whether or not these poles are present in the CPA. These aspects are presently under investigation.

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# Evaluation of the Free Energy of an Anharmonic Crystal

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The anharmonic contributions of order $\eta^4$ to the free energy of a crystal have been evaluated for a central-force nearest-neighbor model in the Ludwig approximation. The accuracy of the Ludwig approximation in evaluating the Brillouin-zone sums occurring in the expressions for the anharmonic contributions to the free energy has been investigated in some detail. It is found that the Ludwig approximation gives exact results for some simple sums. While most of the remaining sums are underestimated by about 18%, the sums occurring in the expression for the second-order quartic anharmonic contribution to the free energy are overestimated by about 20%. The coefficient of the $T^2$ term in the specific heat of lead at high temperatures is also estimated for a Morse potential and is found to be of the same order of magnitude as the experimental value obtained by Leadbetter.

## I. INTRODUCTION

A knowledge of the anharmonic contributions to the free energy is essential for an understanding of the high-temperature behavior of the specific heat of solids. Recent experiments show[1,2] that the linear and the quadratic terms in temperature are present in the expression for the specific heat at high temperatures. Leadbetter[2] has made a detailed analysis of his experimental results for the specific heat of lead and has shown that the anharmonic contribution may be written as

$$C_v^{\mathrm{anh}}/3Nk_B = AT + 2BT^2 , \qquad (1)$$

where $N$ is the number of atoms in the crystal and $k_B$ is Boltzmann's constant. The coefficients $A$ and $B$ are related to the derivatives of the crystal potential. Leadbetter has given experimental estimates for these coefficients for lead and has shown that the theoretical estimate of $A$ made earlier by Maradudin *et al.*[3] agrees quite well with the observed value. The coefficient $B$ was first estimated by the present authors[4] in a somewhat approximate manner and was found to be of the same order of magnitude as the measured value.

In order to evaluate the anharmonic contributions, the traditional approach is to use the perturbation theory. This leads to an anharmonic contribution to the free energy which is an infinite series in the perturbing potential. The perturbation is itself an infinite series expansion of the potential energy of the crystal. If we use an ordering scheme suggested by Van Hove[5] and introduce an ordering parameter $\eta$, the Hamiltonian of the crystal can be written as

$$H = H_0 + \sum_{n=1}^{\infty} \eta^n H_{n+2} , \tag{2}$$

where $H_0$ is the harmonic part. The lowest-order anharmonic contributions to the free energy are found to be of order $\eta^2$. The evaluation of the $\eta^2$ contribution has been described by Maradudin *et al.*[3] Recently, Shukla and Cowley[6] have derived expressions for all the $\eta^4$ contributions to the free energy. These contributions are responsible for the $T^2$ term in the specific heat. However, there are considerable computational difficulties in the evaluation of the $\eta^4$ contributions to the free energy since the theoretical expressions for these involve Brillouin-zone sums over three to six wave vectors and the same number of polarization indices. Though the advent of high-speed computers has made it possible to do these sums numerically, it is of interest to evaluate the sums analytically. As we shall see in Sec. III, the exact analytic solution is possible only in certain simple cases. However, the more complicated sums occurring in the expressions for the free energy can be evaluated by making an approximation which was first suggested by Ludwig.[7] In this approximation the frequencies in the first Brillouin zone are taken to be equal to an average frequency.

It is the purpose of this paper to assess the accuracy of Ludwig approximation in the evaluation of the $\eta^4$ contributions to the free energy and to estimate the coefficient of the $T^2$ term in the specific heat. It is hoped that the values of the anharmonic sums obtained here will be useful as a check on the computational results.

## II. EXPRESSIONS FOR THE ANHARMONIC CONTRIBUTIONS OF $O(\eta^4)$ TO THE FREE ENERGY

The expressions for the various anharmonic contributions may be derived using different versions of the perturbation theory. This has previously been done by several authors.[3,6,8,9] Alternatively, it is possible to derive an exact expression for the free energy of anharmonic crystal where the anharmonic terms of all orders are retained in terms of the Fourier transform of the one-phonon Green's function. Therefore, if different anharmonic contributions to the self-energy of phonons are known, the expressions for the free energy can be derived. This has previously been demonstrated by Pathak and Varshni[10] for the second-order quartic contribution which is of order $\eta^4$. The other contributions to this order can be derived using the above prescription. We shall not do this in this paper. However, for the sake of consistency we give below the expressions for the various anharmonic contributions of order $\eta^4$ to the free energy in the high-temperature limit as obtained by Shukla and Cowley[6] using the diagrammatic technique of the perturbation theory:

$$F^{(61)} = \frac{(k_B T)^3}{48N^2} \sum_{1,2,3} \frac{\phi(1,-1,2,-2,3,-3)}{(\omega_1\omega_2\omega_3)^2} , \tag{3a}$$

$$F^{(42)} \equiv F_a^{(42)} + F_b^{(42)} = -\frac{(k_B T)^3}{16N^2} \sum_{1,2,3,4} \frac{\phi(1,-1,2,3)\phi(-2,-3,4,-4)}{(\omega_1\omega_2\omega_3\omega_4)^2} \Delta(\vec{q}_2+\vec{q}_3) - \frac{(k_B T)^3}{48N^2} \sum_{1,2,3,4} \frac{\phi(1,2,3,4)\Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3+\vec{q}_4)}{(\omega_1\omega_2\omega_3\omega_4)^2} , \tag{3b}$$

$$F^{(34)} \equiv F_a^{(34)} + F_b^{(34)} = -\frac{(k_B T)^3}{16N^2} \sum_{1,2,\cdots,6} \frac{\phi(1,3,4)\phi(-1,5,6)\phi(2,-3,-4)\phi(-2,-5,-6)}{(\omega_1\omega_2\omega_3\omega_4\omega_5\omega_6)^2} \times \Delta(\vec{q}_1+\vec{q}_3+\vec{q}_4)\Delta(-\vec{q}_1+\vec{q}_5+\vec{q}_6)\Delta(\vec{q}_2-\vec{q}_3-\vec{q}_4)\Delta(\vec{q}_2+\vec{q}_5+\vec{q}_6) - \frac{(k_B T)^3}{24N^2} \sum_{1,2,\cdots,6} \frac{\phi(1,2,3)\phi(-1,4,5)\phi(-2,-5,6)\phi(-3,-4,-6)}{(\omega_1\omega_2\omega_3\omega_4\omega_5\omega_6)^2}$$

$$\times\Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\Delta(-\vec{q}_1+\vec{q}_4+\vec{q}_5)\Delta(\vec{q}_2+\vec{q}_5-\vec{q}_6)\Delta(\vec{q}_3+\vec{q}_4+\vec{q}_6)\,, \tag{3c}$$

$$F^{(31,51)}=-\frac{(k_BT)^3}{12N^2}\sum_{1,2,3,4}\frac{\phi(1,2,3)\phi(-1,-2,-3,4,-4)\Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)}{(\omega_1\omega_2\omega_3\omega_4)^2}\,, \tag{3d}$$

$$\begin{aligned}F^{(32,41)}&\equiv F_a^{(32,41)}+F_b^{(32,41)}\\&=\frac{(k_BT)^3}{8N^2}\sum_{1,2,\cdots,5}\frac{\phi(1,3,4)\phi(-2,-3,-4)\phi(-1,2,5,-5)}{(\omega_1\omega_2\omega_3\omega_4\omega_5)^2}\,\Delta(\vec{q}_1+\vec{q}_3+\vec{q}_4)\Delta(\vec{q}_2+\vec{q}_3+\vec{q}_4)\Delta(\vec{q}_1-\vec{q}_2)\\&\quad+\frac{(k_BT)^2}{8N^2}\sum_{1,2,\cdots,5}\frac{\phi(-1,-2,3)\phi(-3,-4,-5)\phi(1,2,4,5)}{(\omega_1\omega_2\omega_3\omega_4\omega_5)^2}\,\Delta(\vec{q}_1+\vec{q}_2-\vec{q}_3)\Delta(\vec{q}_3+\vec{q}_4+\vec{q}_5)\Delta(\vec{q}_1+\vec{q}_2+\vec{q}_4+\vec{q}_5)\,,\end{aligned} \tag{3e}$$

where $\phi(1, 2, \cdots, n)$ is the Fourier transform of the fourth-order derivative of the crystal potential and $i$ stands for the double suffix $(\vec{q}_i j_i)$. $F^{(ij)}$ means the contribution coming from the direct term $(H_i)^j$, and $F^{(ij,kl)}$ denotes the contribution coming from the cross term $(H_i)^j(H_k)^l$. $F^{(32,41)}$, for example, is the contribution to the free energy arising from the cubic anharmonicity in second order and the quartic anharmonicity in first order.

## III. EVALUATION OF THE BRILLOUIN-ZONE SUMS IN LUDWIG APPROXIMATION

The expressions for the free energy given by Eqs. (3) contain sums over three to six wave vectors and the same number of polarization indices. The summations have to be carried out over the first Brillouin zone. This clearly involves considerable computer time. However, if we use the Ludwig approximation,[7] the Brillouin-zone sums can be done analytically. In the Ludwig approximation each factor $1/\omega^2(\vec{q}j)$ appearing in these sums is replaced by $1/\langle\omega^2\rangle$ and taken outside the summation sign. $\langle\omega^2\rangle$ is defined by

$$\langle\omega^2\rangle=\frac{1}{3N}\sum_{\vec{q}j}\omega^2(\vec{q}j)\,. \tag{4}$$

The physical idea behind the Ludwig approximation is essentially the same as in Einstein model of a solid. To evaluate each of the contributions given by Eqs. (3), we now consider a central-force model of a face-centered-cubic lattice with nearest-neighbor interactions in the leading-term approximation. In this approximation

$$\frac{\partial^n\phi}{\partial x\partial y\cdots\partial z}\simeq\frac{xy\cdots z}{r^n}\,\phi^n\,, \tag{5}$$

where $\phi^n$ is the $n$th derivative of the potential $\phi$ with respect to the scalar distance $r$, evaluated at the nearest-neighbor distance $r_0$. Recently, Leech and Reissland[11] have estimated the magnitude of the error caused by this approximation to be about 30%. However, a considerable simplification results from this approximation and we shall make it in the present calculations. For the model we have assumed, it can be easily shown that

$$\langle\omega^2\rangle=4\phi''/M\,. \tag{6}$$

In the leading-term approximation $\phi(1, 2, \cdots, n)$ is given by[3]

$$\begin{aligned}\phi(1,2,\ldots,n)=(2M^{n/2}r_0^n)^{-1}\,\phi^n&\\\times\sum_l[\vec{r}_0^{\,l}\cdot\vec{e}(1)]\cdots[\vec{r}_0^{\,l}\cdot\vec{e}(n)]&\\\times(1-e^{-2\pi i\vec{q}_1\cdot\vec{r}_0^{\,l}})\cdots(1-e^{-2\pi i\vec{q}_n\cdot\vec{r}_0^{\,l}})\,,&\end{aligned} \tag{7}$$

where $\vec{r}_0^{\,l}=\frac{1}{2}a_0\vec{l}$ is the translation vector in the face-centered-cubic lattice and $a_0$ is the lattice parameter. $\vec{e}(\vec{q}j)$ is the polarization vector for the normal mode $(\vec{q}j)$. If the $\Delta(\vec{q})$ function appearing in Eqs. (3) is expressed as

$$\Delta(\vec{q})=\frac{1}{N}\sum_l e^{2\pi i\vec{q}\cdot\vec{r}_0^{\,l}}\,, \tag{8}$$

a considerable simplification results in the evaluation of the sums as will be seen later. The sums over $j$ in Eqs. (3) are readily carried out with the aid of the fact that

$$\sum_j[\vec{r}_0^{\,l}\cdot\vec{e}(\vec{q}j)][\vec{r}_0^{\,m}\cdot\vec{e}(\vec{q}j)]=\vec{r}_0^{\,l}\cdot\vec{r}_0^{\,m}\,. \tag{9}$$

The sums in Eqs. (3) can now be done analytically with the help of Eqs. (6)–(9). To illustrate this we discuss below the evaluation of some complicated anharmonic sums. From Eq. (3d) and Eqs. (6)–(9), we obtain

$$\begin{aligned}F^{(31,51)}=\gamma\sum_{1,2,3,4}\sum_{l,m,n}[\vec{r}_0^{\,l}\cdot\vec{e}(1)]\cdots[\vec{r}_0^{\,l}\cdot\vec{e}(3)][\vec{r}_0^{\,m}\cdot\vec{e}(1)]\cdots[\vec{r}_0^{\,m}\cdot\vec{e}(3)][\vec{r}_0^{\,m}\cdot\vec{e}(4)]^2&\\\times(1-e^{-2\pi i\vec{q}_1\cdot\vec{r}_0^{\,l}})\cdots(1-e^{-2\pi i\vec{q}_3\cdot\vec{r}_0^{\,l}})(1-e^{-2\pi i\vec{q}_1\cdot\vec{r}_0^{\,m}})\cdots(1-e^{-2\pi i\vec{q}_3\cdot\vec{r}_0^{\,m}})(1-e^{-2\pi i\vec{q}_4\cdot\vec{r}_0^{\,m}})&\end{aligned}$$

$$\times\left(1-e^{+2\pi i\vec{q}_4\cdot\vec{r}_0^{\,m}}\right)e^{2\pi i(\vec{q}_1+\vec{q}_2+\vec{q}_3)\cdot\vec{r}_0^{\,n}}\Big) , \qquad (10)$$

where

$$\gamma=-\frac{(k_BT)^3}{48\times256}\,\frac{1}{N^3r_0^8}\,\frac{\phi'''\phi^{\mathrm{v}}}{(\phi'')^4} , \qquad (11)$$

and $r_0=a_0/\sqrt{2}$ is the equilibrium separation between nearest neighbors. The advantage of expressing the $\Delta$ function in the form given by Eq. (8) is that Eq. (10) can be factorized. If we do the sum first over $j$ and then over $\vec{q}$ in Eq. (10) with the aid of the relations (8) and (9), we obtain

$$F^{(31,51)}=2\gamma N^4(\tfrac{1}{2}a_0)^8\sum_{\vec{l},\vec{m};\vec{n}}m^2[\,1-\Delta(\vec{m})]\{(\vec{l}\cdot\vec{m})$$
$$\times[\Delta(\vec{n})-\Delta(\vec{n}-\vec{l})-\Delta(\vec{n}+\vec{m})+\Delta(\vec{n}-\vec{l}+\vec{m})]\}^3 . \qquad (12)$$

In a similar fashion the expressions for $F^{(34)}$ and $F^{(32,41)}$ can be written as

$$F_a^{(34)}=-\frac{1}{(4)^{13}}N(k_BT)^3\,\frac{(\phi''')^4}{(\phi'')^6}\sum_{\vec{k},\vec{l},\vec{m},\vec{p};\vec{n}_1,\vec{n}_2}(\vec{l}\cdot\vec{m})(\vec{k}\cdot\vec{p})(\vec{l}\cdot\vec{k})^2(\vec{m}\cdot\vec{p})^2[\Delta(\vec{n}_1+\vec{n}_2)-\Delta(\vec{n}_1+\vec{n}_2+\vec{p})-\Delta(\vec{n}_1+\vec{n}_2-\vec{k})$$
$$+\Delta(\vec{n}_1+\vec{n}_2+\vec{p}-\vec{k})+\Delta(\vec{n}_1+\vec{n}_2+\vec{l}+\vec{p})-\Delta(\vec{n}_1+\vec{n}_2+\vec{l})+\Delta(\vec{n}_1+\vec{n}_2+\vec{l}-\vec{k})-\Delta(\vec{n}_1+\vec{n}_2+\vec{l}+\vec{p}-\vec{k})-\Delta(\vec{n}_1+\vec{n}_2-\vec{m})$$
$$+\Delta(\vec{n}_1+\vec{n}_2-\vec{m}+\vec{p})+\Delta(\vec{n}_1+\vec{n}_2-\vec{m}-\vec{k})-\Delta(\vec{n}_1+\vec{n}_2-\vec{m}-\vec{k}+\vec{p})+\Delta(\vec{n}_1+\vec{n}_2+\vec{l}-\vec{m})-\Delta(\vec{n}_1+\vec{n}_2+\vec{l}-\vec{m}+\vec{p})$$
$$-\Delta(\vec{n}_1+\vec{n}_2+\vec{l}-\vec{m}-\vec{k})+\Delta(\vec{n}_1+\vec{n}_2+\vec{l}-\vec{m}-\vec{n}+\vec{p})][\Delta(\vec{n}_1)-\Delta(\vec{n}_1+\vec{l})-\Delta(\vec{n}_1-\vec{k})$$
$$+\Delta(\vec{n}_1+\vec{l}-\vec{k})]^2[\Delta(\vec{n}_2)-\Delta(\vec{n}_2-\vec{m})-\Delta(\vec{n}_2+\vec{p})+\Delta(\vec{n}_2-\vec{m}+\vec{p})]^2 , \qquad (13a)$$

$$F_b^{(34)}=-\frac{2}{3\times(4)^{13}}N(k_BT)^3\,\frac{(\phi''')^4}{(\phi'')^6}\sum_{\vec{k},\vec{l},\vec{m},\vec{p};\vec{n}_1,\vec{n}_2,\vec{n}_3}(\vec{l}\cdot\vec{m})(\vec{l}\cdot\vec{k})(\vec{l}\cdot\vec{p})(\vec{m}\cdot\vec{k})(\vec{m}\cdot\vec{p})(\vec{k}\cdot\vec{p})[\Delta(\vec{n}_1)-\Delta(\vec{n}_1+\vec{l})$$
$$-\Delta(\vec{n}_1-\vec{m})+\Delta(\vec{n}_1+\vec{l}-\vec{m})][\Delta(\vec{n}_2)-\Delta(\vec{n}_2+\vec{l})-\Delta(\vec{n}_2-\vec{k})+\Delta(\vec{n}_2+\vec{l}-\vec{k})][\Delta(\vec{n}_3)-\Delta(\vec{n}_3+\vec{l})-\Delta(\vec{n}_3-\vec{p})$$
$$+\Delta(\vec{n}_3+\vec{l}-\vec{p})][\Delta(\vec{n}_1-\vec{n}_3)-\Delta(\vec{n}_1-\vec{n}_3-\vec{m})-\Delta(\vec{n}_1-\vec{n}_3+\vec{p})+\Delta(\vec{n}_1-\vec{n}_3+\vec{p}-\vec{m})][\Delta(\vec{n}_1-\vec{n}_2)-\Delta(\vec{n}_1-\vec{n}_2-\vec{m})$$
$$-\Delta(\vec{n}_1-\vec{n}_2+\vec{k})+(\vec{n}_1-\vec{n}_2+\vec{k}-\vec{m})][\Delta(\vec{n}_2-\vec{n}_3)-\Delta(\vec{n}_2-\vec{n}_3-\vec{k})-\Delta(\vec{n}_2-\vec{n}_3+\vec{p})+\Delta(\vec{n}_2-\vec{n}_3+\vec{p}-\vec{k})] , \qquad (13b)$$

$$F_a^{(32,41)}=\frac{1}{(4)^9}N(k_BT)^3\,\frac{(\phi''')^2\phi^{\mathrm{iv}}}{(\phi'')^5}\sum_{\vec{l},\vec{m},\vec{p};\vec{n}}(\vec{l}\cdot\vec{p})(\vec{m}\cdot\vec{p})(\vec{l}\cdot\vec{m})^2\{[\Delta(\vec{n})-\Delta(\vec{n}-\vec{l})$$
$$-\Delta(\vec{n}+\vec{m})+\Delta(\vec{n}+\vec{m}-\vec{l})]^3+4\Delta(\vec{p}-\vec{m}-\vec{l})+8\Delta(\vec{m}+\vec{p})\Delta(\vec{m}-\vec{l})\} , \qquad (14a)$$

$$F_b^{(32,41)}=\frac{2}{(4)^{11}}\,\frac{(\phi''')^2\phi^{\mathrm{iv}}}{(\phi'')^5}N(k_BT)^3\sum_{\vec{l},\vec{m},\vec{p};\vec{n}_1,\vec{n}_2}(\vec{l}\cdot\vec{m})^2(\vec{l}\cdot\vec{p})^2(\vec{m}\cdot\vec{p})[\Delta(\vec{n}_1)-\Delta(\vec{n}_1+\vec{m})-\Delta(\vec{n}_1-\vec{l})-\Delta(\vec{n}_1+\vec{m}-\vec{l})]^2$$
$$\times[\Delta(\vec{n}_2)-\Delta(\vec{n}_2+\vec{p})-\Delta(\vec{n}_2-\vec{l})+\Delta(\vec{n}_2+\vec{p}-\vec{l})]^2[\Delta(\vec{n}_2-\vec{n}_1)-\Delta(\vec{n}_2-\vec{n}_1+\vec{p})-\Delta(\vec{n}_2-\vec{n}_1-\vec{m})+\Delta(\vec{n}_2-\vec{n}_1+\vec{p}-\vec{m})] . \qquad (14b)$$

The sums over $\vec{n}$, $\vec{n}_1$, $\vec{n}_2$, and $\vec{n}_3$ in Eqs. (12)–(14) extend over all the atoms in the lattice, and the sums over all the other integers extend over nearest-neighbors only. When the summands in the above expressions are expanded and the sums over the various integers carried out, most of the terms vanish due to (i) the properties of $\Delta$ functions and (ii) the cubic symmetry of the lattice. For example, each term obtained after expanding the summand in Eq. (12) vanishes for $|\vec{n}|>\sqrt{8}$. The remaining contributions, $F^{(61)}$ and $F^{(42)}$, can be evaluated in a similar way. The results obtained are

$$F^{(61)}=\tfrac{1}{64}N(k_BT)^3\,\frac{\phi^{\mathrm{iv}}}{(\phi'')^3} , \qquad (15a)$$

$$F^{(42)}\equiv F_a^{(42)}+F_b^{(42)}$$
$$=-\left(\frac{120}{2048}+\frac{19}{2048}\right)N(k_BT)^3\,\frac{(\phi^{\mathrm{iv}}\ )^2}{(\phi'')^4} , \qquad (15b)$$

$$F^{(34)}\equiv F_a^{(34)}+F_b^{(34)}$$
$$=-\left(\frac{2049}{(4)^9}+\frac{480}{(4)^9}\right)N(k_BT)^3\,\frac{(\phi''')^4}{(\phi'')^6} , \qquad (15c)$$

$$F^{(31,51)}=-\tfrac{3}{128}N(k_BT)^3\,\frac{\phi'''\phi^{\mathrm{v}}}{(\phi'')^4} , \qquad (15d)$$

$$F^{(32,41)}\equiv F_a^{(32,41)}+F_b^{(32,41)\prime}$$
$$=\left(\frac{684}{(4)^7}+\frac{255}{(4)^7}\right)N(k_BT)^3\,\frac{\phi^{\mathrm{iv}}\ (\phi^{\mathrm{iv}})^2}{(\phi'')^5} . \qquad (15e)$$

In Sec. IV we shall use the above results to estimate the coefficient of $T^2$ term in the specific heat of lead.

## IV. $T^2$ CONTRIBUTION TO THE SPECIFIC HEAT AT HIGH TEMPERATURES

In order to have a numerical estimate of the $T^2$ term in the specific heat at high temperatures we choose here a Morse potential to represent the interaction between atoms. This can be written as

$$\phi(r) = D(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}) , \tag{16}$$

where $\alpha$ and $D$ are parameters which have been determined by Girifalco and Weizer[12] for a number of crystals. Substituting $\phi''$ from Eq. (16) in Eqs. (15), we obtain for the total anharmonic contribution of order $\eta^4$ to the free energy in the Ludwig approximation (LA):

$$F = -SN(k_B T)^3/D^2 , \tag{17}$$

where

$$S = 0.266 . \tag{18}$$

However, if we use the values of the sums in Eqs. (3) as obtained by Shukla and Cowley,[6] we have

$$S = 0.137 . \tag{19}$$

To compare the Ludwig-approximation results with the computed results we have listed the individual contributions to free energy of a crystal to order $\eta^4$ in Table I. The first column in the table depicts the various anharmonic contributions. The second column gives the results obtained from the Ludwig approximation. The numbers in the third column are based on the computed values[3,6] of the anharmonic sums. The fourth column gives the percentage deviation of the Ludwig-approximation result from the computational result. The $\eta^2$ contributions, $F^{(41)}$ and $F^{(32)}$, that were obtained by Maradudin *et al.*[3] have also been listed in Table I for the sake of completeness. The $\eta^2$ and $\eta^4$ contributions are expressed in the units of $N(k_B T)^2/D$ and $N(k_B T)^3/D^2$, respectively.

It is evident from the table that the Ludwig approximation gives exact results for $F^{(41)}$ and $F^{(61)}$, and it underestimates the magnitudes of most of the remaining anharmonic contributions by about 18%. However, the Ludwig approximation overestimates the magnitudes of $F_a^{(42)}$ and $F_b^{(42)}$ by about 20%. Though the Ludwig approximation underestimates the magnitudes of most of the anharmonic sums the magnitude of the total anharmonic contribution of order $\eta^4$ is overestimated.

From Eqs. (1) and (17), the coefficient of the $T^2$ term in the specific heat at high temperatures can now easily be seen to be

$$2B = 2Sk_B^2/D^2 . \tag{20}$$

TABLE I. Anharmonic contributions to the free energy for a Morse potential.

| Various contributions | LA | Computed values | % deviation |
|---|---|---|---|
| $F^{(41)}$ | 0.6562 | 0.6562 | 0 |
| $F^{(32)}$ | −0.2109 | −0.2524 | −16 |
| $F^{(61)}$ | 0.1211 | 0.1211 | 0 |
| $F_a^{(42)}$ | −0.7177 | −0.5742 | +25 |
| $F_b^{(42)}$ | −0.1137 | −0.0996 | +15 |
| $F_a^{(34)}$ | −0.1583 | −0.1936 | −18 |
| $F_b^{(34)}$ | −0.0371 | −0.0466 | −20 |
| $F^{(31,51)}$ | −0.2632 | −0.3155 | −16 |
| $F_a^{(32,41)}$ | 0.6564 | 0.6626 | −1 |
| $F_b^{(32,41)}$ | 0.2457 | 0.3087 | −20 |

For lead if we use the value of the parameter $D = 3.76\times10^{-13}$ erg as calculated by Girifalco and Weizer,[12] we obtain from Eqs. (18)–(20)

$$B = 3.5\times10^{-8}\,{}^\circ\mathrm{K}^{-2} \text{ LA}$$
$$= 1.8\times10^{-8}\,{}^\circ\mathrm{K}^{-2} \text{, computed.} \tag{21}$$

The experimental value of $B$ obtained by Leadbetter[2] is $6\times10^{-8}\,{}^\circ\mathrm{K}^{-2}$. Considering the uncertainty involved in the experimental value and the approximate nature of the model used in the calculations, the agreement between the measured and the estimated values may be said to be satisfactory.

It is of interest to compare the relative magnitudes of the $T^2$ and $T$ terms in the specific heat of lead in the high-temperature region. From Eq. (1) and the values of the $\eta^2$ contributions, $F^{(41)}$ and $F^{(32)}$, given in Table I, the coefficient of the $T$ term in the specific heat is

$$A = -1.1\times10^{-4}\,{}^\circ\mathrm{K}^{-1} \text{ LA}$$
$$= -1.0\times10^{-4}\,{}^\circ\mathrm{K}^{-1} \text{ computed.} \tag{22}$$

Using the values of $B$ and $A$ from Eqs. (21) and (22), we obtain the following for the ratio of the two anharmonic contributions to the specific heat:

$$2BT/A = -6.4\times10^{-4}T \text{ LA}$$
$$= -3.6\times10^{-4}T \text{ computed.} \tag{23}$$

Since for lead the Debye temperature is about 95 °K and the melting point is about 600 °K, we choose here $T = 500$ °K. At this temperature the ratio in Eq. (23) comes out to be −0.38 in Ludwig approximation. However, if the computed values of the anharmonic sums are used, the ratio is −0.18. In any case we find that the $T^2$ contribution to the specific heat is quite significant at high temperatures, in agreement with the conclusions of Leadbetter.[2]

## V. CONCLUSION

In this paper we have used the Ludwig approximation to evaluate the sums in the expressions for the anharmonic contributions of order $\eta^4$ to the free energy of a face-centered-cubic lattice with nearest-neighbor central-force interactions in the high-temperature limit. The Ludwig approximation has offered a considerable simplification and we have been able to do the sums analytically. As we saw in Sec. IV, the Ludwig approximation gives exact values of some of the anharmonic sums and it underestimates the magnitudes of most of the other sums by about 18%. However, the magnitude of the second-order quartic anharmonic contribution is overestimated by about 20%. Though the Ludwig approximation gives a good estimate of the of the $\eta^2$ contribution, it overestimates the $\eta^4$ contribution by a factor of 1.9. The main advantage of this approximation lies in the fact that we can do the summations analytically. The Ludwig approximation, therefore, could serve as a check on the computed values of the anharmonic sums.

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# Relativistic Energy Band Structure and Properties of $\gamma$-Uranium*

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The electronic band structure of the high-temperature phase of uranium has been determined by means of the symmetized relativistic augmented-plane-wave method. Six different crystal potentials (three atomic starting configurations, $5f^4\,7s^2$, $5f^3\,6d^1\,7s^2$, and $5f^2\,6d^2\,7s^2$, each taken together with $\alpha = 2/3$ and $\alpha = 1$ approximations for exchange) were employed in the warped-muffin-tin approximation. The relativistic effects are found to be very important and result in $5f$ bands which overlap and hybridize strongly with the very broad "$7s$-$p$" and broad $6d$ bands (which in the absence of the $5f$ states are found to be those typical of a high-atomic-number transition metal). The nonrelativistic energy bands are found to be incorrect in many ways. A calculated density of states shows considerable structure reflecting the $s$-$d$-$f$ hybridization and a relatively high density of states (1.45 states per atom eV) at the Fermi energy. The Fermi surface is found to be complicated and to consist of two hole and one electron surfaces.

## I. INTRODUCTION

Of all the actinide metals, uranium is perhaps the most famous because of its early unique role in the field of atomic energy. As with the other actinides, its unusual electronic properties—ranging from magnetism (especially in the case of its dilute alloys and intermetallics) to superconductivity (when subjected to pressure at low temperature)—are not well known and even less well understood.[1,2] One major difficulty, both for the experimentalist and the theorist, is the large number of crystallographic transformations which the metal undergoes as a function of temperature and pressure; in addition to the three well-known phases—the orthorhombic phase, called $\alpha_0$ ($T < 940$ K), the tetragonal $\beta$ phase ($940 < T < 1048$ K), and the body-centered-cubic $\gamma$ phase ($T > 1048$ K) which exists up to the melting point at 1405 K—there are several other transformations all in a small range of temperature around 43 K. The high-temperature $\gamma$ phase, the simplest modifica-