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Theory of the Anharmonic Properties of Solids*

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A theory is presented with which one can calculate the anharmonic properties of solids such as thermal expansion, temperature dependence of elastic constants, dependence of elastic constants under stresses, and the deviation of the specific heat from the Dulong-Petit law at high temperatures. The theory is applied to sodium under the assumption of a special force interaction between nearest neighbors only. In the approximation used, three parameters enter. The three parameters are obtained from experimental measurements of the elastic constants near 0°K, the temperature dependence of the compressibility, and the thermal expansion. Then the variation of the volume with pressure and the deviation of the specific heat from the Dulong-Petit law at high temperatures are calculated. A satisfactory agreement with experiment is obtained. Another prediction of the theory, that the temperature derivative of the compressibility is proportional to the specific heat, also shows satisfactory agreement with the experimental measurements for sodium.

I. INTRODUCTION

At low temperatures a solid consists of atoms arranged in a regular array performing small vibrations about their equilibrium positions. In most solids the displacements from the equilibrium positions are small enough at low temperatures that the potential energy can be expanded in a Taylor's series about the equilibrium positions and only the first nonzero term kept, the higher order terms being neglected. This approximation is called the harmonic approximation. As the temperature of a solid is increased to temperatures near its melting point the vibrations of the atoms increase in magnitude so that higher order terms in the Taylor's series expansion become more important, making the harmonic approximation less accurate. For example, in the harmonic approximation the volume of a solid is independent of the temperature. Quantitatively this is a good approximation since the total change in volume of a solid from 0°K to its melting point is of the order of 5%. At low temperatures the change in volume is very small becoming increasingly greater at higher temperatures. In general the harmonic approximation describes the main quantitative features of a solid, but does not explain important qualitative characteristics of a solid such as thermal expansion, temperature variation of the elastic constants, deviations of the specific heat at high temperatures from the Dulong-Petit law, etc.

This paper presents a theory that goes to the next higher order approximation than the harmonic approximation and is capable of explaining anharmonic effects such as thermal expansion. Various other authors have presented theories of anharmonic effects.[1–7] Grüneisen's[1] treatment of solids assumed a special form of central force interaction between atoms. The anharmonic property that his theory most conspicuously explained was thermal expansion. Born[2] and his collaborators present a very complete theory of the thermodynamics of solids. However, they also assumed a special form of central force interaction between atoms.

The elastic constants of a solid in the harmonic approximation are independent of the temperature. The temperature variation can be explained by the anharmonic terms. Born and his collaborators[2] explain the temperature variation of the compressibility, but limit the applicability of their results by their assumption of a special central force between atoms. Zener[7] gives a good physical picture of the cause of the temperature dependence of the elastic constants but does not give any quantitative results which can be compared with experiment. A new method of calculating the temperature dependence of the adiabatic elastic constants which can be used with a more general force between atoms is presented in Sec. II.

In the harmonic approximation both the Debye and Born-von Kármán[8] theories of specific heat predict a lattice specific heat of $3R$ per mole at high temperatures. Experimentally, however, the total specific heat is practically always greater than $3R$ at high temperatures. In many cases only a small part of this difference can be attributed to the electronic specific heat. Peierls[9] shows that deviations from the Dulong-Petit law are caused by anharmonic terms. However, he does not explicitly evaluate his expression and therefore cannot compare it with experiment. The deviation from the Dulong-Petit

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[1] E. Grüneisen, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1926), Vol. 10, pp. 1–59.

[2] M. Born, J. Chem. Phys. **7**, 591 (1939); Proc. Cambridge Phil. Soc. **36**, 160 (1940). M. Born, Proc. Cambridge Phil. Soc. **39**, 100 (1943); M. Born and M. Bradburn, Proc. Cambridge Phil. Soc. **39**, 104 (1943); M. M. Gow, Proc. Cambridge Phil. Soc. **40**, 151 (1944); R. Furth, Proc. Roy. Soc. (London) **183**, 87 (1944).

[3] D. J. Hooton, Phil. Mag. **46**, 422–432 (1955).

[4] J. S. Dugdale and D. K. C. MacDonald, Phys. Rev. **96**, 57 (1954).

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[6] G. Leibfried, *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), Vol. 7, Part 1, pp. 269–290.

[7] C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, 1948), Chap. III.

[8] J. deLaunay, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), pp. 220–303.

[9] R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, 1955), Chap. II.

law which is proportional to the absolute temperature at high temperatures has been previously explicitly evaluated only for the case of a linear chain with central force interaction between nearest neighbors.[4,5] Again no comparison with experiment can be obtained since no one dimensional solids exist. In Sec. III, the term in the specific heat which is proportional to the absolute temperature at high temperatures is calculated for a three dimensional solid permitting a comparison with experiment.

The thermal expansion and its dependence under stresses and the dependence of elastic constants under stresses are also consequences of the theory.

II. TEMPERATURE VARIATION OF ELASTIC CONSTANTS

The main difference between the theory presented here for the temperature variation of elastic constants and that of others such as Born,[2] is that the constants are determined by calculating changes in energy under stress variations instead of strain variations. This has the advantage that the effect of the stress can be put directly into the Hamiltonian of the system and its effect can be directly calculated, in contrast to the other methods where the macroscopic strain does not appear explicitly in the Hamiltonian.

For simplicity a calculation of only the adiabatic compressibility will be given. Other constants can be calculated in a completely analogous way if the pressure is replaced by the appropriate stress corresponding to the elastic constant.

A fundamental assumption that will be made is that in considering the motion of the ion cores of a solid we can replace the effect of the valence electrons by a potential energy which only depends on the coordinates of the ions. This assumption is a common one in solid state physics and is called the Born-Oppenheimer or adiabatic approximation[10] and can be shown to give only a small error in the energy states of a solid.

The Hamiltonian for the ion cores with no external stresses can be written as

$$H_0=\sum_a(P_a^2/2M)+U(\mathbf{r}_1,\cdots\mathbf{r}_N), \tag{1}$$

where the sum is over all ions, and the potential U is a function of only the N ion-core positions. For simplicity a solid with only one ion per unit cell is considered.

The potential can be expanded about its minimum in a Taylor series:

$$\begin{aligned}U(\mathbf{r}_1,\cdots,\mathbf{r}_N)=U_0&-\tfrac{1}{2}\sum U_{ij}(n,n')X_i(n)X_j(n')\\&-\tfrac{1}{3}\sum U_{ijl}(n,n',n'')X_i(n)X_j(n')X_l(n'')\\&-\tfrac{1}{4}\sum U_{ijlm}(n,n',n'',n''')X_i(n)X_j(n')\\&\qquad\times X_l(n'')X_m(n''')+\cdots,\end{aligned} \tag{2}$$

where

$$\begin{aligned}U_{ij}(n,n')&=-\frac{\partial^2U}{\partial X_i(n)\partial X_j(n')},\\U_{ijl}(n,n',n'')&=-\frac{1}{2}\frac{\partial^3U}{\partial X_i(n)\partial X_j(n')\partial X_l(n'')},\\U_{ijlm}(n,n',n'',n''')&=-\frac{1}{6}\frac{\partial^4U}{\partial X_i(n)\partial X_j(n')\partial X_l(n'')\partial X_m(n''')},\end{aligned} \tag{2'}$$

and each summation is over all subscripts and all arguments. Here n denotes the lattice site at $\mathbf{r}(n)=n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3$, where $\mathbf{a}_i$ are the primitive lattice vectors and n_i are integers, and $\mathbf{X}(n)=[X_1(n),X_2(n),X_3(n)]$ denotes the displacement from the potential minimum of the atom at the nth site in Cartesian coordinates.

Under a constant external pressure P, the Hamiltonian for the solid becomes

$$H=H_0+P\sum_{\text{surface}}\Delta\mathbf{s}\cdot\mathbf{X}_s, \tag{3}$$

where P is the applied pressure, $\Delta\mathbf{s}$ is the average area per surface atom, $\mathbf{X}_s$ is the displacement of a surface atom.

An idealized pressure is used which acts only on the surface atoms but should give the same results as a physical pressure produced by atoms from other materials colliding with the first few layers of atoms of the solid under consideration.

Assume that the problem for the Hamiltonian H_0 has been solved so that $H_0\psi_m=E_m\psi_m$. Consider P to be small in order that its effect can be calculated by perturbation theory. This is no restriction since we are interested in the limit as $P\to 0$. To first order the eigenenergies of Eq. (3) are

$$\begin{aligned}E_m'&=E_m+P\sum_{\text{surface}}\int\psi_m{}^*\Delta\mathbf{s}\cdot X_s\psi_m d\tau\Big/\int\psi_m{}^*\psi_m d\tau\\&=E_m+P\langle\Delta V\rangle_m,\end{aligned} \tag{4}$$

where $\langle\Delta V\rangle_m$, is for the state ψ_m, the average change in volume from the volume where the potential energy is a minimum, U_0. Note that as yet no approximation has been made, harmonic or otherwise, so that $\langle\Delta V\rangle_m\neq 0$.

But $\langle\Delta V\rangle_m$ is just the measured volume change so it will be called ΔV_m. Differentiating Eq. (4) with respect to P and setting $P=0$ gives

$$\partial E_m'/\partial P|_{P=0}=\Delta V_m\equiv V_m-V_0. \tag{5}$$

To find the volume at temperature T the canonical ensemble average of ΔV_n is taken[11]:

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[10] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York and London, 1940), p. 470.

[11] R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, Oxford, 1950), Chap. XIII.

$$\Delta V(T) \equiv V(T) - V_0$$

$$= \sum_m \left(\frac{\partial E_m'}{\partial P}\bigg|_{P=0} e^{-BE_m} \right) \Big/ \sum_m e^{-BE_m}, \tag{6}$$

where $B = 1/kT$.

By second order perturbation theory the effect of the pressure P on E_m' can be found to order P^2. From this the compressibility of the solid can be calculated because of the following reasoning. If the pressure exerted on the solid is varied from 0 to P very slowly compared to the vibration frequencies in the solid, then, according to the adiabatic approximation,[12] if the system had initially energy E_m it will end up with energy E_m'. The internal energy of a solid can thus be determined as a function of the external pressure. If the solid were initially at temperature T, its enthalpy‡ is[11]

$$E(T) = -\partial \ln Q/\partial B,$$

where

$$Q = \textstyle\sum_m e^{-BE_m}. \tag{7}$$

The increase in enthalpy of the solid produced by an adiabatically applied pressure is $\int_0^P (V - V_0) dP$. For small volume changes, Hookes' law states that the relative change in volume is proportional to the pressure, i.e.,

$$[V - V(T)]/V(T) = -\beta_s(T)P.$$

Here $V(T)$ is the initial volume at temperature T and zero pressure, V is the volume at pressure P, and $\beta_s(T)$ is the adiabatic compressibility. If one denotes by $\Delta E(T)$ the change in enthalpy of the solid which was initially at temperature T, one obtains

$$\Delta E(T) = \int_0^P (V - V_0)\, dP = -\tfrac{1}{2}\beta_s(T)V(T)P^2 + [V(T) - V_0]P, \tag{8}$$

$$\beta_s(T) = -\frac{1}{V(T)} \frac{\partial^2 \Delta E(T)}{\partial P^2}\bigg|_{P=0}. \tag{8'}$$

As pointed out previously if the solid is in an energy state E_m and then a pressure P is adiabatically applied, the solid will end up with energy E_m'. The probability at temperature T that the solid have an energy state E_m is proportional to $\exp(-E_m/kT)$. But this is the same probability that after the pressure P is applied it will have energy E_m'. Thus

$$\Delta E(T) = \textstyle\sum_m [(E_m' - E_m)e^{-BE_m}] / \sum_m e^{-BE_m}. \tag{9}$$

From Eq. (8′) and because E_m does not depend on P,

$$\beta_s(T) = -\frac{1}{V(T)} \times \sum_m \left(\frac{\partial^2 E_m'}{\partial P^2}\bigg|_{P=0} e^{-E_m/kT} \right) \Big/ \sum_m e^{-E_m/kT}. \tag{10}$$

The problem of calculating $\beta_s(T)$ thus reduces to the calculation of the dependence of E_m' to second order in P.

Although ideas from perturbation theory were used in deriving Eqs. (6) and (10), the dependence of E_m' on P will be calculated by a different method than perturbation theory, one which is much simpler.

When the solid is under no external pressure, the force in the i direction on the atom at the lattice site $\mathbf{r}(n)$ is given, using Eq. (2), by

$$f_i(n) = -\frac{\partial U}{\partial X_i(n)} = \sum U_{ij}(n,n')X_j(n') + \sum U_{ijl}(n,n',n'')X_j(n')X_l(n'') + \sum U_{ijlm}(n,n',n'',n''') \times X_j(n')X_l(n'')X_m(n'''), \tag{11}$$

where each summation is over all *repeated* subscripts and arguments. Of course when all X_j are zero, $f_i(n)$ is also zero because the potential energy was chosen to have its minimum value there.

Now when an external pressure is exerted on the solid, the total potential energy is $U + P \sum_{\text{surface}} \Delta\mathbf{s}\cdot\mathbf{X}_s$ as in Eq. (3). $f_i(n)$ is not zero any more for the surface atoms when all $X_i = 0$. This means that the total potential energy has its minimum at new lattice site positions because of the applied pressure. In other words, a pressure applied to a solid at absolute zero changes its volume. By choosing a new origin such that all $f_i(n) = 0$, the potential energy will have the same form as Eq. (2) except that now the U_{ij}, U_{ijl}, and U_{ijlm} will be different because they are evaluated at new positions. Thus the problem is only to find the unperturbed solution involving H_0, Eq. (1), and to determine how the U_{ij}, U_{ijl}, and U_{ijlm} depend on the pressure.

The eigenenergies of H_0 to terms proportional to T at high temperatures are[13]

$$E_m = U_0 + \textstyle\sum_j (n_j + \frac{1}{2})\hbar\omega_j, \tag{12}$$

where ω_j are the frequencies of the normal modes of the solid and depend on only $U_{ij}(n,n')$, and the index m denotes the selection of the n_j.

Since, as was shown above, H in Eq. (3) can be put in the same form as H_0,

$$E_m' = U_0' + \textstyle\sum_j (n_j + \frac{1}{2})\hbar\omega_j', \tag{13}$$

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[12] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 209.

‡ $E(T)$ represents the enthalpy and not the internal energy since Q is the partition function for constant pressure and not constant volume.

[13] See reference 10, p. 477.

where U_0' is the new minimum of the energy and ω_j' are the new normal modes of the solid which depend on only the new $U_{ij}'(n,n')$. The $U_{ij}'(n,n')$ depend on the new equilibrium lattice sites which in turn depend on the pressure. The ω_j' are therefore functions of the pressure only.

By considering the solid at 0°K, one obtains from Eqs. (8), (12), and (13) that

$$\Delta E(0)=E_{m0}'-E_{m0}=U_0'+\tfrac{1}{2}\sum_j\hbar\omega_j'-U_0-\tfrac{1}{2}\sum_j\hbar\omega_j=-\tfrac{1}{2}\beta_s(0)V(0)P^2+[V(0)-V_0]P. \tag{14}$$

From Eqs. (13) and (14) it follows that

$$E_m'=U_0+\tfrac{1}{2}\sum_j\hbar\omega_j-\tfrac{1}{2}\beta_s(0)V(0)P^2+P[V(0)-V_0]+\sum_j n_j\hbar\omega_j', \tag{15}$$

$$\left.\frac{\partial^2 E_m'}{\partial P^2}\right|_{P=0}=-\beta_s(0)V(0)+\sum_i n_j\hbar\left.\frac{\partial^2\omega_j'}{\partial P^2}\right|_{P=0}. \tag{15'}$$

From this and Eqs. (7) and (8′), one obtains

$$\beta_s(T)=\beta_s(0)\frac{V(0)}{V(T)}-\frac{1}{V(T)}\times\sum_i\hbar\left.\frac{\partial^2\omega_j'}{\partial P^2}\right|_{P=0}\Big/ e^{(B\hbar\omega_j)}-1. \tag{16}$$

Here the well-known result that

$$n(T)=\frac{1}{\exp(\hbar\omega_j/kT)-1}$$

is used. To determine $V(T)$ use is made of Eqs. (6), (12), and (15), giving

$$V(T)-V(0)=\sum_i\hbar\omega_j\frac{1}{\omega_j}\left.\frac{\partial\omega_j'}{\partial P}\right|_{P=0}\left(\frac{1}{e^{B\hbar\omega_j}-1}\right). \tag{17}$$

The thermal expansion now becomes

$$\alpha_V(T)=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)=\frac{1}{V}\frac{\partial}{\partial T}\sum_i\gamma_j\frac{\hbar\omega_j}{e^{B\hbar\omega_j}-1}, \tag{18}$$

where

$$\gamma_j=\left.\frac{\partial\ln\omega_j'}{\partial P}\right|_{P=0}.$$

It is of interest to note that Eq. (18) is equivalent to the Grüneisen rule

$$\alpha_V(T)=\gamma'\beta_T C(T)/V(T), \tag{19}$$

where

$$\gamma'=-\partial\ln\omega_j/\partial\ln V,$$

and β_T is the compressibility at constant temperature, as is shown in Appendix I.

Using the results of Eqs. (16) and (17) and calculating to terms proportional to T at high temperatures one obtains

$$\beta_s(T)=\beta_s(0)\left(1-\frac{1}{V(0)}\sum_i\gamma_j\frac{\hbar\omega_j}{e^{B\hbar\omega_j}-1}\right)+\frac{1}{V(0)}\sum_i\frac{\delta_j\hbar\omega_j}{e^{B\hbar\omega_j}-1}, \tag{20}$$

where

$$\delta_j=\frac{1}{\omega_j}\left.\frac{\partial^2\omega_j'}{\partial P^2}\right|_{P=0}.$$

In a completely analogous manner one can show for a cubic crystal that

$$S_{44}(T)=\frac{1}{C_{44}(T)}=\frac{1}{V(T)}\frac{\partial^2E(T)}{\partial\tau_1^2}=S_{44}(0)\left(1-\frac{1}{V(0)}\sum_i\gamma_j\frac{\hbar\omega_j}{e^{B\hbar\omega_j}-1}\right)+\frac{1}{V(0)}\sum_i\delta_j^{(1)}\frac{\hbar\omega_j}{e^{B\hbar\omega_j}-1}, \tag{21}$$

and

$$2[S_{11}(T)-S_{12}(T)]=\frac{2}{C_{11}(T)-C_{12}(T)}=\frac{1}{V(T)}\frac{\partial^2E(T)}{\partial\tau_2^2}=2[S_{11}(0)-S_{12}(0)]\left(1-\frac{1}{V(0)}\sum_i\gamma_j\frac{\hbar\omega_j}{e^{B\hbar\omega_j}-1}\right)+\frac{1}{V(0)}\sum_i\delta_j^{(2)}\frac{\hbar\omega_j}{e^{B\hbar\omega_j}-1}. \tag{22}$$

Here τ_1 is the stress that produces a shear in the (100) plane along the [010] direction, τ_2 is the stress that produces a shear in the (110) plane along the $[\bar{1}10]$ direction, and

$$\delta_j^{(1)}=\left.\frac{\partial^2\omega_j}{\partial\tau_1^2}\right|_{\tau_1=0},\quad \delta_j^{(2)}=\left.\frac{\partial^2\omega_j}{\partial\tau_2^2}\right|_{\tau_2=0}.$$

Expressions can also be obtained for the elastic constants of crystal structures other than cubic but for simplicity the discussion here will be limited to cubic crystals.

The remaining step is to calculate δ_j, $\delta_j^{(1)}$, and $\delta_j^{(2)}$. To do this will require the assumption of a specific model for the solid. In order to make the calculation as simple as possible and still applicable to an actual solid the following model is taken:

(a) A body-centered cubic crystal structure composed of only one type of atom.

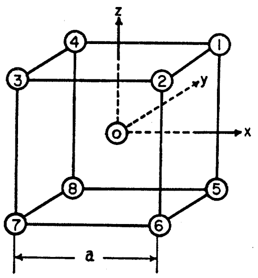

FIG. 1. Labeling of the atoms in a unit cube of a body-centered cubic lattice as used in the text.

(b) Only nearest-neighbor interactions are important. A third assumption will be made further on.

It should be emphasized that assumptions (a), (b), and (c) (to follow) are made only for calculational simplicity. The theory is not restricted to these assumptions but can be used for any general force between neighbors.

From the fact that the force in Eq. (11) and all its derivatives are invariant under a uniform translation, the following relations are obtained.

$$\begin{aligned}\textstyle\sum_n U_{ij}(n,n') &= \textstyle\sum_{n'} U_{ij}(n,n') = 0,\\ \textstyle\sum_n U_{ijl}(n,n',n'') &= \textstyle\sum_{n'} U_{ijl}(n,n',n'')\\ &= \textstyle\sum_{n''} U_{ijl}(n,n',n'') = 0,\\ \textstyle\sum_n U_{ijlm}(n,n',n'',n''') &\\ &= \textstyle\sum_{n'} U_{ijlm}(n,n',n'',n''')\\ &= \textstyle\sum_{n''} U_{ijlm}(n,n',n'',n''')\\ &= \textstyle\sum_{n'''} U_{ijlm}(n,n',n'',n''') = 0.\end{aligned} \tag{23}$$

Because of the above relations the force in Eq. (11) can be written as

$$\begin{aligned}f_i(n) = &\textstyle\sum U_{ij}(n,n')[X_j(n')-X_j(n)]\\ &+\textstyle\sum U_{ijl}(n,n',n'')[X_j(n')-X_j(n)]\\ &\times[X_l(n'')-X_l(n)]+\textstyle\sum U_{ijlm}(n,n',n'',n''')\\ &\times[X_j(n')-X_j(n)][X_l(n'')-X_l(n)]\\ &\times[X_m(n''')-X_m(n)],\end{aligned} \tag{24}$$

where the sums are over repeated subscripts and repeated primed arguments.

From assumptions (a) and (b), $U_{ij}(n,n')=0$ unless n equals n' or one of its eight nearest neighbors, $U_{ijl}(n,n',n'')=0$ unless $n=n'=n''$ or both n' and n'' are nearest neighbors to n and similarly for $U_{ijlm}(n,n',n'',n''')$. Equation (24) now becomes

$$\begin{aligned}f_i(n) = &\textstyle\sum U_{ij}(n,n')[X_j(n')-X_j(n)]\\ &+\textstyle\sum U_{ijl}(n,n')[X_j(n')-X_j(n)]\\ &\times[X_l(n')-X_l(n)]+\textstyle\sum U_{ijlm}(n,n')\\ &\times[X_j(n')-X_j(n)][X_l(n')-X_l(n)]\\ &\times[X_m(n')-X_m(n)],\end{aligned} \tag{24'}$$

where the sums are over n' and repeated subscripts, n' being one of the 8 nearest neighbors to n;

$$U_{ijl}(n,n') \equiv U_{ijl}(n,n',n'),$$

and

$$U_{ijlm}(n,n') \equiv U_{ijlm}(n,n',n',n').$$

$U_{ij}(n,n')$ is a tensor of rank two, $U_{ijl}(n,n')$ is a tensor of rank three, and $U_{ijlm}(n,n')$ is a tensor of rank four.

Consider the cube formed by an atom and its 8 nearest neighbors as labeled in Fig. 1. There is now one remaining assumption that has to be made. Assumption (c);

$$\begin{aligned}U_{ij}(0,1)&=\alpha \text{ (independent of } i \text{ and } j),\\ U_{ijl}(0,1)&=\beta \text{ (independent of } i,\ j, \text{ and } l),\\ U_{ijlm}(0,1)&=\gamma \text{ (independent of } i,\ j,\ l, \text{ and } m).\end{aligned}$$

This assumption is not a central force interaction. A central force interaction would require $U_{ij}(0,1)$ to be independent of i and j but $U_{ijl}(0,1)$ and $U_{ijlm}(0,1)$ would not be independent of i, j, l, and m. The force constants between other neighbors can be obtained from the transformation properties of tensors. They are given in Table I.

Only δ_j will be calculated. $\delta_j^{(1)}$ and $\delta_j^{(2)}$ can be obtained in an analogous manner, but they require numerical evaluation. The calculation of δ_j requires no numerical work and gives a simple result.

The secular equation for ω_j in the harmonic approximation is[14]

$$\begin{vmatrix} 1-C_1C_2C_3-\Omega^2 & S_1S_2C_3 & S_1C_2S_3\\ S_1S_2C_3 & 1-C_1C_2C_3-\Omega^2 & C_1S_2S_3\\ S_1C_2S_3 & C_1S_2S_3 & 1-C_1C_2C_3-\Omega^2\end{vmatrix}=0. \tag{25}$$

Here $S_j=\sin(k_ja/2)$, $C_j=\cos(k_ja/2)$, $\Omega^2=\frac{3}{8}(\pi^2\omega^2M/\alpha)$, and M is the mass of an ion core.

Comparing the secular equation (25) with the secular equation in the acoustic limit,[15] one obtains $C_{11}=C_{12}=C_{44}$. The values[16–18] of the elastic constants for three body centered cubic alkali metals are given in Table II. As can be seen the relation $C_{11}=C_{44}=C_{12}$ is approximately satisfied only by sodium and thus some comparison with experiment can be expected for sodium.

The approach here to calculate δ_j will be, as mentioned previously, to determine the dependence of α on P and then from Eq. (25) obtain ω_j as a function of P.

TABLE I. Values of the force constants between nearest neighbors.[a]

Particle pair No.	U_{ij}	U_{ijl}	U_{ijlm}
0, 1	α	β	γ
0, 7	α	β	γ
0, 2	$(-1)^y\alpha$	$(-1)^y\beta$	$(-1)^y\gamma$
0, 8	$(-1)^y\alpha$	$(-1)^{y+1}\beta$	$(-1)^y\gamma$
0, 3	$(-1)^Z\alpha$	$(-1)^{Z+1}\beta$	$(-1)^Z\gamma$
0, 5	$(-1)^Z\alpha$	$(-1)^Z\beta$	$(-1)^Z\gamma$
0, 4	$(-1)^x\alpha$	$(-1)^x\beta$	$(-1)^x\gamma$
0, 6	$(-1)^x\alpha$	$(-1)^{x+1}\beta$	$(-1)^x\alpha$

[a] $(-1)^y$ means (-1) taken to the power of the number of y's in the $ijlm$ subscripts of the U's. Similarly for $(-1)^x$ and $(-1)^Z$.

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[14] See reference 8, p. 272.

[15] See reference 8, p. 266.

[16] Charles S. Smith (private communication).

[17] S. L. Quimby and S. Siegel, Phys. Rev. **54**, 293 (1938).

[18] O. Bender, Ann. Physik **34**, 359 (1939).

The force on an atom with no external pressure is given by Eq. (24). Now apply a pressure P to the solid. Imagine the solid cut along an internal (100) plane. Let all atoms be fixed at the positions where the potential energy is a minimum. The force per unit area along the cut plane is now P, or the force per atom on either side of the plane is $Pa^2(1+\epsilon)^2$, where the length of the edge of the unit cube is changed from a to $a(1+\epsilon)$ under a pressure P. This determines the relative displacement of the atoms from the positions they had in minimizing the potential energy under zero pressure. Using Eq. (24′) and the fact that from symmetry, the displacement of the atom of a cubic solid under pressure is uniform in all directions, one obtains

$$Pa^2(1+\epsilon)^2=-6\alpha\epsilon a-9\beta(\epsilon a)^2-(27/2)\gamma(\epsilon a)^3. \tag{26}$$

Here α, β, and γ are the force constants at zero pressure. Solving for ϵ to second order in P from Eq. (26), one obtains

$$\epsilon=-\frac{Pa}{6\alpha}-9\left(\frac{a}{6\alpha}\right)^3\beta P^2+2\left(\frac{a}{6\alpha}\right)^2P^2. \tag{27}$$

Using Eq. (2′) and the fact that ϵ is small so that a Taylor series expansion can be used, one obtains for the new α' at pressure P,

$$\begin{aligned}\alpha'=U_{ij}'(0,1)&=U_{ij}(0,1)+\sum_l\frac{\partial U_{ij}}{\partial X_l}\Delta X_l\\&\quad+\tfrac{1}{2}\sum_{l,m}\frac{\partial^2U_{ij}}{\partial X_l\partial X_m}\Delta X_l\Delta X_m\\&=U_{ij}(0,1)+2\sum_l U_{ijl}(0,1)(\tfrac{1}{2}\epsilon a)+3\sum_{l,m}U_{ijlm}(0,1)(\tfrac{1}{2}\epsilon a)^2\\&=\alpha+3\beta a\epsilon+(27/4)\gamma(a\epsilon)^2\\&=\alpha-\frac{Pa^2\beta}{2\alpha}-\left(\frac{a}{2\alpha}\right)^2P^2\left[\frac{\beta^2a^2}{2\alpha}-\tfrac{3}{4}\gamma a^2-\tfrac{2}{3}\beta a\right].\end{aligned} \tag{28}$$

The secular equation (25) for the frequencies assumes the Born-von Kármán boundary condition. In the approach presented here the boundary conditions are different from the Born-von Kármán one. However, Born[19] has shown that the error introduced in the frequency spectrum is of order $1/N$, where N is the total number of atoms, a negligible amount. Also the determination of ϵ in Eq. (27) is for an interior atom. The ϵ associated with surface atoms will be different. Since ϵ is assumed to be the same for all atoms, a negligible error of the order of $1/N$ is introduced.

As the pressure is applied to the solid only α and ω^2 change in the secular equation (25) for ω. The C_j's and S_j's remain constant. In fact, Eq. (25) implies that ω^2/α is a constant independent of the pressure. This permits us to obtain ω as a function of pressure. A straightforward calculation then gives,

$$\gamma_j=\left.\frac{\partial\ln\omega_j'}{\partial P}\right|_{P=0}=-\frac{a^2\beta}{4\alpha^2}, \tag{29}$$

$$\delta_j=\left.\frac{1}{\omega_j}\frac{\partial^2\omega_j'}{\partial P^2}\right|_{P=0}=\frac{3}{16}\frac{a^4}{\alpha^2}\left(\frac{\gamma}{\alpha}+\frac{8}{9}\frac{\beta}{a\alpha}-\frac{\beta^2}{\alpha^2}\right), \tag{30}$$

independent of the normal mode.

The compressibility $\beta_s=-V^{-1}\partial V/\partial P$ is seen from Eq. (26), where $dV/V=3\epsilon$, to be equal to

$$\beta_s(0)=a/2\alpha. \tag{31}$$

Using the values of Eq. (29) in Eq. (20) and using the relation of Eq. (33), one finally obtains that

$$\beta_s(T)=\beta_s(0)-\int_0^T\frac{C(T')dT'}{V(0)}\times\left[\frac{\beta_s(0)\beta a^2}{12\alpha^2}+\frac{3}{16}\frac{a^4}{\alpha^2}\left(\frac{\gamma}{\alpha}-\frac{\beta^2}{\alpha^2}\right)\right]. \tag{32}$$

Here

$$\int_0^T C(T')dT'=\sum_i\frac{\hbar\omega_j}{\exp(B\hbar\omega_j)-1},$$

where $C(T)$ is the specific heat in the harmonic approximation. Therefore for a body-centered cubic solid where assumptions (b) and (c) are valid

$$\frac{\partial\beta_s(T)}{\partial T}=\frac{C(T)}{V(0)}\left[-\frac{\beta_s(0)a^2\beta}{12\alpha^2}-\frac{3}{16}\frac{a^4}{\alpha^2}\left(\frac{\gamma}{\alpha}-\frac{\beta^2}{\alpha^2}\right)\right]. \tag{33}$$

The temperature variation of the compressibility is proportional to the specific heat.

The dependence of the volume with pressure will next be calculated neglecting zero point energy. Since the lattice parameter a changes to $a(1+\epsilon)$ under a pressure change, where ϵ is related to P from Eq. (26), straightforward differentiation gives a Taylor series to order P^3 for the change in volume at 0°K as

$$-\frac{\Delta V}{V}=\beta_s(0)P-\tfrac{1}{2}[\beta_s(0)P]^2\left(2-\frac{\beta a}{\alpha}\right)+\tfrac{1}{6}[\beta_s(0)P]^3\times\left[\frac{34}{9}-\frac{6\beta a}{\alpha}-\frac{3}{2}\frac{\gamma a^2}{\alpha}+3\left(\frac{\beta a}{\alpha}\right)^2\right]. \tag{34}$$

TABLE II. The elastic constants of some alkalis in units of 10^{11} dynes/cm^2.

Element	Structure	C_{11}	C_{12}	C_{44}	Temperature	Reference
Li	bcc	1.34	1.13	0.96	195°K	a
Na	bcc	0.608	0.463	0.593	80°K	b
K	bcc	0.459	0.372	0.263	77°K	c

[a] See reference 16.
[b] See reference 17.
[c] See reference 18.

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[19] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), p. 391.

III. DEVIATION OF THE LATTICE SPECIFIC HEAT FROM THE DULONG-PETIT LAW

A classical calculation will be made of the next higher approximation to the specific heat than the harmonic approximation. At low temperatures where quantum effects are important the anharmonic effects will be very small. It is only at the higher temperatures where the quantum mechanical effects are small that the anharmonic effects are important, and thus a classical calculation will suffice.

Integrating Eq. (24′), one obtains for the potential energy

$$\begin{aligned}U=U_0&-\tfrac{1}{2}\sum U_{ij}(n,n')X_i(n)[X_j(n')-X_j(n)]\\&-\tfrac{1}{3}\sum U_{ijl}(n,n')X_i(n)[X_j(n')-X_j(n)]\\&\times[X_l(n')-X_l(n)]-\tfrac{1}{4}\sum U_{ijlm}(n,n')X_i(n)\\&\times[X_j(n')-X_j(n)][X_l(n')-X_l(n)]\\&\qquad\times[X_m(n')-X_m(n)],\end{aligned}\tag{35}$$

where here and in Eq. (37) the sums are over n, n', and repeated subscripts. Using the labeling as in Fig. 1, $U_{ij}(0,1)=U_{ij}(0,7)$ (see Table I). Now if the origin is shifted to particle 7, by translational symmetry particle 7 can now be called particle 0 and particle 0 can now be called particle 1. It is then seen that $U_{ij}(0,7)=U_{ij}(1,0)$. Therefore $U_{ij}(1,0)=U_{ij}(0,1)$. In the same way it can be shown that

$$\begin{aligned}U_{ij}(n,n')&=U_{ij}(n',n),\\U_{ijl}(n,n')&=-U_{ijl}(n',n),\\U_{ijlm}(n,n')&=U_{ijlm}(n',n).\end{aligned}\tag{36}$$

Using the relations in Eq. (36), it can be seen that Eq. (35) can be put into the form

$$\begin{aligned}U=U_0&+\tfrac{1}{4}\sum U_{ij}(n,n')[X_i(n')-X_i(n)]\\&\times[X_j(n')-X_j(n)]+\tfrac{1}{6}\sum U_{ijl}(n,n')\\&\times[X_i(n')-X_i(n)][X_j(n')-X_j(n)]\\&\times[X_l(n')-X_l(n)]+\tfrac{1}{8}\sum U_{ijlm}(n,n')\\&\times[X_i(n')-X_i(n)][X_j(n')-X_j(n)]\\&\qquad\times[X_l(n')-X_l(n)][X_m(n')-X_m(n)].\end{aligned}\tag{37}$$

The normal modes of the solid are next introduced[20]:

$$X_i(n)=\sum_{\mathbf{k},\sigma}a_\sigma(\mathbf{k},t)\xi_{i,\sigma}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}(n)}/(MN)^{\frac{1}{2}}.\tag{38}$$

The total number of lattice sites is N. σ describes the polarization of the normal mode in respect to its wave number $\mathbf{k}$. For a simple lattice without a basis, the situation considered here, σ has 3 values. The $\xi_{i,\sigma}(\mathbf{k})$ are components of the unit vector in the direction of the displacement of the atom. They have the property that

$$\begin{aligned}\textstyle\sum_i \xi_{i,\sigma}^*(\mathbf{k})\xi_{i,\sigma'}(\mathbf{k})&=\delta_{\sigma,\sigma'},\\\xi_{i,\sigma}^*(-\mathbf{k})&=\xi_{i,\sigma}(\mathbf{k}).\end{aligned}\tag{39}$$

The $a_\sigma(\mathbf{k},t)$ are the normal modes and have the property that

$$a_\sigma^*(-\mathbf{k},t)=a_\sigma(\mathbf{k},t).\tag{39′}$$

There is the further relation that

$$(1/N)\textstyle\sum_n f(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}(n)}=f(\mathbf{k})\delta(\mathbf{k},\mathbf{g}),\tag{39″}$$

where $f(\mathbf{k})$ is any function depending on $\mathbf{k}$ and

$$\begin{aligned}\delta(\mathbf{k},\mathbf{g})&=0\quad\text{if}\quad\mathbf{k}\neq\mathbf{g}\\&=1\quad\text{if}\quad\mathbf{k}=\mathbf{g}.\end{aligned}$$

Here $\mathbf{g}$ is defined by

$$\exp[i\mathbf{g}\cdot\mathbf{r}(n)]=1.\tag{39‴}$$

New normal modes can be introduced which are real.[20]

$$\begin{aligned}b_\sigma(\mathbf{k})&=\frac{a_\sigma(\mathbf{k})+a_\sigma^*(\mathbf{k})}{\sqrt{2}},\\b_\sigma(-\mathbf{k})&=\frac{a_\sigma(\mathbf{k})-a_\sigma^*(\mathbf{k})}{i\sqrt{2}}.\end{aligned}\tag{40}$$

In Eq. (40) $\mathbf{k}$ is limited to vary over that half of the first Brillouin zone which includes $\mathbf{k}$ but not $-\mathbf{k}$.

The enthalpy of the solid as a function of temperature can be obtained by

$$E(T)=-\partial\ln Q_c/\partial B,\tag{41}$$

where Q_c is the classical partition function

$$Q_c=\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\cdots e^{-BE}db_\sigma(\mathbf{k})\cdots dp_\sigma(\mathbf{k})\cdots;$$

and

$$E=\sum_{\mathbf{k},\sigma}[\tfrac{1}{2}p_\sigma^2(\mathbf{k})+U(b_\sigma(\mathbf{k}))].$$

The integration is with respect to all of the normal coordinates $b_\sigma(\mathbf{k})$ and their conjugate momenta $p_\sigma(\mathbf{k})$. The normal coordinates are substituted for the X_i in the potential energy terms, Eq. (35).

The potential energy can be separated into $U(b_\sigma(\mathbf{k}))=U_2(b_\sigma(\mathbf{k}))+U_3(b_\sigma(\mathbf{k}))+U_4(b_\sigma(\mathbf{k}))$; where $U_2(b_\sigma(\mathbf{k}))$ which equals[20] $\frac{1}{2}\sum_{\mathbf{k},\sigma}b_\sigma^2(\mathbf{k})\omega_\sigma^2(\mathbf{k})$, $U_3(b_\sigma(\mathbf{k}))$, and $U_4(b_\sigma(\mathbf{k}))$ are the terms in the potential energy that contained X_i to second order, third order, and fourth order, respectively. These terms now contain $b_\sigma(\mathbf{k})$ to the same order as they contained X_i since the transformation to normal coordinates is a linear one. As is usually done,[21] the exponential containing U_3 and U_4 is expanded in a power series:

$$Q_c=\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\cdots\exp\left\{-\tfrac{1}{2}\sum_{\mathbf{k},\sigma}\frac{p_\sigma^2(\mathbf{k})+b_\sigma^2(\mathbf{k})\omega_\sigma^2(\mathbf{k})}{kT}\right\}\times\left(1-\frac{U_3}{kT}-\frac{U_4}{kT}+\frac{1}{2}\frac{U_3^2}{(kT)^2}\right)db_\sigma(\mathbf{k})\cdots dp_\sigma(\mathbf{k})\cdots.$$

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[20] See reference 10, pp. 125-133.

[21] See reference 9, pp. 34–39.

The integration over U_3 is zero since U_3 is odd in the $b_\sigma(\mathbf{k})$ while the exponential is even, leaving $Q_c = Q_0 + Q_1 + Q_2$, where

$$Q_0 = (2\pi kT)^{3N} / \prod_{\mathbf{k},\sigma} \omega_\sigma(\mathbf{k})$$

$$= \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \cdots \exp\left\{ -\tfrac{1}{2} \sum_{\mathbf{k},\sigma} \frac{p_\sigma^2(\mathbf{k}) + b_\sigma^2(\mathbf{k})\omega_\sigma^2(\mathbf{k})}{kT} \right\} \times db_\sigma(\mathbf{k}) \cdots dp_\sigma(\mathbf{k}) \cdots,$$

$$Q_1 = \frac{1}{2} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \cdots \times \exp\left\{ -\tfrac{1}{2} \sum_{\mathbf{k},\sigma} \frac{p_\sigma^2(\mathbf{k}) + b_\sigma^2(\mathbf{k})\omega_\sigma^2(\mathbf{k})}{kT} \right\} \times \left[\frac{U_3(b_\sigma(\mathbf{k}))}{kT} \right]^2 db_\sigma(\mathbf{k}) \cdots dp_\sigma(\mathbf{k}) \cdots, \tag{42}$$

$$Q_2 = -\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \cdots \times \exp\left\{ -\tfrac{1}{2} \sum_{\mathbf{k},\sigma} \frac{p_\sigma^2(\mathbf{k}) + b_\sigma^2(\mathbf{k})\omega_\sigma^2(\mathbf{k})}{kT} \right\} \times \frac{U_4(b_\sigma(\mathbf{k}))}{kT} db_\sigma(\mathbf{k}) \cdots dp_\sigma(\mathbf{k}) \cdots.$$

Substituting in for U_4 and utilizing the cubic symmetry of the lattice in a straightforward but tedious calculation,[22] one obtains for Q_2

$$Q_2 = -\frac{48 Q_0 \gamma}{M^2 N kT} I^2,$$

where

$$I = \sum_{i,j} \sum_{\mathbf{k},\sigma} \frac{\xi_{i,\sigma}^*(\mathbf{k}) \xi_{j,\sigma}(\mathbf{k}) \sin^2[\frac{1}{2}\mathbf{k}\cdot\mathbf{r}(0,1)]}{\omega_\sigma^2(\mathbf{k})}. \tag{43}$$

Here $\mathbf{r}(0,1)$ means $\mathbf{r}(1) - \mathbf{r}(0)$, the distance between nearest neighbors. By cubic symmetry $\mathbf{r}(0,1)$ may be replaced by $\mathbf{r}(0,j)$ where j can be any of the 8 nearest neighbors. Neighbor one is taken in order to be definite.

To evaluate I, consider Eq. (24′) in the harmonic approximation. Using $f_i(n) = M[d^2X_i(n)/dt^2]$, and substituting a normal mode for the displacements one obtains[20]

$$M\omega_\sigma^2(\mathbf{k})\xi_{i,\sigma}(\mathbf{k}) = \sum_{j,\Delta n'} U_{ij}(\Delta n')[e^{i\mathbf{k}\cdot\mathbf{r}(\Delta n')} - 1]\xi_{j,\sigma}(\mathbf{k})$$

$$= 2 \sum_{j,\Delta n'} U_{ij}(\Delta n')\xi_{j,\sigma}(\mathbf{k}) \sin^2[\tfrac{1}{2}\mathbf{k}\cdot\mathbf{r}(\Delta n')],$$

where $\mathbf{r}(\Delta n') \equiv \mathbf{r}(n') - \mathbf{r}(n)$ and $U_{ij}(\Delta n') \equiv U_{ij}(n,n')$, and $\sum_{\Delta n'}$ means $\sum_{n'}$ keeping n fixed, i.e., sum over nearest neighbors. Multiply both sides of the above equation by $\xi_{i,\sigma}^*(\mathbf{k})$ and sum with respect to i. Using Eq. (39) one obtains

$$1 = \frac{2}{M} \sum_{i,j,\Delta n} U_{ij}(\Delta n) \frac{\xi_{i,\sigma}^*(\mathbf{k})\xi_{j,\sigma}(\mathbf{k}) \sin^2[\frac{1}{2}\mathbf{k}\cdot\mathbf{r}(\Delta n)]}{\omega_\sigma^2(\mathbf{k})}. \tag{44}$$

Summing both sides in respect to $\mathbf{k}$ and σ gives

$$3N = \frac{2}{M} \sum_{\Delta n} \sum_{\mathbf{k},\sigma} \sum_{i,j} U_{ij}(\Delta n) \frac{\xi_{i,\sigma}^*(\mathbf{k})\xi_{j,\sigma}(\mathbf{k}) \sin^2[\frac{1}{2}\mathbf{k}\cdot\mathbf{r}(\Delta n)]}{\omega_\sigma^2(\mathbf{k})}.$$

If the summation is first done with respect to $\mathbf{k}$, σ, i, and j, the sum, from cubic symmetry, is independent of Δn, giving after summing over the eight nearest neighbors

$$3N = \frac{16\alpha}{M} \sum_{\mathbf{k},\sigma} \sum_{i,j} \frac{\xi_{i,\sigma}^*(\mathbf{k})\xi_{j,\sigma}(\mathbf{k}) \sin^2[\frac{1}{2}\mathbf{k}\cdot\mathbf{r}(0,1)]}{\omega_\sigma^2(\mathbf{k})} = \frac{16\alpha I}{M}, \tag{45}$$

or

$$I = 3NM/16\alpha.$$

Therefore from Eq. (43)

$$Q_2 = -27 Q_0 N \gamma kT (16\alpha^2)^{-1}. \tag{46}$$

It remains to evaluate Q_1, a more involved procedure. Substituting the expression for U_3 in Eq. (42) and integrating, one obtains a complicated expression which contains, among others, a double sum over nearest neighbors. If the sums are first performed over all the other variables, leaving the double sums over nearest neighbors undone, only two different types of terms are obtained, because of the cubic symmetry. For one the same nearest neighbor is involved twice and for the other two different nearest neighbors are involved. The result is, after another tedious but straightforward calculation,[22]

$$Q_1 = \frac{16}{3} \frac{kTQ_0}{M^3 N} \{ 16\beta^2 \sum G_{i,i',\sigma}(\mathbf{k}) G_{j,j',\sigma'}(\mathbf{k}') \times G_{l,l',\sigma''}(\mathbf{k}'') + 48\beta \sum U_{i'j'l'}(0,2) \times F_{i,i',\sigma}(\mathbf{k}) F_{j,j',\sigma'}(\mathbf{k}') F_{l,l',\sigma''}(\mathbf{k}'') \}, \tag{47}$$

where

$$G_{i,i',\sigma}(\mathbf{k}) = \omega_\sigma^{-2}(\mathbf{k}) \xi_{i,\sigma}(\mathbf{k}) \xi_{i',\sigma}^*(\mathbf{k}) \sin^2[\tfrac{1}{2}\mathbf{k}\cdot\mathbf{r}(0,1)],$$

$$F_{i,i',\sigma}(\mathbf{k}) = \omega_\sigma^{-2}(\mathbf{k}) \xi_{i,\sigma}(\mathbf{k}) \xi_{i',\sigma}^*(\mathbf{k}) \times \sin[\tfrac{1}{2}\mathbf{k}\cdot\mathbf{r}(0,1)] \sin[\tfrac{1}{2}\mathbf{k}\cdot\mathbf{r}(0,2)],$$

and $\mathbf{g}$ are the reciprocal space vectors that have the property that $\exp[i\mathbf{g}\cdot\mathbf{r}(n)] = 1$; the sums are over i, j, l, i', j', l', σ, σ', σ'', $\mathbf{k}$, and $\mathbf{k}'$, with the restriction

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[22] Peierls in reference 9 presents a calculation of the same term in the specific heat as presented here. The presentation here evaluates Peierls' $b(\mathbf{f},s;\mathbf{f}',s';\mathbf{f}'',s'')$, Eq. (2.40), and $c(\mathbf{f},s;\mathbf{f}',s';\mathbf{f}'',s'';\mathbf{f}''',s''')$ Eq. (2.52) for the particular model used. The other new step performed in this paper and not done elsewhere is the evaluation of the complicated sums.

that $\mathbf{k}+\mathbf{k}'+\mathbf{k}''=\mathbf{g}$. The difficulty in evaluating the sums of Eq. (47) comes about because the sums over $\mathbf{k}$ and $\mathbf{k}'$ are coupled to one another by the restriction that $\mathbf{k}+\mathbf{k}'+\mathbf{k}''=\mathbf{g}$.

The second set of sums on the right hand side of the Eq. (47) will now be shown to be zero. Another property of the vectors $\mathbf{g}$ are that all physical properties that depend on $\mathbf{k}$ will be the same for wave number vectors $\mathbf{k}$ replaced by $\mathbf{k}+\mathbf{g}$.[20] In particular the second set of sums on the right-hand side of the Eq. (47) should be the same if $\mathbf{k}$ is replaced by $\mathbf{k}+\mathbf{g}$. Let $\mathbf{g}=2\pi[(\mathbf{j}-\mathbf{k})/a]$. This $\mathbf{g}$ satisfies the condition that $\exp[i\mathbf{g}\cdot\mathbf{r}(\Delta n)]=1$. From Fig. 1 it is seen that $\mathbf{r}(0,1)=(\mathbf{i}+\mathbf{j}+\mathbf{k})a/2$ and $\mathbf{r}(0,2)=(\mathbf{i}-\mathbf{j}+\mathbf{k})a/2$. As $\mathbf{k}$ is replaced by $\mathbf{k}+\mathbf{g}$, one has

$$\begin{aligned}\sin[\tfrac{1}{2}\mathbf{k}\cdot\mathbf{r}(0,1)]\sin[\tfrac{1}{2}\mathbf{k}\cdot\mathbf{r}(0,2)]\rightarrow&\\ \sin[\tfrac{1}{2}\mathbf{k}\cdot\mathbf{r}(0,1)]&\sin[\tfrac{1}{2}\mathbf{k}\cdot\mathbf{r}(0,2)-\pi]\\ &=-\sin[\tfrac{1}{2}\mathbf{k}\cdot\mathbf{r}(0,1)]\sin[\tfrac{1}{2}\mathbf{k}\cdot\mathbf{r}(0,2)].\end{aligned}$$

Thus the second set of sums changes sign under this substitution. The only way that this is possible and the sum still be invariant under the transformation $\mathbf{k}\rightarrow\mathbf{k}+\mathbf{g}$ is for the sum to be zero.

The first set of sums on the right-hand side of Eq. (47) will now be evaluated. Now

$$\frac{1}{N}\sum f(\mathbf{k},\mathbf{k}',\mathbf{k}'')e^{i(\mathbf{k}+\mathbf{k}'+\mathbf{k}'')\cdot\mathbf{r}(n)}=\sum f(\mathbf{k},\mathbf{k}',\mathbf{k}'')$$

from Eq. (39″), where the sum on the left-hand side is over $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{k}''$, that on the right-hand side over $\mathbf{k}$ and $\mathbf{k}'$ subject to the restriction that $\mathbf{k}+\mathbf{k}'+\mathbf{k}''=\mathbf{g}$. Therefore Eq. (47) can be put into the form

$$Q_1=\frac{256}{3}\frac{kTQ_0\beta^2}{M^3N^2}\sum_n\left[\sum_{\mathbf{k},\sigma}\sum_{i,i'}e^{i\mathbf{k}\cdot\mathbf{r}(n)}\times\frac{\xi_{i,\sigma}(\mathbf{k})\xi_{i',\sigma}(\mathbf{k})\sin^2[\frac{1}{2}\mathbf{k}\cdot\mathbf{r}(0,1)]}{\omega_\sigma^2(\mathbf{k})}\right]^3. \tag{48}$$

The problem is now reduced to evaluating the bracketed term of Eq. (48) raised to the third power. Multiply both sides of Eq. (44) by $e^{i\mathbf{k}\cdot\mathbf{r}(n)}$ and then sum over $\mathbf{k}$ and σ. Because $\sum_k e^{i\mathbf{k}\cdot\mathbf{r}(n)}=0$ unless $\mathbf{r}(n)=0$, one obtains

$$\frac{3NM}{2}\delta_{\mathbf{r}(n),0}=8\alpha\sum_{\mathbf{k},\sigma}\sum_{i,i'}e^{i\mathbf{k}\cdot\mathbf{r}(n)}\times\frac{\xi_{i,\sigma}^*(\mathbf{k})\xi_{i',\sigma}(\mathbf{k})\sin^2[\frac{1}{2}\mathbf{k}\cdot\mathbf{r}(0,1)]}{\omega_\sigma^2(\mathbf{k})}.$$

Equation (48) now becomes

$$Q_1=\frac{256}{3}\frac{kTQ_0\beta^2}{M^3N^2}\left(\frac{3NM}{16\alpha}\right)^3=\frac{9}{16}NkT\frac{Q_0\beta^2}{\alpha^3}. \tag{49}$$

The enthalpy of the solid becomes, using Eqs. (41), (42), (46), and (49),

$$E(T)=3NkT+\left(\frac{9}{16}\frac{\beta^2}{\alpha^3}-\frac{27}{16}\frac{\gamma}{\alpha^2}\right)N(kT)^2. \tag{50}$$

The specific heat per mole, at constant pressure, becomes

$$C_p=\frac{\partial E}{\partial T}=3R\left[1+\left(\frac{3}{8}\frac{\beta^2}{\alpha^3}-\frac{9}{8}\frac{\gamma}{\alpha^2}\right)kT\right]. \tag{51}$$

Equation (51) is the classical result for C_p. At the temperatures where the term proportional to T will be important, there will be still some small quantum effects present. These effects, being small, do not have to be known very accurately. Their effect is approximated as shown in the following equation.

$$C_p=3Rf\left(\frac{\theta}{T}\right)\left[1+\left(\frac{3}{8}\frac{\beta^2}{\alpha^3}-\frac{9}{8}\frac{\gamma}{\alpha^2}\right)kT\right], \tag{52}$$

where $f(\theta/T)$ is the Debye function given by

$$3\left(\frac{T}{\theta}\right)^3\int_0^{\theta/T}\frac{e^xx^4}{(e^x-1)^2}dx,$$

and θ is the Debye temperature.[23]

There should be some discussion why the specific heat was said to be for constant pressure and not for constant volume as is often stated elsewhere.[24] From thermodynamics

$$C_p-C_v=-T\left(\frac{\partial V}{\partial T}\right)_P^2\bigg/\left(\frac{\partial V}{\partial P}\right)_T.$$

In the harmonic approximation C_p and C_v are equal because $(\partial V/\partial T)_P$ is zero. It is usually stated[24] that the harmonic approximations to the specific heat such as the Debye and Born-von Kármán theories calculate the specific heat at constant volume, since in the aprpoximation used the volume does not change. This is not quite true since, as just pointed out, in the harmonic approximation $C_p=C_v$. The Debye and Born-von Kármán theories calculate neither C_p nor C_v but only the first approximation to both. The paper here has presented the next higher approximation to the specific heat, the first one where C_p and C_v will differ. C_p has been calculated here because the Hamiltonian that was solved [see Eqs. (1) and (2)] was for zero pressure. If C_v were to be calculated, the Hamiltonian of Eq. (3) would have to be used, with P determined by the condition that the volume remains constant. C_v calculated this way differs from C_p just as predicted from thermodynamics as shown in Appendix II.

The reason why the Debye theory usually agrees better with experimental values of C_v rather than C_p is

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[23] See reference 10, p. 110.

[24] See reference 10, pp. 136–137; reference 9, p. 39.

TABLE III. The experimental data for sodium used in calculating the parameters of the theory.[a, b] All quantities are expressed in cgs units. The units of α, β, and γ are dynes/cm, dynes/cm^2 and dynes/cm^3, respectively.

$V(0)$/mole	a	$\frac{\alpha_V(T)V(0)}{C(T)}$	$\frac{\partial\beta_s(T)}{\partial T}\frac{V(0)}{C(T)}$	$\alpha=\frac{1}{6}a(C_{11}+C_{12}+C_{44})$	β	γ
22.77[c]	4.22×10^{-8} [c]	1.92×10^{-11} [d]	1.58×10^{-21} [e]	1.17×10^{3}	-0.590×10^{11}	-0.105×10^{19}

[a] $C(T)$, the specific heat in the harmonic approximation, is assumed to have the Debye values obtained from J. A. Beattie [J. Math. and Phys. **6**, 1 (1926–1927)] using a Debye temperature of 170°K.

[b] The values for C_{11}, C_{12}, and C_{44} are given in Table II.

[c] See reference 27.

[d] S. Siegel and S. L. Quimby, Phys. Rev. **54**, 76 (1938).

[e] See reference 17.

because the term in Eq. (52) that is linear in T is usually positive, and C_p therefore usually becomes greater than the Dulong-Petit limit. C_v is always smaller than C_p and will therefore usually agree better with the Dulong-Petit value, the limiting value of the harmonic approximation.

IV. COMPARISON WITH EXPERIMENT

The theory presented above involves three parameters, α, β, and γ. Fortunately, though, the theory predicts more than three quantities and thus it can be checked against experiment. From Eq. (31)

$$\tfrac{1}{3}(C_{11}+2C_{12})=2\alpha/a.$$

Since the theory requires that $C_{11}=C_{12}=C_{44}$, α will be determined by taking an average of the experimental values of C_{11}, C_{12}, C_{44} and setting it equal to $2\alpha/a$. The parameter β is determined from experimental values of the thermal expansion by using Eqs. (18) and (29). The parameter γ is determined from experimental values of the temperature variation of the compressibility using Eq. (33). In this way one obtains

$$\beta=-\frac{4\alpha^2}{a^2}\frac{\alpha_V(T)}{C(T)}V(0), \tag{53}$$

$$\gamma=\alpha\left(\frac{4\alpha_V(T)V(0)\alpha}{a^2C(T)}\right)^2-\frac{16}{3}\frac{\alpha^3V(0)}{a^4C(T)}\left(\frac{\partial\beta_s(T)}{\partial T}-\frac{\beta_s(0)\alpha_V(T)}{3}\right). \tag{54}$$

Since sodium is the only element that satisfies the approximations made in this paper, the prediction of the theory can be compared only to the experimental measurements made on sodium. Table III gives the pertinent data and references used in determining the parameters of the theory.

Figure 2 shows the comparison between the theory [Eq. (52)] and experiment[25] of $C_p/3R$ for sodium. A Debye temperature of 160°K was assumed. The contribution of the electronic specific heat[26] was added to Eq. (52), but it gives a term linear in temperature which is only a few percent of the anharmonic contribution. The difference between the two curves is also shown. This difference does not appear to have any dependence proportional to T. The approximation used here calculates the specific heat to terms proportional to T at high temperatures. The approximations of next order would give a dependence proportional to $a_2T^2+a_3T^3+\cdots$. The theory satisfactorily agrees with experiment since the linear term in T is accounted for by the theory. Also shown in Fig. 2 is the specific heat in the harmonic approximation with the electronic specific heat added. The harmonic approximation alone fails to account for the high temperature specific heat of sodium.

Using Eq. (34) and the values in Table III, one obtains $-\Delta V/V=\beta_sP-2.07(\beta_sP)^2+5.4(\beta_sP)^3$. This theoretical curve for sodium is compared with experiment[27] in Fig. 3. The value of the compressibility used is that given in reference 27, $\beta_s=1.39\times10^{-5}$ atmos^{-1}. Curve C in Fig. 3 represents the equation $-\Delta V/V=\beta_sP$. The experimental curve A can be represented by $-\Delta V/V=\beta_sP-2.41(\beta_sP)^2+5.0(\beta_sP)^3$. The P^2 term in the theoretical expression is about 14% lower than the

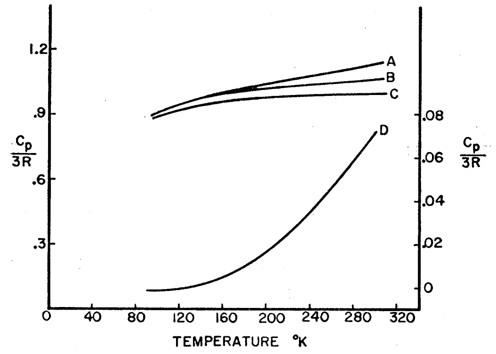

FIG. 2. $C_p/3R$ for sodium. Curve A is the experimental results.[25] Curve B is the curve,

$$\frac{C_p}{3R}=f\left(\frac{160°}{T}\right)[1+2.34\times10^{-4}T]+0.20\times10^{-4}T,$$

predicted by theory taking into account the first anharmonic contribution of the lattice and the electronic specific heat. Here $f(160°/T)$ is the Debye function for a Debye temperature of 160°K. Curve C is the curve predicted by the harmonic approximation with the electronic specific heat added. Curve D is the difference between curves A and B plotted on the expanded scale to the right.

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[25] Dauphinee, MacDonald, and Preston-Thomas, Proc. Roy. Soc. (London) **A221**, 267 (1954).

[26] See reference 10, p. 155.

[27] C. A. Swenson, Phys. Rev. **99**, 423 (1955).

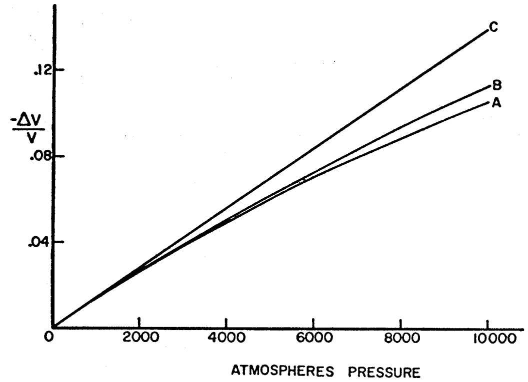

FIG. 3. $-\Delta V/V$ *vs* pressure for sodium. Curve A is the experimental results[27] which can be represented by $-\Delta V/V=\beta_sP-2.41(\beta_sP)^2+5.0(\beta_sP)^3$. Curve B is the theoretical curve $-\Delta V/V=\beta_sP-2.07(\beta_sP)^2+5.4(\beta_sP)^3$. Curve C is the curve $-\Delta V/V=\beta_sP$.

experimental value while the P^3 term is about 8% higher than experiment. Considering the approximations made in the theory, this is a satisfactory agreement between theory and experiment.

Another prediction of the theory is that the temperature derivative of the adiabatic compressibility for sodium should be proportional to the specific heat [see Eq. (33)]. By use of the measured values[17] of the temperature derivative of the compressibility in the high-temperature region where the compressibility varies linearly with temperature, and also by use of the measured value of the compressibility itself at 180°K, Eq. (33) is used to calculate the compressibility at other temperatures. As can be seen in Fig. 4, the agreement for Na is well within the experimental errors, though more precise experimental data are needed for a critical check on the theory.

V. SUMMARY

A theory is presented which correlates the thermal expansion and the temperature variation of the compressibility of the alkalis with the deviation of the specific heat from the Dulong-Petit law and the change in the volume with pressure. The theory of the temperature variation of elastic constants satisfies the condition that Lazarus[28] found experimentally must be true; the elastic constants must be both explicit functions of temperature and volume or pressure. In Eqs. (20)–(22), the δ_j's and γ_j's are functions of only the pressure, independent of the temperature, while the $n_j=1/(e^{B\hbar\omega_j}-1)$ are functions of only the temperature.

The temperature dependence of elastic constants can be understood physically. The second derivative of the energy with respect to the stress gives the elastic constant. Neglecting the zero-point energy, when a stress is applied at 0°K the problem involved is just a static one. The atoms are stationary at their equilibrium positions and the stress just changes their equilibrium positions. However, at nonzero temperatures, an applied stress will also change the vibrational energy of the solid. The second derivative of the internal energy with respect to the stress now has a part due to the vibrational energy which will depend on the temperature. This temperature-dependent part explains the temperature variation of the elastic constants. It should be noted that the temperature variation of the elastic constants is not due to thermal expansion as is sometimes mentioned in the literature. In fact, if the potential energy can be expanded in a Taylor series of only even powers of the displacements from the minimum, then the thermal expansion will be zero. However, there will still be a temperature dependence of the elastic constants since this depends on both the odd and even anharmonic terms.

The theory differs from others in that in calculating the thermal expansion and the temperature dependence of the elastic constants, the stresses are used as variables instead of the strains. This has the advantage of greatly simplifying the calculation since the stresses can be inserted directly into the Hamiltonian for the solid. In addition, the adiabatic elastic constants are calculated instead of the isothermal elastic constants. In order to facilitate the actual numerical calculations and to permit the exact summing of the complicated expressions in the specific heat calculation, special assumptions of the force constants between atoms [assumption (c)] were used. The anharmonic effects were calculated to the next higher order approximation than the harmonic approximation. Similar methods can be used to calculate still higher order approximations but those were not presented here. As far as is known to the author, this paper is the first to present an evaluation for a three-dimensional solid of the complicated sums present in the anharmonic contribution to the specific heat.

The theory is compared with experiment for the body-centered cubic alkali Na. Considering the approximations made in the theory and the uncertainties in the experimental results, the agreement with experiment is

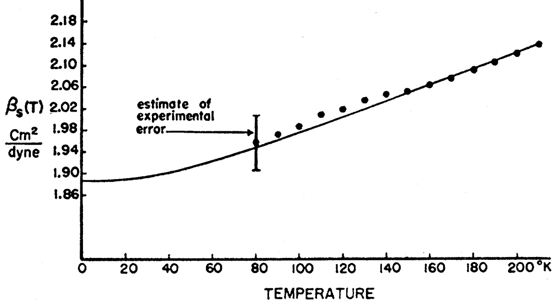

FIG. 4. The adiabatic compressibility of sodium as a function of temperature. The curve was normalized to have the same slope and value of the compressibility at high temperatures as the experimental points. The rest of the temperature dependence was calculated from Eq. (32).

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[28] See D. Lazarus, Phys. Rev. **76**, 544 (1949).

satisfactory. It is unfortunate that the experimental measurements on the alkalis are not more complete in order to permit a more complete comparison between theory and experiment. Only for Na is there a reasonably complete set of measurements and even in that case the situation is not entirely satisfactory. For instance, Swenson[27] obtains a value for the compressibility of Na at 77°K of 1.54×10^{-11} cm^2/dyne, Quimby and Siegel[17] obtain the value at 80°K of 1.96×10^{-11}, and Bender[18] obtains the value at 90°K of 1.20×10^{-11}. It is hoped that in the near future the experimental situation for the alkalis will be improved since it appears that they are one of the better structures for calculating the anharmonic effects.

APPENDIX I

Equation (18) will be shown to reduce to the Grüneisen relation, Eq. (19). The variable is changed to V, the volume, in place of the pressure P. In Eq. (18) γ_j becomes

$$\gamma_j=\left.\frac{\partial \ln\omega_j'}{\partial P}\right|_{P=0}=\frac{\partial \ln\omega_j'}{\partial V}\frac{\partial V}{\partial P}=\gamma_j'\beta_s(T),$$

where $\gamma_j'=-\partial \ln\omega_j'/\partial \ln V$ and $\beta_s(T)$ is the adiabatic compressibility. Using the approximation of the Grüneisen theory that $\gamma_j'=\gamma'$ independent of the normal mode j, Eq. (18) becomes

$$\alpha_V=\frac{\gamma'}{V(T)}\frac{\partial}{\partial T}\sum_j \beta_s(T)\frac{\hbar\omega_j}{e^{B\hbar\omega_j}-1}.$$

Within the approximations made in the calculation, the above becomes

$$\alpha_V=\gamma'\beta_T(T)C(T)/V(T),$$

the Grüneisen relation.

APPENDIX II

The Hamiltonian in Eq. (3) for pressure P can be transformed to be of the same form as the Hamiltonian of Eq. (1) for zero pressure as shown in the discussion following Eq. (11). If a is the lattice constant at zero pressure then the lattice constant changes to $a(1+\epsilon)$ under a pressure P, where ϵ is related to P by Eq. (27). The potential energy terms in the Hamiltonian of Eq. (3) are now in the same form as that in Eq. (2) with new U_0', U_{ij}', U_{ijl}', and U_{ijlm}'. In deriving $E(T)$ of Eq. (50), U_0, the zero of potential energy, was assumed zero. As shown in Eq. (8) U_0' then becomes $-\frac{1}{2}\beta_s(T)V(T)P^2$. U_{ij}' is given by Eq. (28), and U_{ijl}' and U_{ijlm}' can also be obtained in a similar manner. The $E(T)$ at pressure P can be obtained from Eq. (50) by adding U_0' and replacing α, β, and γ by $\alpha'=U_{ij}'(0,1)$, $\beta'=U_{ijl}'(0,1)$, and $\gamma'=U_{ijlm}'(0,1)$. However, since the term containing α', β', and γ' is already of order T^2, the primed quantities can be replaced by the unprimed quantities within the desired approximation. Finally,

$$E(T)=-\tfrac{1}{2}\beta_s(T)V(T)P^2+E_0(T),$$

where $E_0(T)$ is given by Eq. (50), the energy at zero pressure. P is determined by the condition that the volume remain constant. Thus, classically,

$$P\approx\frac{[V(T)-V(0)]}{\beta_s(T)V(T)}\approx\frac{T\alpha_V(T)}{\beta_s(T)}.$$

To order T^2, at high temperatures,

$$E(T)=\frac{-V(0)}{\beta_s(0)}\frac{[T\alpha_V(T)]^2}{2}+E_0(T).$$

The specific heat at constant volume is

$$C_v(T)=\frac{\partial E(T)}{\partial T}=C_p(T)-\frac{V(0)}{\beta_s(0)}T\alpha_V^2(T),$$

since $\partial E_0(T)/\partial T=C_p(T)$. Thus

$$C_p(T)-C_v(T)=TV(0)\alpha_V^2(T)/\beta_s(T).$$

This expression agrees within the approximations made with the thermodynamic relation[29]

$$C_p(T)-C_v(T)=TV(T)\alpha_V^2(T)/\beta_T(T),$$

giving added weight to the statement made in the paper that C_p was calculated and not C_v.

Note added in proof.—It is of interest to note that C_v is also not constant at high temperatures though it varies more slowly than C_p. Using the experimental values for Na one obtains classically to order T including the electronic contribution

$$C_v/3R=(1-0.40\times10^{-4}T).$$

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[29] See reference 10, p. 137.