

Anharmonic Free Energy of Crystals at Low Temperatures and at Absolute Zero*

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The method of long waves is used to show that the anharmonic contribution to the Helmholtz free energy of crystals has a lowest order temperature dependence of T^4 at low temperatures. The anharmonic correction to the low-temperature Debye temperature is obtained in terms of the ratio of the anharmonic to harmonic free energies at low temperature. Approximate expressions are developed for the anharmonic zero-point energy for the case where all atoms in the crystal have the same mass. These expressions are shown to be simply related to the corresponding anharmonic contributions to the high-temperature free energy. Numerical evaluation of these approximations is carried out for fcc and hcp lattices for a model of two-body central forces represented by a Lennard-Jones form. The various contributions to the zero-point energy are compared for these two lattices, and an application to the inert gas crystals shows that the anharmonic contribution is sufficient to make the fcc structure stable at $T=0$ for Ne and Ar, but not for Kr and Xe. An approximation is developed for the low-temperature anharmonic free energy for the case of one atom per unit cell, and this approximation is evaluated for the fcc lattice for the Lennard-Jones model. The results of the present paper are compared numerically with previously published calculations, and qualitative agreement is found in general.

I. INTRODUCTION

In a recent paper,¹ the anharmonic contributions to the Helmholtz free energy and the specific heat at constant volume of crystals at high temperatures have been discussed. The present paper is concerned with the anharmonic contributions to the zero-point energy of crystals, and to the Helmholtz free energy and the specific heat at constant volume of crystals at low temperatures. The work is based on the standard treatment of the lattice dynamics problem^{2,3} in which the potential energy of the system of vibrating ions is expanded in a Taylor series in the displacements of the ions from their equilibrium positions. The terms of third and fourth order in the displacements are treated as perturbations, and give rise to the anharmonic contributions to the Helmholtz free energy, F_3 and F_4 , respectively. These contributions have been derived by Ludwig⁴ and also by Maradudin *et al.*⁵:

$$F_3 = -(\hbar^2/16NM_c^3) \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}'', s's's''} |B_{\mathbf{k}s, \mathbf{k}'s', \mathbf{k}''s''}|^2 \\ \times (\omega_{\mathbf{k}s} \omega_{\mathbf{k}'s'} \omega_{\mathbf{k}''s''})^{-1} [(\bar{n}_{\mathbf{k}s} \bar{n}_{\mathbf{k}'s'} + \bar{n}_{\mathbf{k}s} + \frac{1}{2}) \\ \times (\omega_{\mathbf{k}s} + \omega_{\mathbf{k}'s'} + \omega_{\mathbf{k}''s''})^{-1} + (2\bar{n}_{\mathbf{k}s} \bar{n}_{\mathbf{k}'s'} - \bar{n}_{\mathbf{k}s} \bar{n}_{\mathbf{k}'s'}) \\ + \bar{n}_{\mathbf{k}'s'}] (\omega_{\mathbf{k}s} + \omega_{\mathbf{k}'s'} - \omega_{\mathbf{k}''s''})^{-1}], \quad (1.1)$$

$$F_4 = (\hbar^2/8NM_c^2) \sum_{\mathbf{k}\mathbf{k}', s's'} C_{\mathbf{k}s, -\mathbf{k}s', -\mathbf{k}'s'} \\ \times (\omega_{\mathbf{k}s} \omega_{\mathbf{k}'s'})^{-1} (\bar{n}_{\mathbf{k}s} + \frac{1}{2}) (\bar{n}_{\mathbf{k}'s'} + \frac{1}{2}), \quad (1.2)$$

where

$$B_{\mathbf{k}s, \mathbf{k}'s', \mathbf{k}''s''} = \delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}'') \sum_{n'n'', \rho\rho', \rho''} B_{n\rho, n'\rho', n''\rho''} \\ \times \exp[i\mathbf{k} \cdot \mathbf{r}_{nj} + i\mathbf{k}' \cdot \mathbf{r}_{n'j'} + i\mathbf{k}'' \cdot \mathbf{r}_{n''j''}] \\ \times v_{\mathbf{k}, \rho s} v_{\mathbf{k}', \rho' s'} v_{\mathbf{k}'', \rho'' s''}, \quad (1.3)$$

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¹ D. C. Wallace, Phys. Rev. **131**, 2046 (1963).

² M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford at the Clarendon Press, Oxford, England, 1954).

³ R. E. Peierls, *Quantum Theory of Solids* (Oxford at the Clarendon Press, Oxford, England, 1955).

⁴ W. Ludwig, J. Phys. Chem. Solids **4**, 283 (1958).

⁵ A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. (N. Y.) **15**, 337, 360 (1961).

$$C_{\mathbf{k}s, -\mathbf{k}s', \mathbf{k}'s'} = \sum_{n'n''n''', \rho\rho', \rho''} C_{n\rho, n'\rho', n''\rho''} \\ \times \exp[i\mathbf{k} \cdot (\mathbf{r}_{nj} - \mathbf{r}_{n'j'}) + i\mathbf{k}' \cdot (\mathbf{r}_{n''j''} - \mathbf{r}_{n''j''})] \\ \times v_{\mathbf{k}, \rho s} v_{-\mathbf{k}, \rho' s'} v_{\mathbf{k}', \rho'' s''}, \quad (1.4)$$

$$\delta(\mathbf{k}) = N^{-1} \sum_n \exp(i\mathbf{k} \cdot \mathbf{r}_n), \quad (1.5)$$

$$\bar{n}_{\mathbf{k}s} = [\exp(\hbar\omega_{\mathbf{k}s}/KT) - 1]^{-1}. \quad (1.6)$$

The notation used here is the same as in Ref. 1, with some additions. The symbol n labels a unit cell in the crystal, j labels an ion in the unit cell, i labels a Cartesian coordinate, and ρ stands for a pair of indices, (j, i) . There are N unit cells in the crystal, J ions per unit cell, M_j is the mass of an ion of type j , and M_c is the total mass of ions in one unit cell. The equilibrium position of ion (n, j) is $\mathbf{r}_{nj} = \mathbf{r}_n + \mathbf{r}_j$. The normal coordinates of the harmonic lattice dynamics problem are enumerated by the wave vector \mathbf{k} and the polarization index s ; the associated circular frequencies are $\omega_{\mathbf{k}s}$ and the eigenvector components are $v_{\mathbf{k}, \rho s}$. Finally, $B_{n\rho, n'\rho', n''\rho''}$ and $C_{n\rho, n'\rho', n''\rho''}$ are coefficients of terms of third and fourth order, respectively, in the potential energy expansion.

In Sec. II it is shown that F_3 and F_4 are each proportional to T^4 in the limit of low temperatures. Approximate expressions for the zero-point and low-temperature forms of F_3 and F_4 are developed in Sec. III. The zero-point approximations are evaluated in Sec. IV for face-centered cubic (fcc) and hexagonal close-packed (hcp) lattices for the case of two-body central forces represented by a Lennard-Jones form. In addition, the low-temperature approximations are evaluated for the fcc lattice for the same model. In Sec. V, the results of these calculations are applied to the inert gas crystals.

II. TEMPERATURE DEPENDENCE AT LOW TEMPERATURES

It is desired to find the lowest order temperature dependence of F_3 and F_4 at very low temperatures. The terms in (1.1) and (1.2) which are independent of

the occupation numbers \bar{n}_{ks} , etc., are zero-point contributions to the free energy. The lowest order temperature dependence arises from the terms which are linear in the occupation numbers. In (1.2), these linear terms contain the factor $\frac{1}{2}(\bar{n}_{ks} + n_{k's'})$. Since the coefficient of each such factor is symmetric in the index pairs \mathbf{k}, s and \mathbf{k}', s' , then $\frac{1}{2}(\bar{n}_{ks} + \bar{n}_{k's'})$ can be replaced by $\bar{n}_{k's'}$. Similarly in (1.1) the factors linear in the occupation numbers can be written

$$\bar{n}_{k''s''} [(\omega_{ks} + \omega_{k's'} + \omega_{k''s''})^{-1} + (\omega_{ks} + \omega_{k's'} - \omega_{k''s''})^{-1}].$$

When (1.3)–(1.5) are inserted into (1.1) and (1.2), and only terms linear in occupation numbers are kept, the following low-temperature forms are obtained.

$$\begin{aligned} F_3 = & -(\hbar^2/16N^2M^2c^3) \sum_{n \dots n^{iv}, \rho \dots \rho^v} B_{0\rho, n'\rho', n''\rho''} \\ & \times B_{0\rho''', n'''\rho^{iv}, n^{iv}\rho^v} \sum_{\mathbf{k}k', s, s'} \exp[i\mathbf{k} \cdot (\mathbf{r}_n + \mathbf{r}_j - \mathbf{r}_{j''})] \\ & \times \exp[i\mathbf{k}' \cdot (\mathbf{r}_n + \mathbf{r}_{n'j'} - \mathbf{r}_{n''j''})] v_{\mathbf{k}, \rho s} v_{-\mathbf{k}, \rho''s''} v_{\mathbf{k}', \rho's'} \\ & \times v_{-\mathbf{k}', \rho^{iv}s'} (\omega_{ks} \omega_{k's'})^{-1} \sum_{\mathbf{k}''s''} \exp[i\mathbf{k}'' \cdot (\mathbf{r}_n + \mathbf{r}_{n'j'} \\ & - \mathbf{r}_{n^{iv}j^v})] v_{\mathbf{k}'', \rho''s''} v_{-\mathbf{k}'', \rho''s''} \bar{n}_{\mathbf{k}'', s''} (\omega_{k''s''})^{-1} \\ & \times [(\omega_{ks} + \omega_{k's'} + \omega_{k''s''})^{-1} \\ & + (\omega_{ks} + \omega_{k's'} - \omega_{k''s''})^{-1}]; \quad (2.1) \end{aligned}$$

$$\begin{aligned} F_4 = & (\hbar^2/8NM^2c^2) \sum_{n' n'' n''', \rho \dots \rho'''} C_{0\rho, n'\rho', n''\rho'', n'''\rho'''} \\ & \times \sum_{\mathbf{k}, s} \exp[i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_{n'j'})] v_{\mathbf{k}, \rho s} v_{-\mathbf{k}, \rho's} (\omega_{ks})^{-1} \\ & \times \sum_{\mathbf{k}', s'} \exp[i\mathbf{k}' \cdot (\mathbf{r}_{n'j'} - \mathbf{r}_{n''j''})] \\ & \times v_{\mathbf{k}', \rho's'} v_{-\mathbf{k}', \rho''s''} \bar{n}_{\mathbf{k}', s'} (\omega_{k's'})^{-1}. \quad (2.2) \end{aligned}$$

Here the unit cell specified by $n=0$ is at the origin of coordinates ($\mathbf{r}_n=0$).

The temperature dependence of the low-temperature form of F_4 is determined by the sum over \mathbf{k}', s' . This sum is real, since for every \mathbf{k}' in the sum there is a $-\mathbf{k}'$, while in general $v_{\mathbf{k}, \rho s}^* = v_{-\mathbf{k}, \rho s}$ and $\omega_{ks} = \omega_{-ks}$. Also, at low temperatures it is only necessary to consider the long-wavelength acoustic modes in the sum, because of the factor $\bar{n}_{\mathbf{k}', s'}$. Furthermore, the method of long waves² can be used to obtain an expansion of the summand in powers of $k' = |\mathbf{k}'|$ when s' is restricted to acoustic modes; this leads to an expansion of F_4 in powers of T . Thus the exponential is expanded for $\mathbf{k}' \cdot (\mathbf{r}_{n'j'} - \mathbf{r}_{n''j''}) \ll 1$, since \mathbf{k}' is small for long wavelengths, and since the coefficient $C_{0\rho, n'\rho', n''\rho'', n'''\rho'''}$ tends to vanish for large $|\mathbf{r}_{n'j'} - \mathbf{r}_{n''j''}|$. The eigenvectors for the acoustic modes can be expanded as²

$$v_{\mathbf{k}, \rho s} = v_{0, is} + ikv_{1, \rho s} + \frac{1}{2}k^2v_{2, \rho s}, \quad (2.3)$$

to order k^2 , where v_0, v_1 , and v_2 depend on the direction of \mathbf{k} but not on the magnitude. In addition, $v_{0, is}$ depends on ρ only through the index i , but is independent of j . When the eigenvectors and the exponential are expanded in the sum over \mathbf{k}', s' in (2.2), the zeroth order term is $v_{0, i's'} v_{0, i''s''}$. This term gives no contribution to (2.2) since it is independent of n'', n''', j'', j''' , and a sum such as $\sum_{n'', j'', n''', j'''} C_{0\rho, n'\rho', n''\rho'', n'''\rho'''}$ can be extracted. But this sum vanishes identically.⁶ In addition, the

terms linear in k' give no contribution to the sum since these terms are imaginary while the sum is real. There are six terms of order k'^2 in the expansion:

$$\begin{aligned} & k'^2 v_{1, \rho''s''} v_{1, \rho''s''} \\ & k' [\mathbf{k}' \cdot (\mathbf{r}_{n'j'} - \mathbf{r}_{n''j''})] v_{0, i's'} v_{1, \rho''s''}, \\ & -k' [\mathbf{k}' \cdot (\mathbf{r}_{n'j'} - \mathbf{r}_{n''j''})] v_{1, \rho''s''} v_{0, i's'}, \quad (2.4) \\ & -\frac{1}{2} [\mathbf{k}' \cdot (\mathbf{r}_{n'j'} - \mathbf{r}_{n''j''})]^2 v_{0, i's'} v_{0, i's'}, \\ & \frac{1}{2} k'^2 v_{0, i's'} v_{2, \rho''s''}, \\ & \frac{1}{2} k'^2 v_{2, \rho''s''} v_{0, i's'}. \end{aligned}$$

The last two terms give no contribution to (2.2) for the same reason that the zeroth order term gives no contribution. The contributions of the first four terms do not vanish in general, and they give rise to a T^4 dependence for F_4 at low temperatures. This is shown by writing

$$\omega_{k's'} = c_{s'}(\Theta', \Phi')k' \quad (2.5)$$

for the acoustic phonons of small k' , where the angles Θ' and Φ' denote the direction of \mathbf{k}' . The sum over \mathbf{k}' is then transformed to an integral over all \mathbf{k}' space, and the integration on the magnitude of \mathbf{k}' is carried out. In order to state the results, it is convenient to make the following definitions.

$$G(\mathbf{r}_{nj})_{\rho\rho'} = N^{-1} \sum_{\mathbf{k}, s} \exp(i\mathbf{k} \cdot \mathbf{r}_{nj}) v_{\mathbf{k}, \rho s} v_{-\mathbf{k}, \rho's} (\omega_{ks})^{-1}; \quad (2.6)$$

$$\begin{aligned} H(\mathbf{r}_{nj})_{\rho\rho'} = & (4\pi)^{-1} \sum'_s \int d\Omega \\ & \times h(\mathbf{r}_{nj}, \Theta, \Phi)_{s, \rho\rho'} [c_s(\Theta, \Phi)]^{-5}; \quad (2.7) \end{aligned}$$

where $k'^2 h(\mathbf{r}_{n'j'} - \mathbf{r}_{n''j''}, \Theta', \Phi')_{s', \rho''\rho'''}$ is the sum of the first four terms listed in (2.4). In (2.7) the $\int d\Omega$ is over all angles (Θ, Φ) , and the prime on \sum'_s means that the sum is restricted to acoustic modes only. \mathbf{G} and \mathbf{H} are both real matrix functions. The leading term in the expansion of F_4 in powers of T at low temperatures is denoted by F_{4t} and is

$$\begin{aligned} F_{4t} = & (NV_c \pi^2/240M^2c^2) [(KT)^4/\hbar^2] \sum_{n' n'' n''', \rho \dots \rho'''} \\ & \times C_{0\rho, n'\rho', n''\rho'', n'''\rho'''} G(\mathbf{r}_j - \mathbf{r}_{n'j'})_{\rho\rho'} \\ & \times H(\mathbf{r}_{n'j'} - \mathbf{r}_{n''j''})_{\rho''\rho'''}, \quad (2.8) \end{aligned}$$

where V_c is the volume of one unit cell.

The same procedure can be applied to the sum over \mathbf{k}'', s'' in (2.1) to determine the temperature dependence of F_3 at low temperatures. This sum is also real, with the first contributing terms in the expansion of the exponential and eigenvectors again of order k''^2 , for the same reasons as above. The expansion of the exponential for $\mathbf{k}'' \cdot (\mathbf{r}_n + \mathbf{r}_{n'j'} - \mathbf{r}_{n^{iv}j^v}) \ll 1$ is justified as above, with the additional remark that when $|\mathbf{r}_n|$ becomes large, the other sums in F_3 tend to vanish because of random phases among the terms. This effect has been verified numerically in the high-temperature calculations.¹

⁶ Reference 1, Eq. (2.2).

It is also possible to show that the frequency denominators in the sum over \mathbf{k}'', s'' in (2.1) may be expanded in a power series for $\omega_{\mathbf{k}'', s''} < (\omega_{\mathbf{k}s} + \omega_{\mathbf{k}'s'})$, without introducing any error in the leading term in the low-temperature expansion of F_3 .⁷ When this is done the factor $[(\omega_{\mathbf{k}s} + \omega_{\mathbf{k}'s'} + \omega_{\mathbf{k}'', s''})^{-1} + (\omega_{\mathbf{k}s} + \omega_{\mathbf{k}'s'} - \omega_{\mathbf{k}'', s''})^{-1}]$ is replaced by $2(\omega_{\mathbf{k}s} + \omega_{\mathbf{k}'s'})^{-1}$ to obtain the leading term in the expansion of the summand in powers of k'' . Finally, (2.5) is used for $\omega_{\mathbf{k}'', s''}$, and the sum is transformed to an integral over all \mathbf{k}'' space. The leading term in the low-temperature expansion of F_3 is denoted by F_{3t} and is

$$F_{3t} = - (NV_c \pi^2 / 480 M_c^3) [(KT)^4 / \hbar^2] \sum_{n \dots n^{iv}, \rho \dots \rho^{iv}} \times B_{0\rho, n' \rho', n'' \rho''} B_{0\rho''', n''' \rho''', n^{iv} \rho^{iv}} \times K(\mathbf{r}_n + \mathbf{r}_j - \mathbf{r}_{j'''}, \mathbf{r}_n + \mathbf{r}_{n'j'} - \mathbf{r}_{n''j''})_{\rho\rho''', \rho'\rho^{iv}} \times H(\mathbf{r}_n + \mathbf{r}_{n'j'} - \mathbf{r}_{n^{iv}j^{iv}})_{\rho'\rho^{iv}}, \quad (2.9)$$

where the real matrix function \mathbf{K} is given by

$$K(\mathbf{r}_{nj}, \mathbf{r}_{n'j'})_{\rho\rho', \rho''\rho'''} = N^{-2} \sum_{\mathbf{k}\mathbf{k}', s s'} \exp(i\mathbf{k} \cdot \mathbf{r}_{nj} + i\mathbf{k}' \cdot \mathbf{r}_{n'j'}) \times \mathcal{V}_{\mathbf{k}\rho s \mathbf{v} - \mathbf{k}, \rho' s' \mathbf{v} \mathbf{k}', \rho'' s'' \mathbf{v} - \mathbf{k}', \rho''' s'''} \times \{2[\omega_{\mathbf{k}s} \omega_{\mathbf{k}'s'} (\omega_{\mathbf{k}s} + \omega_{\mathbf{k}'s'})]^{-1}\}. \quad (2.10)$$

Ludwig⁴ and Leibfried and Ludwig⁸ have approximated F_3 at low temperatures by taking $(\omega_{\mathbf{k}s} \omega_{\mathbf{k}'s'} \omega_{\mathbf{k}'', s''})^2$ out of the denominator of (2.1), averaging this separately, and putting $(\omega_{\mathbf{k}s} \omega_{\mathbf{k}'s'} \omega_{\mathbf{k}'', s''})$ back into the numerator. A similar approximation was applied to F_4 . In this manner, they arrived at a T^4 dependence for F_3 and F_4 at low temperatures. It is not certain in advance, however, that this procedure will give the correct temperature dependence, since the powers of ω in the integrals discussed above determine the temperature dependence. Indeed, if this approximation were made first and the method of long waves were applied as above, a T^6 dependence would result for F_{3t} and F_{4t} .

Barron and Klein⁹ have shown that the terms in (1.1) and (1.2) which are linear in the occupation numbers can be accounted for approximately by introducing corrections to the normal mode frequencies. Thus if the harmonic contribution to the Helmholtz free energy, F_H , is written as a sum of contributions from each normal mode, $f_H(\omega_{\mathbf{k}s})$, and if the anharmonic effects are represented by the additive corrections $\delta\omega_{\mathbf{k}s}$ to each $\omega_{\mathbf{k}s}$, then

$$F_H = \sum_{\mathbf{k}, s} f_H(\omega_{\mathbf{k}s}); \quad (2.11)$$

$$F_H + F_3 + F_4 = \sum_{\mathbf{k}, s} f_H(\omega_{\mathbf{k}s} + \delta\omega_{\mathbf{k}s}); \quad (2.12)$$

⁷ To show this, transform the sums over \mathbf{k} and \mathbf{k}' in (2.1) to integrals, expand the integrand for small k, k' , and integrate over the range $0 \leq \omega_{\mathbf{k}s} + \omega_{\mathbf{k}'s'} \leq \omega_{\mathbf{k}'', s''}$. The resulting contribution to F_3 is found to contain terms proportional to T^{10} and higher powers, by carrying out the integration over \mathbf{k}' .

⁸ G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 275.

⁹ T. H. K. Barron and M. L. Klein, *Phys. Rev.* **127**, 1997 (1962).

where

$$\delta\omega_{\mathbf{k}s} = (\delta\omega_{\mathbf{k}s})_3 + (\delta\omega_{\mathbf{k}s})_4. \quad (2.13)$$

Since $\delta\omega_{\mathbf{k}s}$ is presumably small compared to $\omega_{\mathbf{k}s}$, (2.12) can be expanded:

$$F_H + F_3 + F_4 = \sum_{\mathbf{k}, s} f_H(\omega_{\mathbf{k}s}) + \sum_{\mathbf{k}, s} \delta\omega_{\mathbf{k}s} (\partial f_H / \partial \omega_{\mathbf{k}s}) + \dots \quad (2.14)$$

Barron and Klein transformed the parts of F_3 and F_4 which are linear in the occupation numbers into the form of the first correction term in (2.14). Their results, in the present notation, are given by

$$(\delta\omega_{\mathbf{k}s})_3 = - (\hbar / 16 N M_c^3) \sum_{\mathbf{k}'\mathbf{k}'', s' s''} |B_{\mathbf{k}s, \mathbf{k}'s', \mathbf{k}''s''}|^2 \times (\omega_{\mathbf{k}s} \omega_{\mathbf{k}'s'} \omega_{\mathbf{k}''s''})^{-1} [(\omega_{\mathbf{k}'s'} + \omega_{\mathbf{k}''s''} + \omega_{\mathbf{k}s})^{-1} + (\omega_{\mathbf{k}'s'} + \omega_{\mathbf{k}''s''} - \omega_{\mathbf{k}s})^{-1}]; \quad (2.15)$$

$$(\delta\omega_{\mathbf{k}s})_4 = (\hbar / 8 N M_c^2) \sum_{\mathbf{k}', s'} C_{\mathbf{k}s, -\mathbf{k}s, \mathbf{k}'s', -\mathbf{k}'s'} \times (\omega_{\mathbf{k}s} \omega_{\mathbf{k}'s'})^{-1}. \quad (2.16)$$

Now it is well known² that the leading term in the low-temperature expansion of F_H is proportional to T^4 ; this temperature dependence results from the fact that $\omega_{\mathbf{k}s}$ is proportional to k for the long-wavelength acoustic modes. Thus, if $(\omega_{\mathbf{k}s} + \delta\omega_{\mathbf{k}s})$ is proportional to k for the long-wavelength acoustic modes, comparison of (2.11) and (2.12) shows that each term in the expansion (2.14) is proportional to T^4 at low temperatures. Hence the work of Barron and Klein shows that F_3 and F_4 are each proportional to T^4 at low temperatures if $(\delta\omega_{\mathbf{k}s})_3$ and $(\delta\omega_{\mathbf{k}s})_4$, as given by (2.15) and (2.16), are each proportional to k for the long-wavelength acoustic modes. It is possible to show, by using the method of long waves and a procedure equivalent to that used in the discussion of (2.1) and (2.2) above, that $(\delta\omega_{\mathbf{k}s})_3$ and $(\delta\omega_{\mathbf{k}s})_4$ are proportional to k for the long-wavelength acoustic modes.

To conclude this section, some low-temperature thermodynamics are discussed. The leading term in the low-temperature expansion of F_H is

$$F_{Ht} = - (NJ) (\pi^4 / 5) (KT) (T / \Theta_H)^3, \quad (2.17)$$

where the harmonic low-temperature Debye temperature Θ_H is defined by

$$(K\Theta_H)^{-3} = \frac{V_c}{72 \hbar^3 \pi^3 J} \sum' \int d\Omega [c_s(\Theta, \phi)]^{-3}. \quad (2.18)$$

The harmonic plus anharmonic contribution to the low-temperature specific heat at constant volume is

$$C_{Vt} = - (12/T) (F_{Ht} + F_{At}), \quad (2.19)$$

where

$$F_{At} = F_{3t} + F_{4t}. \quad (2.20)$$

It is convenient to define a low-temperature Debye temperature Θ_A , which includes the effect of anharmonicity, by an equation analogous to (2.17):

$$F_{Ht} + F_{At} = - (NJ) (\pi^4 / 5) (KT) (T / \Theta_A)^3. \quad (2.21)$$

Since $F_{At} \ll F_{Ht}$ is implied by the perturbation treatment of the anharmonicity, (2.17) and (2.21) can be combined to give

$$\Theta_A = \Theta_H [1 - F_{At}/3F_{Ht}], \quad (2.22)$$

to first order in (F_{At}/F_{Ht}) .

III. ZERO-POINT AND LOW-TEMPERATURE APPROXIMATIONS

In the zero-point form of F_3 , denoted by F_{30} , the sums over $\mathbf{k}s$, $\mathbf{k}'s'$, $\mathbf{k}''s''$ are all coupled through the frequency denominators. This fact makes it quite difficult to carry out an accurate evaluation of F_{30} for a three-dimensional crystal, even with the aid of present-day high-speed computers. The situation is similar in the low-temperature form F_{3t} , where the sums over $\mathbf{k}s$, $\mathbf{k}'s'$ are coupled through the frequency denominators. It is therefore desirable to approximate the zero-point and low-temperature expressions. Furthermore, it is convenient to develop the approximations by methods similar to the high-temperature approximation of Ref. 1, since this approximation proved to be simple and yet reasonably accurate, and also since the high-temperature work will be of some help in estimating the errors of the zero-point and low-temperature approximations.

Flinn and Maradudin¹⁰ have recently described a different approximation for the zero-point and low-temperature anharmonic free energy contributions for a fcc lattice with nearest-neighbor interactions. Their work, which includes a numerical evaluation of a double sum over wave vectors and polarizations, is compared with the present work in Appendix II.

For the case where all atoms of the crystal have the same mass, the high-temperature approximation was shown to be equivalent to replacing the frequency denominators of the appropriate limiting forms of (1.1) and (1.2) by their averages.¹ For simplicity, the work of this section will be restricted to this case, although this restriction is not essential. In addition, when all $M_j = M$, it is convenient to normalize the eigenvectors to unity:

$$\sum_{\rho} v_{\mathbf{k}, \rho s} v_{-\mathbf{k}, \rho s'} = \delta_{ss'} \quad (\text{orthonormality}), \quad (3.1)$$

$$\sum_s v_{\mathbf{k}, \rho s} v_{-\mathbf{k}, \rho' s} = \delta_{\rho\rho'} \quad (\text{completeness}). \quad (3.2)$$

The zero-point forms are, when all masses are the same,

$$F_{30} = -(\hbar^2/48NM^3) \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}'', s s' s''} |B_{\mathbf{k}s, \mathbf{k}'s', \mathbf{k}''s''}|^2 \times [\omega_{\mathbf{k}s} \omega_{\mathbf{k}'s'} \omega_{\mathbf{k}''s''} (\omega_{\mathbf{k}s} + \omega_{\mathbf{k}'s'} + \omega_{\mathbf{k}''s''})]^{-1}, \quad (3.3)$$

$$F_{40} = (\hbar^2/32NM^2) \sum_{\mathbf{k}\mathbf{k}', s s'} C_{\mathbf{k}s, -\mathbf{k}s', -\mathbf{k}'s'} \times (\omega_{\mathbf{k}s} \omega_{\mathbf{k}'s'})^{-1}. \quad (3.4)$$

These expressions are now approximated by replacing the denominators by their averages and carrying out the sums over the numerators. The sums of the numerators are evaluated with the aid of (1.3)–(1.5) and

(3.2), and the results are

$$f_{30} = -(N\hbar^2/144M\Omega_2\Omega_1^2) \sum_{nn', \rho\rho', \rho''} (B_{0\rho, n\rho', n'\rho''})^2, \quad (3.5)$$

$$f_{40} = (N\hbar^2/32M\Omega_1^2) \sum_{n, \rho\rho'} C_{0\rho, 0\rho', n\rho'}. \quad (3.6)$$

Here f_{30} denotes an approximation to F_{30} , and similarly for f_{40} , and

$$\Omega_{\mu} = (3JN)^{-1} \sum_{\mathbf{k}, s} M^{\mu/2} \omega_{\mathbf{k}s}^{\mu}. \quad (3.7)$$

Now the sums over B and C coefficients in (3.5) and (3.6) are the same as those which appear in f_{3T} and f_{4T} [Eqs. (4.3) and (4.4), respectively, of Ref. 1]. The further simplification of f_{30} and f_{40} for the cases of two-body forces and central forces proceeds exactly as in f_{3T} and f_{4T} , and needs no further discussion here. As a result of this similarity in the high-temperature and the zero-point approximations, the following ratios hold:

$$(f_{30}/f_{3T}) = \frac{1}{3} (f_{40}/f_{4T}) = \hbar^2 \Omega_2^2 / 12M\Omega_1^2 (KT)^2. \quad (3.8)$$

Furthermore, on account of the similarity of the approximations made in obtaining f_{3T} and f_{4T} on the one hand, and f_{30} and f_{40} on the other hand, the ratios between the zero-point and high-temperature contributions should be given quite accurately by the right-hand quantity in (3.8). Therefore it is convenient to write the approximation as

$$\begin{aligned} F_{30}/F_{3T} &\approx X, \quad F_{40}/F_{4T} \approx 3X, \\ F_{30} + F_{40} &\approx X(F_{3T} + 3F_{4T}); \\ X &= \hbar^2 \Omega_2^2 / 12M\Omega_1^2 (KT)^2. \end{aligned} \quad (3.9)$$

Thus, for example, if F_{3T} is known, the approximate F_{30} calculated from (3.9) should be more accurate than the f_{30} calculated from (3.5). Limits of error have been estimated for the ratios (3.9) for the case of two-body central forces for fcc and hcp lattices; these are discussed in Sec. IV. A further approximation may prove useful, since Ω_2 is quite easy to calculate for any force model, while the evaluation of Ω_1 is generally much more difficult. Thus Ω_1^2 may be replaced by Ω_2 without seriously affecting the accuracy of (3.9). The error of this replacement is also discussed in Sec. IV for the case of two-body central forces.

By analogy with the high-temperature and zero-point approximations, the following approximations are used to simplify the low-temperature forms of F_3 and F_4 for the case where all masses are the same:

$$M^{-1/2} G(\mathbf{r}_{nj})_{\rho\rho'} \approx \Omega_1^{-1} \delta(\mathbf{r}_{nj}) \delta_{\rho\rho'}, \quad (3.10)$$

$$\begin{aligned} M^{-3/2} K(\mathbf{r}_{nj}, \mathbf{r}_{n'j'})_{\rho\rho', \rho''\rho'''} \\ \approx (\Omega_2 \Omega_1)^{-1} \delta(\mathbf{r}_{nj}) \delta(\mathbf{r}_{n'j'}) \delta_{\rho\rho'} \delta_{\rho''\rho'''}. \end{aligned} \quad (3.11)$$

When there is more than one atom per unit cell, there is a further difficulty in trying to approximate F_{3t} and F_{4t} . This difficulty arises from the fact that the sum over polarizations in $\mathbf{H}(\mathbf{r}_{nj})$, Eq. (2.7), is restricted to acoustic modes only, and hence it is not possible to use an eigenvector completeness relation when there

¹⁰ P. A. Flinn and A. A. Maradudin, Ann. Phys. 22, 223 (1963).

are optic modes. For this reason, the remaining discussion of the low-temperature forms will be restricted to the case of one atom per unit cell.

For one atom per unit cell, the index j is dropped, and ρ becomes simply i . In addition, since the dynamical matrices are real, the eigenvectors are also real and (2.7) becomes

$$H(\mathbf{r}_n)_{ii'} = -\frac{1}{2}(4\pi)^{-1} \sum_s \int d\Omega (\hat{\mathbf{k}} \cdot \mathbf{r}_n)^2 v_{0,iss} v_{0,i's} c_s^{-5}, \quad (3.12)$$

where $\hat{\mathbf{k}}$ is a unit vector in the direction of \mathbf{k} . This matrix function may be approximated by replacing $(\hat{\mathbf{k}} \cdot \mathbf{r}_n)^2$ by its average over angles, namely $\frac{1}{3} r_n^2$, replacing c_s^{-5} by its average over s and over angles, and then carrying out the sum over s in the numerator with the aid of

$$\sum_s v_{0,iss} v_{0,i's} = \delta_{ii'}.$$

This procedure gives

$$H(\mathbf{r}_n)_{ii'} \approx -\frac{1}{6} r_n^2 C_{-5} \delta_{ii'}, \quad (3.13)$$

where

$$C_\mu = \frac{1}{3}(4\pi)^{-1} \sum_s \int d\Omega c_s^\mu. \quad (3.14)$$

This approximation to $\mathbf{H}(\mathbf{r}_n)$ gives the correct value of $\text{Tr}[\mathbf{H}(\mathbf{r}_n)]$ for primitive cubic lattices. This may be proved by noting that for a set of \mathbf{k} vectors which are related by cubic point group operations, the set of c_s are the same, while $(\hat{\mathbf{k}} \cdot \mathbf{r}_n)^2$ averages exactly to $\frac{1}{3} r_n^2$ for such a group of \mathbf{k} vectors.

With the aid of (3.10), (3.11), and (3.13), the approximations to F_{3t} and F_{4t} are, respectively,

$$f_{3t} = (NV \epsilon \pi^2 / 2880 M^{3/2}) [(KT)^4 C_{-5} / \hbar^2 \Omega_1 \Omega_2] \\ \times \sum_{nn'n''} B_{0i,ni',n'i''} B_{0i,ni',n'i''} \\ \times B_{0i,ni',n'i''} (\mathbf{r}_n - \mathbf{r}_{n'})^2, \quad (3.15)$$

$$f_{4t} = -(NV \epsilon \pi^2 / 1440 M^{3/2}) [(KT)^4 C_{-5} / \hbar^2 \Omega_1] \\ \times \sum_{nn'} C_{0i,0i,ni',n'i'} (\mathbf{r}_n - \mathbf{r}_{n'})^2. \quad (3.16)$$

If the restriction to two-body forces is made, these expressions can be reduced further with the aid of the symmetry properties of the B and C coefficients.¹ The results are

$$f_{3t} = -(NV \epsilon \pi^2 / 1440 M^{3/2}) [(KT)^4 C_{-5} / \hbar^2 \Omega_1 \Omega_2] \\ \times \sum'_n \sum'_{n'} \sum_{ii'i''} B_{0i,0i',ni',n'i''} B_{0i,0i',n'i''} \mathbf{r}_n \cdot \mathbf{r}_{n'} \\ \times [1 + \delta(\mathbf{r}_n - \mathbf{r}_{n'})], \quad (3.17)$$

$$f_{4t} = (NV \epsilon \pi^2 / 720 M^{3/2}) [(KT)^4 C_{-5} / \hbar^2 \Omega_1] \\ \times \sum'_n \sum_{ii'} C_{0i,0i,ni',n'i'} r_n^2, \quad (3.18)$$

where the prime on \sum'_n means to omit the term $n=0$ ($\mathbf{r}_n=0$). A further simplification is afforded by the fact that the contribution of each term in the \sum'_n of (3.18) is the same for all points \mathbf{r}_n which are obtained from one another by operations of the cubic point group. The same is also true of the \sum'_n of (3.17) when lattices with cubic symmetry are considered.

RESULTS FOR CENTRAL FORCES

The approximations of Sec. III have been evaluated for the case of two-body central potentials represented by a Lennard-Jones form. Thus, the potential energy between two ions a distance r apart is taken as

$$\psi(r^2) = (A_\alpha / r^\alpha) - (B_\beta / r^\beta) \quad (4.1)$$

for all pairs of ions, where A_α , B_β , α , and β are arbitrary positive constants, and $\alpha > \beta$. Calculations have been carried out for several sets of α and β for fcc and hcp lattices. The nearest-neighbor distance ϵ has been chosen as that which minimizes U_0 , the crystal potential energy when all ions are at rest and located at lattice sites. For one or two atoms per unit cell, the minimization of U_0 leads to the relations

$$U_0(\epsilon) = -NJD, \quad (4.2)$$

$$D = (\alpha - \beta) A_\alpha S_\alpha / 2\beta \epsilon^\alpha = (\alpha - \beta) B_\beta S_\beta / 2\alpha \epsilon^\beta, \quad (4.3)$$

where

$$S_\alpha = \sum'_{n,j} (\epsilon / r_{nj})^\alpha. \quad (4.4)$$

Additional relations for the Lennard-Jones model are given in Ref. 1.

All calculations were carried out in terms of dimensionless quantities, which are indicated by a superscript bar. For example

$$\bar{\Omega}_\mu = (\epsilon^2 / D)^{\mu/2} \Omega_\mu, \\ \bar{F}_{30} = (\epsilon^2 M / \hbar^2) (F_{30} / NJ), \\ \bar{F}_{40} = (\epsilon^2 M / \hbar^2) (F_{40} / NJ). \quad (4.5)$$

\bar{F}_{30} and \bar{F}_{40} are dimensionless anharmonic contributions to the zero-point energy per atom of the crystal. As a result of the transformation to dimensionless quantities, it is seen that F_{30} and F_{40} depend on ϵ and M in the manner $(\epsilon^2 M)^{-1}$, in contrast to the high-temperature contributions which do not depend explicitly on these parameters.¹ In reduced form, (3.9) becomes

$$\bar{F}_{30} / \bar{F}_{3T} \approx \bar{X}, \quad \bar{F}_{40} / \bar{F}_{4T} \approx 3\bar{X}, \quad \text{etc.}; \\ \bar{X} = \bar{\Omega}_2^2 / 12 \bar{\Omega}_1^2. \quad (4.6)$$

In the calculation of $\bar{\Omega}_1$, the dynamical matrices were diagonalized by the Jacobi method and the sum of frequencies, appropriately weighted, was carried out over a small part of the Brillouin zone.¹¹ The values of $\bar{\Omega}_1$ and $\bar{\Omega}_2$ for the fcc lattice are listed in Table I. These values are in all cases slightly larger than the correct values for the model, the error being no more than 1 part in 10^8 . Table I also lists the approximate \bar{F}_{30} and \bar{F}_{40} , as obtained from (4.6) and the corresponding accurate values of \bar{F}_{3T} and \bar{F}_{4T} from Table I of Ref. 1. The further approximation of replacing $\bar{\Omega}_1^2$ by $\bar{\Omega}_2$ would lead to the simplification of replacing \bar{X} in (4.6) by

$$\bar{X} \approx \bar{\Omega}_2 / 12. \quad (4.7)$$

¹¹ Reference 1, Sec. III.

TABLE I. Anharmonic contributions to the zero-point free energy for the face-centered cubic lattice.

| α | β | $\bar{\Omega}_1$ | $\bar{\Omega}_2$ | Approximation to | | $\delta\bar{\Omega}_1^2$ |
|----------|---------|------------------|------------------|------------------|----------------|--------------------------|
| | | | | \bar{F}_{30} | \bar{F}_{40} | |
| 12 | 10 | 8.745 | 82.69 | -13.6 | 76.9 | -0.081 |
| 12 | 8 | 7.880 | 67.31 | -11.6 | 64.3 | -0.084 |
| 12 | 6 | 6.917 | 52.10 | -9.88 | 53.2 | -0.089 |
| 12 | 4 | 5.799 | 36.93 | -8.23 | 43.3 | -0.098 |
| 10 | 8 | 7.245 | 57.05 | -9.89 | 51.9 | -0.086 ₅ |
| 10 | 6 | 6.378 | 44.45 | -8.32 | 41.6 | -0.092 ₅ |
| 8 | 6 | 5.794 | 36.89 | -6.95 | 31.5 | -0.098 ₅ |
| 6 | 4 | 4.398 | 21.76 | -4.77 | 15.7 | -0.124 ₅ |

The error of this replacement is listed in Table I in the form of

$$\delta\bar{\Omega}_1^2 = (\bar{\Omega}_1^2 - \bar{\Omega}_2) / \bar{\Omega}_1^2.$$

It is seen that $\bar{\Omega}_2$ overestimates $\bar{\Omega}_1^2$ by about 8–12%. The tabulated values of $\delta\bar{\Omega}_1^2$ are accurate to ± 0.001 , and these values are the same for the hcp lattice, for each α and β , within this error.

It is quite difficult to make a quantitatively reliable estimate of the error of the ratio F_{30}/F_{3T} as given by (3.9) or by (4.6). A qualitative estimate has been made by calculating approximately the ratio of an upper limit to a lower limit of F_{30} for the simplified case where $\omega_{ks} = ck$ for all s , with the Brillouin zone taken as a sphere. By comparing this ratio of limits to the known errors in the approximate calculation of F_{3T} ,¹ it was concluded that the correct ratio F_{30}/F_{3T} should lie between $\frac{1}{2}X$ and $\frac{3}{2}X$ for fcc and hcp lattices with central forces. The error in the ratio F_{40}/F_{4T} , as given by (3.9) or by (4.6), should not exceed 10% for fcc and hcp lattices with central forces.

It is convenient to express the results for the hcp lattice in terms of ratios to corresponding quantities for the fcc lattice. With a given amount of labor, it is generally possible to compute such ratios to greater accuracy than the separate quantities for each lattice. The parameters A_α , B_β , α , β , and M are assumed to be the same for each lattice. The ratio of nearest-neighbor distances is then obtained from (4.3) as

$$[\epsilon_h/\epsilon_f]^{\alpha-\beta} = [S_{\alpha h}S_{\beta f}/S_{\alpha f}S_{\beta h}], \quad (4.8)$$

where subscripts h and f refer to hcp and fcc lattices, respectively. The results are listed in Table II in the form of $\Delta(\epsilon)$, where

$$\epsilon_h/\epsilon_f = 1 + (10^{-6})\Delta(\epsilon). \quad (4.9)$$

This calculation is based on highly accurate S_α which have been computed in the present work. The limits of error of $\Delta(\epsilon)$ are also given; these limits depend only on the known limits of error of the S_α . The ratio of the static lattice binding energies is also obtained from (4.3) and is

$$D_h/D_f = (S_{\beta h}/S_{\beta f})(\epsilon_f/\epsilon_h)^\beta = 1 + (10^{-4})\Delta(D). \quad (4.10)$$

TABLE II. Comparison of nearest-neighbor distance and contributions to the zero-point energy for hexagonal close-packed and face-centered cubic lattices.

| α | β | $\Delta(\epsilon)$ | | $\Delta(D)$ | F_{A0h}/F_{A0f} |
|----------|---------|--------------------|-----------------|-------------|-------------------|
| | | $\Delta(\epsilon)$ | $\Delta(D)$ | | |
| 12 | 10 | -9.37 ± 0.02 | 1.466 ± 0.002 | 1.04 ± 0.02 | |
| 12 | 8 | -8.75 ± 0.01 | 1.3912 ± 0.0007 | 1.04 ± 0.02 | |
| 12 | 6 | -5.574 ± 0.006 | 1.0098 ± 0.0005 | 1.05 ± 0.02 | |
| 12 | 4 | 0.43 ± 0.05 | 0.289 ± 0.003 | 1.05 ± 0.02 | |
| 10 | 8 | -8.13 ± 0.02 | 1.342 ± 0.001 | 1.05 ± 0.02 | |
| 10 | 6 | -3.68 ± 0.01 | 0.8958 ± 0.0006 | 1.05 ± 0.02 | |
| 10 | 4 | 3.70 ± 0.06 | 0.158 ± 0.004 | ... | |
| 8 | 6 | 0.78 ± 0.02 | 0.628 ± 0.001 | 1.05 ± 0.02 | |
| 8 | 4 | 9.62 ± 0.10 | -0.079 ± 0.005 | ... | |
| 6 | 4 | 18.5 ± 0.2 | -0.432 ± 0.008 | 1.06 ± 0.03 | |

The last equality defines $\Delta(D)$; this is also listed in Table II, along with limits of error. The harmonic zero-point energy per atom of the crystal is defined as

$$E_H = (JN)^{-1} \sum_{\mathbf{k}, s} \frac{1}{2} \hbar \omega_{\mathbf{k}s}. \quad (4.11)$$

With the aid of (4.5), the appropriate ratio can be written

$$E_{Hh}/E_{Hf} = (D_h/D_f)^{1/2} (\bar{\Omega}_{1h}\epsilon_f/\bar{\Omega}_{1f}\epsilon_h). \quad (4.12)$$

The result of this calculation is

$$E_{Hh}/E_{Hf} = 1 + (2 \pm 1)(10^{-4}), \quad (4.13)$$

for all (α, β) sets considered here. Finally the ratio of $F_{A0} = F_{30} + F_{40}$ for hcp to that for fcc has been computed, based on the approximations (3.9) and the accurate high-temperature calculations.¹ The results, along with estimated limits of error, are listed in Table II.

Certain of these results are comparable with the findings of Barron and Domb.¹² These authors also found that, at vanishing pressure, D_h is greater than D_f for all except very small values of α and β , and that for $\alpha=12$, $\beta=6$, $D_h > D_f$ by 0.01%. In addition, for the (12,6) potential, they concluded that $(E_{Hh} - E_{Hf})/E_H$ is of the order of 10^{-4} , and possibly of either sign. Their analysis of E_H was based in part upon the empirical relation $E_H = (9/8)K\Theta_\infty$. The present calculations allow an accurate numerical check of this relation; this check is discussed in Appendix I.

The low-temperature approximations (3.17) and (3.18) have been evaluated for the Lennard-Jones models for the fcc lattice. The first step was to calculate the long-wavelength dynamical matrices. A straightforward expansion of the dynamical matrix $\mathbf{a}_\mathbf{k}$ [Ref. 1, Eq. (1.7)], to order k^2 , leads to the following results valid for any primitive cubic lattice²:

$$\lambda(\Theta, \phi) = \mathbf{a}_\mathbf{k}/k^2, \quad \text{to order } k^2; \quad (4.14)$$

$$\begin{aligned} [\lambda(\Theta, \phi)]_{ii} &= \lambda_1(\Theta, \phi) + \hat{k}_i^2 \lambda_2(\Theta, \phi), \\ [\lambda(\Theta, \phi)]_{i'v} &= \hat{k}_i \hat{k}_{i'} \lambda_3(\Theta, \phi), \quad i \neq i', \end{aligned} \quad (4.15)$$

¹² T. H. K. Barron and C. Domb, Proc. Roy. Soc. (London) A227, 447 (1955).

where the angles (Θ, ϕ) denote the direction of \mathbf{k} and \hat{k}_i is the i th Cartesian component of the unit vector \hat{k} . Also,

$$\begin{aligned}\lambda_1 &= \sum'_n [\phi'_{0n} r_{ni}^2 + 2\phi''_{0n} r_{ni}^2 r_{ni}^2], \quad i \neq i', \\ \lambda_2 &= 2 \sum'_n \phi''_{0n} [r_{ni}^4 - r_{ni}^2 r_{ni}^2], \quad i \neq i', \\ \lambda_3 &= 4 \sum'_n \phi''_{0n} r_{ni}^2 r_{ni}^2, \quad i \neq i'.\end{aligned}\quad (4.16)$$

Here ϕ'_{0n} is the first derivative of $\psi(r^2)$, with respect to r^2 , evaluated at $r^2 = r_n^2$, and ϕ''_{0n} is the second derivative. When ϵ is chosen so as to minimize U_0 , the sum involving ϕ'_{0n} in λ_1 vanishes for a primitive cubic lattice, and λ_3 becomes $2\lambda_1$. For the Lennard-Jones model under consideration, the λ coefficients can be obtained from the expressions

$$\lambda_1 + \lambda_2 = [\alpha\beta D/2(\alpha - \beta)] [(\alpha + 2)S_{\alpha 4} S_{\alpha}^{-1} - (\beta + 2)S_{\beta 4} S_{\beta}^{-1}], \quad (4.17)$$

$$\text{Tr}\lambda = 3\lambda_1 + \lambda_2 = D\alpha\beta/3,$$

$$\lambda_3 = 2\lambda_1,$$

where

$$S_{\alpha 4} = \sum'_n (r_{ni}/\epsilon)^4 (\epsilon/r_n)^{\alpha+4}, \quad \text{any } i. \quad (4.18)$$

The $S_{\alpha 4}$ have also been calculated in the present work. The eigenvalues of the matrix $\lambda(\Theta, \phi)$ are $M[c_s(\Theta, \phi)]^2$. The dimensionless matrices $\bar{\lambda} = D^{-1}\lambda$ were calculated as a function of (Θ, ϕ) , the matrices were diagonalized by the Jacobi method, and the averages over angles were carried out by numerical integration. Some values of the dimensionless quantities $\bar{C}_\mu = (M/D)^{\mu/2} C_\mu$ are listed in Table III; these are accurate to 1 part in 10^3 . In addition, the approximation (3.13) for the $\mathbf{H}(\mathbf{r}_n)$ matrices was checked numerically for all the (α, β) sets and for several lattice vectors \mathbf{r}_n . The approximation was found to be quite good; for example, for $\alpha = 12$, $\beta = 6$, and $\mathbf{r}_n = (\epsilon/\sqrt{2})(1, 1, 0)$, the dimensionless matrix $\bar{H}(\mathbf{r}_n) = \epsilon^{-2}(M/D)^{-5/2}\mathbf{H}(\mathbf{r}_n)$ is

$$\bar{H}(\mathbf{r}_n) = \begin{bmatrix} -0.00379 & 0.00187 & 0 \\ 0.00187 & -0.00379 & 0 \\ 0 & 0 & -0.00350 \end{bmatrix},$$

while the approximation (3.13) gives $[\bar{H}(\mathbf{r}_n)]_{ii'} \approx -0.00369\delta_{ii'}$ for \mathbf{r}_n a nearest-neighbor vector.

The sums over lattice points in (3.17) and (3.18) converge rapidly with increasing distance from the origin, and for the range of forces considered here these sums can be restricted to nearest neighbors only. The relative contribution of further distant neighbors is about 2% for the fcc lattice. After carrying out the indicated sums over nearest neighbors, the results for fcc are

$$\begin{aligned}f_{3t} &= -[N(KT)^4 V_c \epsilon^4 \pi^2 / 15 \hbar^2 M^{3/2}] (C_{-5} / \Omega_1 \Omega_2) \\ &\quad \times [150(\phi'')^2 + 120\epsilon^2 \phi'' \phi''' + 28\epsilon^4 (\phi''')^2], \quad (4.19)\end{aligned}$$

$$\begin{aligned}f_{4t} &= [N(KT)^4 V_c \epsilon^2 \pi^2 / 15 \hbar^2 M^{3/2}] (C_{-5} / \Omega_1) \\ &\quad \times [15\phi'' + 20\epsilon^2 \phi''' + 4\epsilon^4 \phi''''], \quad (4.20)\end{aligned}$$

TABLE III. Anharmonic contributions to the low-temperature free energy for the face-centered cubic lattice.

| α | β | \bar{C}_{-3} | \bar{C}_{-5} | \bar{f}_{3t} | \bar{f}_{4t} | $\bar{\Delta}\Theta_A$ |
|----------|---------|----------------|----------------|----------------|----------------|------------------------|
| 12 | 10 | 0.03785 | 0.005533 | -0.52 | 0.86 | 8.9 |
| 12 | 8 | 0.05393 | 0.01012 | -0.72 | 1.17 | 8.6 |
| 12 | 6 | 0.08536 | 0.02216 | -1.10 | 1.84 | 8.8 |
| 12 | 4 | 0.1630 | 0.06691 | -2.10 | 3.68 | 9.8 |
| 10 | 8 | 0.07239 | 0.01676 | -0.89 | 1.44 | 7.6 |
| 10 | 6 | 0.1152 | 0.03723 | -1.37 | 2.22 | 7.5 |
| 10 | 4 | 0.2219 | 0.1145 | ... | ... | ... |
| 8 | 6 | 0.1672 | 0.07100 | -1.84 | 2.89 | 6.3 |
| 8 | 4 | 0.3255 | 0.2241 | ... | ... | ... |
| 6 | 4 | 0.5363 | 0.5387 | -5.2 | 7.6 | 4.7 |

where the derivatives ϕ'' , ϕ''' , and ϕ'''' are evaluated at $r^2 = \epsilon^2$. The function of these derivatives in f_{4t} is the same as that which appears in the approximations f_{4T} and f_{40} for the fcc lattice. Equations (4.19) and (4.20) may be transformed by the introduction of dimensionless quantities, as defined above and in Ref. 1, and the dimensionless free energy contributions may be defined as

$$\bar{f}_{3t} = [\epsilon \hbar^2 D^2 / M V_c (KT)^4] (f_{3t} / N), \quad (4.21)$$

and similarly for \bar{f}_{4t} . These contributions are listed in Table III. It is estimated that the correct \bar{F}_{3t} lies within 50% of \bar{f}_{3t} , while the correct \bar{F}_{4t} lies within 30% of \bar{f}_{4t} .

The correction to the harmonic Debye temperature, due to anharmonicity, is defined by (2.22). If $\Delta\Theta_A$ is defined as

$$\Delta\Theta_A = (\Theta_A - \Theta_H) / \Theta_H, \quad (4.22)$$

then with the aid of (2.17) and (2.18), the appropriate dimensionless quantity is

$$\bar{\Delta}\Theta_A = \Delta\Theta_A [\epsilon (DM)^{1/2} / \hbar] = (10/\pi^2 \bar{C}_{-3}) (\bar{f}_{3t} + \bar{f}_{4t}). \quad (4.23)$$

This quantity is also listed in Table III for the fcc lattice. It is interesting to note that, despite the large variation of \bar{C}_{-3} , \bar{f}_{3t} , and \bar{f}_{4t} with varying α and β , $\bar{\Delta}\Theta_A$ is not very sensitive to the range of forces. In addition, the transformation to dimensionless quantities shows that $\Delta\Theta_A$ is proportional to $M^{-1/2}$.

The zero-point and low-temperature approximations of Leibfried and Ludwig¹³ can be conveniently compared to the present results. With the aid of the definitions (2.18) and (3.14), and after transforming to dimensionless quantities, their expressions for the fcc lattice can be written

$$\bar{f}_{30} = -(81/256)(3\pi^2/\bar{C}_{-3})^{2/3} DP, \quad (4.24)$$

$$\bar{f}_{40} = (81/256)(3\pi^2/\bar{C}_{-3})^{2/3} DQ, \quad (4.25)$$

$$\bar{f}_{3t} = -(81\pi^4/320\sqrt{2})(\bar{C}_{-3}/3\pi^2)^{2/3} DP, \quad (4.26)$$

$$\bar{f}_{4t} = (81\pi^4/480\sqrt{2})(\bar{C}_{-3}/3\pi^2)^{2/3} DQ. \quad (4.27)$$

¹³ Reference 8, Eqs. (12.8) and (12.9).

TABLE IV. Anharmonic contributions to the zero-point and low-temperature free energy for the face-centered cubic lattice, according to the approximation of Leibfried and Ludwig⁸ as represented by (4.24)–(4.27).

| α | β | \bar{f}_{30} | \bar{f}_{40} | \bar{f}_{3t} | \bar{f}_{4t} |
|----------|---------|----------------|----------------|----------------|----------------|
| 12 | 6 | -10.8 | 53.9 | -0.24 | 0.81 |
| 10 | 6 | -8.4 | 39.8 | -0.28 | 0.89 |

These authors have tabulated the dimensionless quantities DP and DQ (their Table XIV) for several Lennard-Jones potentials. With the aid of these tabulated values, (4.24)–(4.27) have been evaluated for the sets of α and β which correspond to those used in the present work; the results are listed in Table IV. By comparison with Table I, it is seen that the zero-point approximations of Leibfried and Ludwig agree well with the zero-point approximations of the present work. The low-temperature approximations as given by (4.26) and (4.27), however, do not agree with the present results (Table III) within the estimated limits of error of the latter. Nevertheless, the sum $\bar{f}_{3t} + \bar{f}_{4t}$, according to the approximation of Leibfried and Ludwig, differs no more than 30% from the present results for the same sum. This may be considered satisfactory agreement for the two different calculations.

V. APPLICATION TO INERT GAS CRYSTALS

The results of Sec. IV have been applied to the solidified inert gases. The constants A_α and B_β , of (4.1), have been computed for the (12,6) potential from the data in Appendix II of the article of Dobbs and Jones.¹⁴ The nearest-neighbor distance ϵ , and the several contributions to the energy at absolute zero, are listed in Table V for Ne, Ar, Kr, and Xe in the fcc structure. Table V also lists the observed nearest-neighbor distance $a_0/\sqrt{2}$, where a_0 is the cubic lattice parameter.¹⁵ The calculated ϵ agrees with the measured, within experimental error, except for Ar. In spite of this agreement, the calculated ϵ appears to show a trend of being smaller than the observed, the more so the smaller the mass. Such a trend is expected to result from the determination of ϵ by minimizing U_0 alone, instead of $U_0 + NJE_H$. This point is being checked by further calculations.

The total (positive) binding energy of the crystal at $T=0$ is

$$L_0 = NJ(D - E_H) - F_{A0};$$

this quantity is listed in Table V, along with limits of error due to the possible errors in the calculation of E_H and F_{A0} , but with no consideration of possible errors in the experimentally determined A_α and B_β . The calculated L_0 values deviate from the measured values¹⁵

¹⁴ E. R. Dobbs and G. O. Jones, Rept. Progr. Phys. **20**, 516 (1957).

¹⁵ Measured values of a_0 and L_0 are taken from Appendix I of Ref. 14.

in an apparently unsystematic way; the difference varies from $\sim 2\%$ of the observed value for Ar up to $\sim 11\%$ for Ne. The calculated differences between L_0 for the fcc lattice and L_0 for the hcp lattice are also listed in Table V, along with error limits which reflect only the possible errors in the calculation. The anharmonic contribution to the zero-point energy is sufficient to make the fcc lattice stable at $T=0$ for Ne and Ar, but not for Kr and Xe. Finally, the anharmonic corrections to the low-temperature Debye temperatures are also listed in Table V, in the form of $\Delta\theta_A$. These corrections are quite large, mainly as a result of the small binding energies of these crystals. However, an additional correction of the opposite sign should result if ϵ is made larger, by minimizing $U_0 + NJE_H$ instead of U_0 alone.

In connection with the question of the relative stability of the fcc and hcp structures at absolute zero, Jansen and Zimering¹⁶ have concluded that the stabilization of the fcc for Ne, Ar, Kr, and Xe may be explained by two and three atom exchange energies, as calculated in second-order perturbation.

VI. DISCUSSION

Several qualitative features of the approximate calculations of Sec. IV are of interest. Firstly it should be noted that, according to (1.1), F_3 is negative at all temperatures for any force model for any lattice. It is not possible to determine the sign of F_4 from the general expression (1.2). For the models for which calculations were carried out, the zero-point, low-temperature, and high-temperature contributions to F_4 are all positive and greater in magnitude than the corresponding contributions to F_3 , so that $F_3 + F_4$ is positive in all cases. This leads to a negative anharmonic specific heat at constant volume in all cases studied.

The dimensionless quantity \bar{F}_{A0} decreases markedly with increasing range of forces; this reflects the fact that the \bar{F}_{40} contribution dominates \bar{F}_{A0} . The quantity $\bar{f}_{3t} + \bar{f}_{4t}$ increases with increasing range of forces, in contrast to the zero-point and high-temperature limits.

In the zero-point anharmonic free energy, the approximations (3.9) show that F_3 contributes proportionately only one-third as much as in the high-temperature limit. This allows the possibility that the total zero-point and high-temperature contributions could have opposite sign. Since $F_{4T} > 0$ and $F_{3T} < 0$, the approximate condition for this to occur is, according to (3.9), $F_{4T} < |F_{3T}| < 3F_{4T}$. On the basis of the calculations of Ref. 1, however, it appears quite unlikely that this condition will be fulfilled, at least for fcc and hcp lattices.

The present treatment of the low-temperature limit, Sec. II, is quite different from the treatment of Leibfried and Ludwig.⁸ Although the contributions \bar{f}_{3t} and \bar{f}_{4t} , as calculated by the present approximations (Table

¹⁶ L. Jansen and S. Zimering, Phys. Letters **4**, 95 (1963).

TABLE V. Applications to the inert gas crystals. Dimensions are as follows: A_α is \AA^{12} erg, B_β is \AA^6 erg, ϵ and $a_0/\sqrt{2}$ are \AA , and all energy contributions are in cal/mole.

| Element | A_α | B_β | ϵ | $a_0/\sqrt{2}$ | D | E_H | F_{A0} | L_0 Calculated | L_0 Observed | $L_{0A} - L_{0f}$ | $\Delta\Theta_A$ |
|---------|-----------------|------------------|------------|-----------------|------|-------|----------|---------------------|-------------------|-------------------|------------------|
| Ne | $3.68(10^{-9})$ | $8.51(10^{-12})$ | 3.00 | 3.08 ± 0.11 | 610 | 187 | 23.0 | 400 ± 6 | 450 ± 10 | -1.2 ± 0.8 | 0.258 |
| Ar | $1.63(10^{-7})$ | $1.05(10^{-10})$ | 3.71 | 3.75 ± 0.01 | 2097 | 199 | 7.59 | 1890 ± 2 | 1850 ± 12 | -0.23 ± 0.27 | 0.080 |
| Kr | $5.67(10^{-7})$ | $2.28(10^{-10})$ | 4.01 | 4.02 ± 0.02 | 2841 | 148 | 3.10 | 2690 ± 1 | 2590 ± 50 | 0.10 ± 0.12 | 0.044 |
| Xe | $2.57(10^{-6})$ | $5.65(10^{-10})$ | 4.44 | 4.3 ± 0.1 | 3848 | 124 | 1.61 | 3722 ± 0.5 | 3830 ± 50 | 0.28 ± 0.07 | 0.027 |

III), are several times larger in magnitude than the corresponding results of Leibfried and Ludwig, the two methods give reasonable agreement for the sum $\bar{f}_{3t} + \bar{f}_{4t}$. This is not entirely an accident, since the treatment of Leibfried and Ludwig may be expected to underestimate each contribution, and to underestimate F_{3t} by a larger factor than F_{4t} .

Barron and Klein⁹ have pointed out that the low-temperature Debye temperature as obtained from the specific heat is the same as that which is calculated from the elastic constants at absolute zero. This is correct to the lowest order in anharmonic perturbation, since the higher order terms in the expansion (2.14) are of higher order in anharmonicity, even though these terms are each proportional to T^4 at low temperatures. It is therefore not possible to separate the harmonic and first-order-anharmonic contributions to the low-temperature free energy by comparing the Debye temperatures as determined from specific heat and from elastic constants. However, as it was shown in Sec. IV, the anharmonic correction to the low-temperature Debye temperature is proportional to $M^{-1/2}$ for one atom per unit cell. It is therefore possible, at least in principle, to separate the low-temperature harmonic and anharmonic contributions by measuring the specific heats of different isotopes of the same element.

In a recent article, Overton¹⁷ proposed an empirical expression for the anharmonic specific heat at constant volume, C_{VA} , which was assumed to be valid at all temperatures:

$$C_{VA} = C_{VH}[AT + \text{higher order terms}], \quad (6.1)$$

where C_{VH} is the harmonic lattice specific heat and A is a constant to be determined. Overton used (6.1) to investigate C_{VA} for Na and Cu, by comparing this equation with the appropriately corrected measured values of C_P at temperatures near and below the Debye temperature. Although (6.1) is correct to order T at high temperatures,¹ by virtue of the fact that C_{VH} approaches a constant at high temperatures, there is no basis for supposing that C_{VA} has a leading term which is proportional to TC_{VH} at intermediate temperatures. Indeed, at low temperatures, (6.1) is incorrect because it predicts that C_{VA} goes as T^4 when C_{VH} goes as T^3 , while in fact C_{VA} goes as T^3 at low tempera-

tures. At intermediate temperatures, the form of C_{VA} is quite complicated.

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APPENDIX I. ERRORS IN THE EMPIRICAL RELATION $E_H = (9/8)K\Theta_\infty$

Domb and Salter¹⁸ have tested the empirical relation $E_H \approx (9/8)K\Theta_\infty$ for some simple models for the three primitive cubic lattices. They concluded that the approximation can be used to calculate E_H to an accuracy of 1% for reasonable force models. The present work allows an accurate calculation of the error of this approximation for fcc and hcp lattices for the Lennard-Jones models which have been studied. From the definitions

$$E_H = (JN)^{-1} \sum_{k,s} \frac{1}{2} \hbar \omega_{ks},$$

$$K\Theta_\infty = (5/3)^{1/2} \hbar [(3JN)^{-1} \sum_{k,s} \omega_{ks}^2]^{1/2},$$

the error in the approximation may be written

$$\delta E_H = [E_H - (9/8)K\Theta_\infty] / E_H$$

$$= (\bar{\Omega}_1 - 0.96825\bar{\Omega}_2^{1/2}) / \bar{\Omega}_1.$$

This error is listed in Table VI, is accurate to ± 0.001 , and is the same for fcc and hcp within this accuracy. It is seen that δE_H is negative for the Lennard-Jones models considered, and is greater than 1% for the long-range forces.

TABLE VI. Errors in the empirical relation $E_H = (9/8)K\Theta_\infty$ for face-centered cubic and hexagonal close-packed lattices.

| α | β | δE_H |
|----------|---------|--------------|
| 12 | 10 | -0.007 |
| 12 | 8 | -0.008 |
| 12 | 6 | -0.010 |
| 12 | 4 | -0.015 |
| 10 | 8 | -0.009 |
| 10 | 6 | -0.012 |
| 8 | 6 | -0.015 |
| 6 | 4 | -0.027 |

¹⁷ W. C. Overton, Jr., J. Chem. Phys. **37**, 2975 (1962).

¹⁸ C. Domb and L. Salter, Phil. Mag. **43**, 1083 (1952).

APPENDIX II. FURTHER COMPARISONS WITH
THE LITERATURE

After the present manuscript was completed, the author's attention was drawn to a recent paper by Flinn and Maradudin.¹⁰ They have obtained approximate expressions for the zero-point and low-temperature anharmonic free energy contributions for a fcc lattice with nearest-neighbor interactions through an arbitrary central potential. Their expressions have been translated into the language of the present paper, exactly as in Ref. 1 where a similar comparison was made of the high-temperature approximations. The results of Flinn and Maradudin can be written

$$f_{30} = -(N\hbar^2\epsilon^2\Omega_1^2/M\Phi^3)(0.001037) \\ \times [9(\phi'')^2 + 12\epsilon^2\phi''\phi''' + 4\epsilon^4(\phi''')^2], \quad (\text{II1})$$

$$f_{40} = (N\hbar^2\Omega_1^2/M\Phi^2)(3/256) \\ \times [3\phi'' + 12\epsilon^2\phi''' + 4\epsilon^4\phi''''], \quad (\text{II2})$$

$$f_{3t} = -[N(KT)^4V_e\epsilon^2\pi^2/640\hbar^2M^{1/2}](0.2997C_{-3}\Omega_1/\Phi^3) \\ \times [9(\phi'')^2 + 12\epsilon^2\phi''\phi''' + 4\epsilon^4(\phi''')^2], \quad (\text{II3})$$

$$f_{4t} = [N(KT)^4V_e\pi^2/640\hbar^2M^{1/2}](C_{-3}\Omega_1/\Phi^2) \\ \times [3\phi'' + 12\epsilon^2\phi''' + 4\epsilon^4\phi''''], \quad (\text{II4})$$

where

$$\Phi = \frac{1}{2}\phi' + \epsilon^2\phi''. \quad (\text{II5})$$

There is a basic difference between the method of approximation which was used in Ref. 10 and that which has been used in the present work. Flinn and Maradudin have approximated appropriate limiting forms of (1.1) and (1.2) by omitting certain small terms in the coefficients $B_{n\rho, n'\rho', n''\rho''}$ and $C_{n\rho, n'\rho', n''\rho'', n'''\rho'''}$, while the present method has been to replace certain frequency denominators in these limiting forms by their averages. Just as in the high-temperature approximations, the two methods give very similar results for the zero-point contributions. With the aid of (3.8) and of Eqs. (4.7) and (4.8) of Ref. 1, the present approximations for the fcc lattice can be written

$$f_{30} = -(4N\hbar^2\epsilon^2/M\Omega_1^2\Omega_2) \\ \times [15(\phi'')^2 + 12\epsilon^2\phi''\phi''' + 4\epsilon^4(\phi''')^2], \quad (\text{II6})$$

$$f_{40} = (3N\hbar^2/M\Omega_1^2)[15\phi'' + 20\epsilon^2\phi''' + 4\epsilon^4\phi'''']. \quad (\text{II7})$$

The similarity of (II1) and (II6), and of (II2) and (II7), is brought out by noting that, for nearest neighbors only for the fcc lattice,

$$\Omega_2 = 16[(3/2)\phi' + \epsilon^2\phi'']. \quad (\text{II8})$$

Also $\Omega_1^2 \approx \Omega_2$, and since the ϕ' terms give relatively small contributions to Ω_2 and Φ , then $\Omega_2 \approx 16\Phi$.

TABLE VII. Anharmonic contributions to the zero-point and low-temperature free energy for the face-centered cubic lattice, according to the approximations of Flinn and Maradudin¹⁰ as represented by (II1)–(II5).

| α | α | \bar{f}_{30} | \bar{f}_{40} | \bar{f}_{3t} | \bar{f}_{4t} |
|----------|----------|----------------|----------------|----------------|----------------|
| 12 | 10 | -8.58 | 80.7 | -0.17 | 0.46 |
| 12 | 8 | -6.81 | 65.9 | -0.21 | 0.59 |
| 12 | 6 | -5.06 | 51.5 | -0.28 | 0.84 |
| 12 | 4 | -3.32 | 37.2 | -0.42 | 1.38 |
| 10 | 8 | -5.37 | 52.6 | -0.24 | 0.69 |
| 10 | 6 | -3.85 | 39.7 | -0.31 | 0.94 |
| 8 | 6 | -2.76 | 29.1 | -0.36 | 1.10 |
| 6 | 4 | -1.02 | 17.2 | -0.56 | 1.96 |

Equations (II1) and (II2) have been evaluated for the Lennard-Jones models of the present paper, and the results are listed in Table VII. The values for \bar{f}_{30} are 35–80% smaller than the approximate values of \bar{F}_{30} of Table I. This discrepancy is attributed largely to the fact that the approximate \bar{F}_{30} were calculated from (4.6) with the aid of the accurate high-temperature results, rather than from (II6). The \bar{f}_{40} as given by (II2) are generally in good agreement with the approximate \bar{F}_{40} of Table I. Finally, since the total zero-point anharmonic free energy is dominated by the \bar{F}_{40} contribution, the approximation to $\bar{F}_{30} + \bar{F}_{40}$ as given by Ref. 10 is generally in agreement with the results of Table I within the estimated error of the latter.

The low-temperature contributions (II3) and (II4) are to be compared with the expressions (4.19) and (4.20). It is difficult to make an analytic comparison, but the numerical results for (II3) and (II4) are listed in Table VII. The discrepancy between these values and the corresponding values in Table III is quite large, being a factor of ~ 2 – 3 for \bar{f}_{4t} and a factor of ~ 3 – 10 for \bar{f}_{3t} . This discrepancy may result from the basic difference between the two methods of approximation, in the following way. In the development of Sec. I above, when the exponentials and eigenvectors were expanded in powers of k , the two leading terms in the expansion gave no contribution on account of certain vanishing sums of B and C coefficients. If the B and C coefficients are approximated at this stage, however, these particular sums need not vanish.

The sum $\bar{f}_{3t} + \bar{f}_{4t}$, according to the approximation of Flinn and Maradudin, agrees qualitatively with the present results (Table III). For each α and β , this sum is smaller than the corresponding quantity computed from the values of Table III, varying from 12% smaller for $\alpha=12, \beta=10$, to 44% for $\alpha=6, \beta=4$. In addition, the approximation of Flinn and Maradudin shows the trend of increasing $\bar{f}_{3t} + \bar{f}_{4t}$ with increasing range of forces, just as does the approximation of the present paper.