One now expands $g_i(\omega,\theta,\phi)$ in terms of those Kubic Harmonics[18] $K_m(\theta,\phi)$ which are invariant under the operations of the cubic symmetry group; thus

$$g_i(\omega,\theta,\phi)=\sum\nolimits_m a_{i,m}K_m(\theta,\phi), \quad (K_0=1). \tag{21}$$

The coefficients $a_{i,m}$ in (21) may be determined from the solutions of the secular equation along the various directions (θ_n,ϕ_n) in k-space. The total number of frequencies $G(\omega)d\omega$ lying between ω and $\omega+d\omega$ is then obtained from (21) by integrating it over all solid angles and summing over the three branches. Remembering that the various K_m are orthogonal to each other, we have

$$G(\omega)d\omega\equiv\sum\nolimits_i G_i(\omega)d\omega=\sum\nolimits_i d\omega\int g_i(\omega,\theta,\phi)d\Omega$$
$$=4\pi d\omega\sum\nolimits_i a_{i,0}. \tag{22}$$

This method naturally gives the better approximation to $G(\omega)$ the more numerous are the directions (θ_n,ϕ_n) along which the secular equation is solved. In practice, one solves the secular equation along the three principal directions of a cubic crystal, *viz.*, (100), (110), and (111) [the corresponding direction cosines being (100), $2^{-\frac{1}{2}}(110)$, and $3^{-\frac{1}{2}}(111)$]; the quantities referring to these three directions will be distinguished by subscripts A, B, and C respectively. Then one has to retain only the first three terms in the expansion (21). Apart from normalization factors, the first three appropriate Kubic Harmonics, expressed in Cartesian coordinates, are $(x^2+y^2+z^2=1)$

$$K_0=1, \quad K_1=(x^4+y^4+z^4-\tfrac{3}{5}),$$
$$K_2=x^2y^2z^2+(1/22)K_1-(1/105). \tag{23}$$

Making use of (20) to (23), one obtains for $G(\omega)$ the expression[19]

$$G(\omega)=\frac{V}{(2\pi)^3}\frac{4\pi}{35}\sum_i\left[10k^2\left(\frac{dk}{d\omega}\right)_{i,A}\right.$$
$$\left.+16k^2\left(\frac{dk}{d\omega}\right)_{i,B}+9k^2\left(\frac{dk}{d\omega}\right)_{i,C}\right]. \tag{24}$$

In general, the right-hand side of (24) has to be multiplied by a normalization factor so that one obtains the correct number of normal modes, *viz.*,

$$\int G_i(\omega)d\omega=N_0V \quad (i=1,\ 2 \text{ and } 3), \tag{25}$$

where N_0 is the number of atoms per unit volume. If we denote the maximum value of k along the three directions A, B, and C by $k_A(m)$, $k_B(m)$ and $k_C(m)$ respectively, the normalization factor F is determined by the equation

$$\frac{F}{(2\pi)^3}V\cdot\frac{4\pi}{35}\tfrac{1}{3}[10k_A^3(m)+16k_B^3(m)+9k_C^3(m)]$$
$$=N_0V. \tag{26}$$

As already mentioned in Sec. II, the $\mathbf{k}$ vectors are to be restricted to the first Brillouin zone. For a body-centered cubic lattice—this is the case we are interested in here since sodium has body-centered cubic structure—the first Brillouin zone is a dodecahedron bounded by (110) planes. The distances of these planes from the origin of k-space are given in reference 4, p. 156, and we may determine $k_A(m)$, $k_B(m)$, and $k_C(m)$ by finding the points of intersection of the corresponding $\mathbf{k}$ vectors with (110) plane. One finds[20]

$$k_A(m)=\sqrt{3}(\pi/a), \quad k_B(m)=(\sqrt{\tfrac{3}{2}})(\pi/a),$$
$$k_C(m)=\tfrac{3}{2}(\pi/a). \tag{27}$$

From (26) and (27), one obtains for the normalization factor F:

$$F=0.778.$$

Before we use (24) to calculate the frequency spectrum of sodium, we should mention that the frequency spectrum obtained by Houston's method outlined above contains, in general, a certain number of singularities; the area under them, however, is finite. These singularities are peculiar to Houston's method and arise from the fact that the frequency spectrum is approximated from the solutions of the secular equation along three directions only. Van Hove[21] has investigated

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[17] W. V. Houston, Revs. Modern Phys. **20**, 161 (1948). An account of various methods of calculating the frequency spectrum may be found in reference 1, pp. 70–84.

[18] Kubic Harmonics were introduced by F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).

[19] This is essentially Houston's expression (11) after allowing for a misprint in his equation preceding (11), where the coefficient of $f_1(q)$ should read $-2/(4\pi)^{\frac{1}{2}}$ instead of $-10/(36\pi)^{\frac{1}{2}}$.

[20] Note that in reference 4, a is the lattice constant while here a is distance between the nearest neighbors; moreover, k as defined here is 2π times the k used in Chapter V of reference 4.

[21] L. Van Hove, Phys. Rev. **89**, 1189 (1953).

the nature of the singularities of $G(\omega)$ in one, two, and three dimension. He finds that in three dimensions $G(\omega)$ can only have finite discontinuities. Nakamura,[22] on the basis of an analysis of two dimensions, concludes that Houston's method reproduces fairly accurately the shape of the frequency spectrum up to the first maximum; beyond this, the actual $G(\omega)$ is flatter than that obtained by the Houston method. Since the numerical work involved in systematically improving Houston's approximation is rather large and since the slight flattening of the distribution function beyond the first maximum is likely to affect, if at all, the calculated specific heats in the temperature region $T\sim\Theta$ (effective Debye temperature) only, we shall use here Houston's method. The effect of the flattening of $G(\omega)$ will be discussed qualitatively at the end of this section. For the purposes of numerical integrations, however, the singularities will be replaced by finite peaks of equal area.

Frequency Spectrum

The first step towards obtaining the distribution function $G(\omega)$ is to solve equations (14) for ω^2 along the three directions A, B, and C. The solution is elementary; making use of (16a), we find

Direction A

$(\lambda,\mu,\nu)=(100)$:

$$\omega^2=\frac{12}{a^2\rho}c_{44}\sin^2\left(\frac{ka}{2\sqrt{3}}\right)+\frac{(c_{11}-c_{44})k^2}{\rho[1+k^2/(4\pi e\eta)]},\tag{28a}$$

$(\lambda,\mu,\nu)=(010)$ or (001):

$$\omega^2=\frac{12}{a^2\rho}c_{44}\sin^2\left(\frac{ka}{2\sqrt{3}}\right).\tag{28b}$$

Direction B

$(\lambda,\mu,\nu)=(1,1,0)$:

$$\omega^2=\frac{1}{a^2\rho}(6c_{44}-3\epsilon)\sin^2\left(\frac{ka}{\sqrt{6}}\right)+\frac{(c_{11}-c_{44})k^2}{\rho[1+k^2/(4\pi e\eta)]},\tag{28c}$$

$(\lambda,\mu,\nu)=(1,-1,0)$:

$$\omega^2=\frac{1}{a^2\rho}(6c_{44}+3\epsilon)\sin^2\left(\frac{ka}{\sqrt{6}}\right),\tag{28d}$$

$(\lambda,\mu,\nu)=(001)$:

$$\omega^2=\frac{6}{a^2\rho}c_{44}\sin^2\left(\frac{ka}{\sqrt{6}}\right).\tag{28e}$$

Direction C

$(\lambda,\mu,\nu)=(1,1,1)$:

$$\omega^2=\frac{1}{a^2\rho}\left[3(c_{44}-\epsilon)\sin^2\left(\frac{ka}{2}\right)+3(3c_{44}+\epsilon)\sin^2\left(\frac{ka}{6}\right)\right]+\frac{(c_{11}-c_{44})k^2}{\rho[1+k^2/(4\pi e\eta)]},\tag{28f}$$

$(\lambda,\mu,\nu)=(1,-1,0)$ or $(1,1,-2)$:

$$\omega^2=\frac{1}{a^2\rho}\left[3(c_{44}+\tfrac{1}{2}\epsilon)\sin^2\left(\frac{ka}{2}\right)+3(3c_{44}-\tfrac{1}{2}\epsilon)\sin^2\left(\frac{ka}{6}\right)\right].\tag{28g}$$

It will be seen from (28) that, just as in the case of infinitely long waves (see Sec. II), the elastic waves of any wave number k propagating along one of these three directions are either wholly longitudinal or wholly transverse. In other directions, there is a slight mixing up of the longitudinal and transverse vibrations. Hence the frequency distribution obtained from (28a), (28c), and (28f) will be predominantly due to the longitudinal waves, while that obtained from the remaining equations in (28) will be chiefly due to the transverse waves. We denote these two distribution functions by $G_l(\omega)$ and $G_t(\omega)$ respectively. Obviously

$$G(\omega)=G_l(\omega)+G_t(\omega)\quad\text{and}$$

$$\int G_l(\omega)d\omega=\frac{1}{2}\int G_t(\omega)d\omega=N_0V.$$

The frequency distribution functions $G_l(\omega)$, $G_t(\omega)$ and $G(\omega)$ are now easily obtained with the help of (24), (27), and (28). The elastic constants for sodium used in this calculation were the same as employed by Bauer.[7] These, as well as other constants needed in the calculation, are listed below:

$$\begin{gathered}c_{44}=0.580\times10^{11},\quad c_{11}-c_{44}=0.390\times10^{11},\\ \epsilon=-1.02\times10^{11},\text{ all of them in dynes/cm}^2;\\ n_0=N_0=2.56\times10^{22}/\text{cc},\quad a=(3\sqrt{3}/4n_0)^{\frac{1}{3}},\\ \rho=0.97\text{ g/cc},\end{gathered}\tag{29}$$

$$(4\pi e\eta)^{-1}=\frac{1}{4\pi e}\cdot\frac{M}{\rho}\frac{(c_{11}-c_{44})}{en_0}=0.015\times a^2\quad[\text{see Eq. (16)}].$$

The distribution functions $G_l(\omega)$, $G_t(\omega)$, and G (ω) are plotted against ω in Fig. 1.

Specific Heat of Sodium

From the distribution function $G(\omega)$, the specific heat C_v at constant volume may be obtained in the

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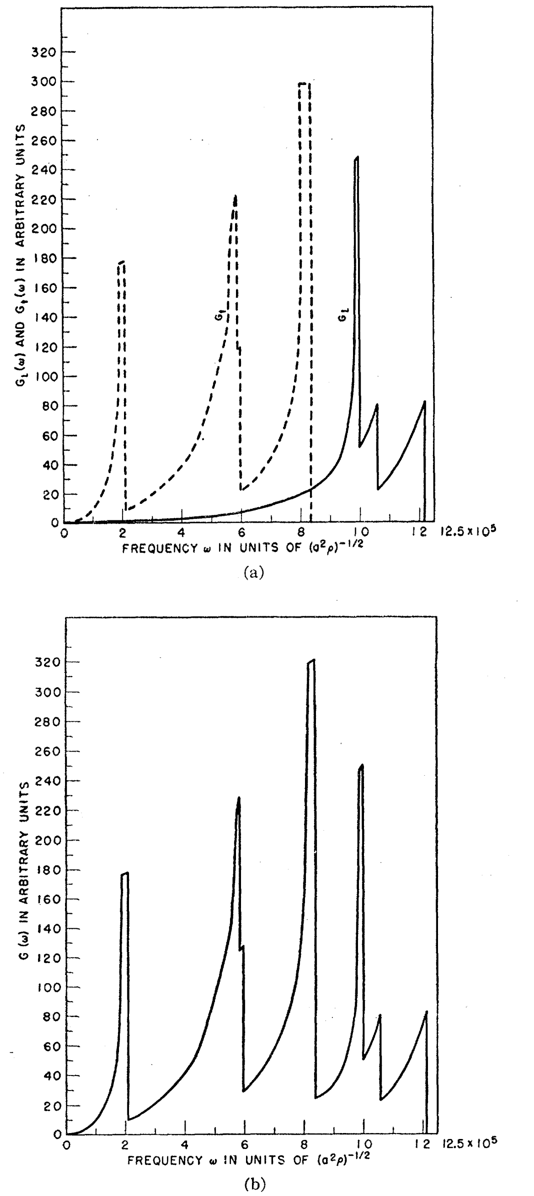
[22] T. Nakamura, Progr. Theoret. Phys. (Japan) 5, 213 (1950).



(a)

(b)

FIG. 1. The frequency spectrum of sodium. The distribution functions $G_l(\omega)$ and $G_t(\omega)$, predominantly due to longitudinal and transverse waves respectively, are given in Fig. 1(a), while $G(\omega)=G_l(\omega)+G_t(\omega)$ is given in Fig. 1(b). (For convenience, the singularities have been replaced by finite peaks of equal area.) The normalized distribution functions may be obtained by multiplying the ordinates in Fig. 1 by $3.9\times10^{-8}(a^2\rho)^{\frac{1}{2}}N_0V$.

usual manner by numerical integration. The results of the entire numerical work of the present paper are estimated to be correct to within about 3 percent. The calculated and experimental specific heats are plotted against the temperature T in Fig. 2. The experimental values of C_v above 20°K are due to Simon and Zeidler,[23] while those below this temperature are due to Pickard and Simon.[24]

A more usual way to study the C_v-T behavior is to insert C_v at a given T in the Debye formula for specific heats, calculate the characteristic temperature Θ and plot Θ against T. If $G(\omega)$ is strictly proportional to ω^2, Θ is independent of temperature; otherwise Θ depends on T. In Fig. 3, we give $\Theta-T$ curves for (*a*) Θ derived from the C_v calculated in the present paper, (*b*) Θ derived from the observed specific heats. As mentioned in the introduction, Bauer,[7] using a two force-constant model, has calculated the specific heat of sodium. For comparison, we give in Fig. 3, curve *c*, Θ's obtained by him on Houston's approximation and finally curves (*d*) and (*e*) which give Θ's obtained by Bauer by flattening in two different ways[25] the frequency distribution function $G(\omega)$ calculated by Houston's method. We should mention that for temperatures above about 120°K, the theoretical Θ-values [presented in the dotted part of the curve (*a*)] are to be regarded as giving merely the general shape of the curve since, at these temperatures, a small error in C_v causes a large error in the corresponding Θ value.

It will be seen from Fig. 3 that the agreement be-

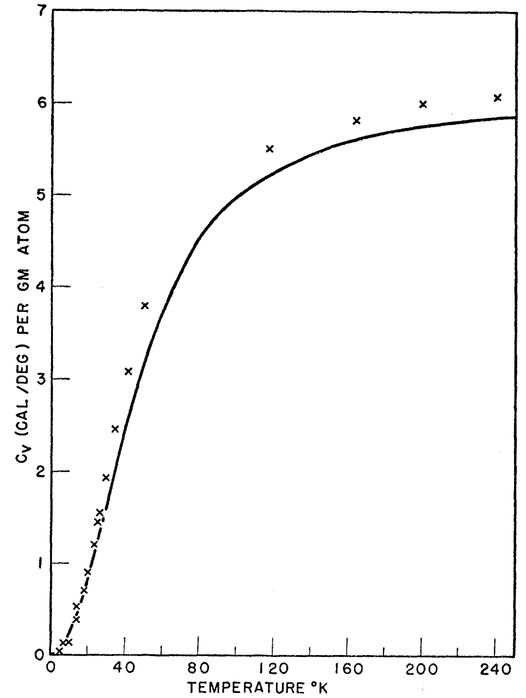


FIG. 2. The calculated and observed lattice specific heats C_v of sodium, as a function of temperature. The experimental points are shown by X. (The electronic specific heat, which was subtracted at low temperatures from the observed C_v, is assumed to be given by the formula to be found in any textbook on the subject.)

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[23] F. E. Simon and W. Zeidler, Z. physik. Chem. **B123**, 383 (1926).

[24] G. L. Pickard and F. E. Simon, Proc. Phys. Soc. (London) **A61**, 1 (1948).

[25] See reference 7, p. 63.

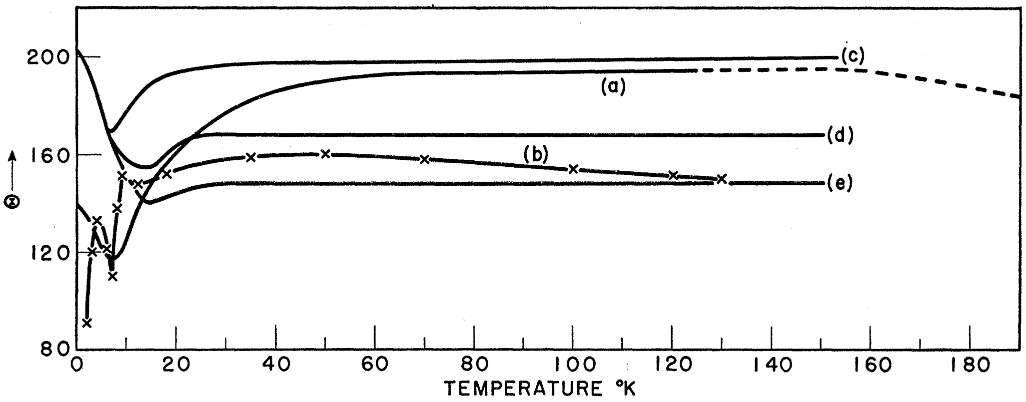

FIG. 3. The effective Debye temperature Θ for sodium, as a function of temperature. Curve (*a*): present calculations; curve (*b*): experimental. Curves (*c*), (*d*) and (*e*) reproduce the theoretical results of Bauer[7]; the explanation of these curves is given in the text.

tween the calculated and observed values of Θ [curves (*a*) and (*b*)] is satisfactory[26] below about 30°K; the discrepancy below about 4°K is presumably due to the uncertainty in the contribution of the electronic specific heat. This specific heat, according to recent investigations by Buckingham,[27] may not be proportional to T as is usually assumed. Above 30°K, the theoretical values are about 15 percent higher than the experimental values. However, it will be noticed that the curve (*a*) lies everywhere much closer to the experimental curve than the curve (*c*) which was obtained by Bauer[7] using Houston's method, i.e., by the same method of calculating the frequency spectrum as employed here. The discrepancy at higher temperatures between the Θ-values calculated here and the experimental values may be due to one or more of the following causes:

(1) The actual frequency distribution beyond the first maximum is flatter than that obtained on Houston's approximation. This will lower the theoretical values at higher temperatures. For example, the curves (*d*) and (*e*) of Bauer lie lower than his curve (*c*).

(2) The assumptions on which the secular equation (14) is derived make the high frequency end of the spectrum somewhat uncertain (see discussion at the end of Sec. II).

(3) Temperature variation of the elastic constants which is neglected in the present calculation. (The values used in the calculation refer to 0°K).

(4) Finally, it will be seen from Fig. 2 that the observed C_v rises above the classical value 6 cal per degree per g atom at about 200°K, while the C_v calculated from the frequency spectrum of normal modes of vibration can never rise above this value. This implies that part of the contribution to the experimental specific heat at this temperature, and therefore possibly at lower temperatures too, comes from sources other than elastic vibrations, e.g., from anharmonicity. If this extraneous specific heat is allowed for, the experimental points in Fig. 3 would tend to lie, at least above about 100°K, a little higher than at present.

Conclusion

From the foregoing discussion we may conclude that, on the whole, the agreement between the experimental values of C_v and those calculated here is satisfactory. In particular, the close agreement between the two sets of values below about 30°K indicates the necessity of using, as has been done in the present paper, some three force-constant model for a metal like sodium which is neither elastically isotropic nor satisfies the Cauchy relation $c_{12}=c_{44}$.

ACKNOWLEDGMENTS

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[26] We should mention that although both curves (*b*) and (*a*) show a minimum at about 7°K, the minimum in the experimental curve is deeper than that in the theoretical curve; this deep minimum in the former is due to a slight hump at about 7°K in the experimental C_v-T curve of reference 24 and does not appear to have been confirmed by the recent work of Hill, Smith, and Parkinson (unpublished); see M. J. Buckingham and M. R. Schafroth, Proc. Phys. Soc. (London) **A67**, 828 (1954), footnote on p. 829. The C_v-T curve obtained from the present calculations has no hump.

[27] M. J. Buckingham, Nature **168**, 281 (1951); see also the reference given in the previous footnote.