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Convergence of the quartic anharmonic contribution to the Helmholtz free energy in metals

R. C. Shukla
Physics Department, Brock University, St. Catharines, Ontario L2S 3A1, Canada
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The convergence of the quartic term of the Helmholtz free energy (F_4) in metals is investigated by comparing the numerical results of F_4 by two methods. In the first method, F_4 is calculated by summing over the direct lattice vectors of the product of the fourth-rank tensor derivatives of a two-body potential and correlation functions involving Brillouin-zone and branch-index summations. In the second method, F_4 is calculated from an alternative expression which requires beforehand the knowledge of wave-vector-dependent fourth-rank tensors. The alternative expression for F_4, which is derived in this paper, is more appropriate for the calculation of F_4 in metals where the forces are long range and oscillatory. Calculations are carried out by the two methods, for different volumes, from almost 0 K to the melting temperature range for Na and K using the same first-principle potential as used by Shukla and Taylor in their previous calculations of F_4. Representing the F_4 results of the two methods by $F_4(s)$, where s is the shell index at which the $\vec{l}$ summation is truncated in the first method and F_4 (Ewald), we find the two methods giving the same answer for F_4 only in some cases. For example, in Na, F_4 (Ewald) agrees exactly with $F_4(s)$, where $s = 18$, at the 90-K volume. The agreement between the two is almost exact at 160-K and 361-K volumes with $s = 17$ and 10, respectively. At the other two volumes referred to $T = 5$ and 293 K, F_4 (Ewald) and $F_4(s)$ differ by about 1% where $s = 22$ and 21, respectively, for these volumes. In K, F_4 (Ewald) and $F_4(s)$ differ by less than 1% in each case for the three volumes corresponding to temperatures 9, 215, and 299 K where for each of these volumes $s = 15$, 7, and 10, respectively. The largest disagreement between F_4 (Ewald) and $F_4(s)$ ($s = 7$) arises for the volume at 99 K. In this case they differ by 3%. It is clear from the above discussion that F_4 (Ewald) and $F_4(s)$ are in agreement with each other for "some" shell index s, but s changes with volume. Thus, without *a priori* knowledge of an exact value of F_4, such as the one obtained by the Ewald procedure, one cannot decide the shell index (s) at which the summation in the first method should be truncated to obtain a correct answer for F_4.

I. INTRODUCTION

In recent years, several anharmonic calculations have been reported in the literature for metallic crystals. For example, the phonon frequency shifts (Δ) and widths (Γ) have been calculated for aluminum,[1] sodium,[2] potassium,[3] rubidium,[4] and lithium.[5] The two lowest-order terms of the Helmholtz free energy, commonly known as the cubic (F_3) and quartic (F_4) terms, and their contributions to the specific heat at constant volume (C_v^A) have been calculated in sodium,[6,7] potassium,[7] rubidium,[4,8] and copper.[9]

In all of these calculations, the anharmonic coefficients, which are Fourier transforms of the third- and fourth-rank tensors, have been obtained from the Cartesian tensor derivatives of a two-body potential, $V(r)$. In different calculations, the real-space summations arising in these Fourier transforms were truncated at the various neighbor positions. For example, Koehler *et al.*[1] have truncated the above-mentioned sums at the eighth-neighbor distance in their calculations of Δ and Γ for Al, whereas in the calculations of Δ and Γ for Na and K, these sums were truncated at the 19th-neighbor distance.[2,3] It is not clear in all the above-cited references how many neighbors should be included in the various calculations of Δ and Γ or F_3 and F_4 for a satisfactory convergence. In fact, these sums are truncated with as few as two-neighbor distances[4] (in Rb) to as many as 23-neighbor distances[7] (in Na and K).

Shukla and Taylor[7] pointed out the difficulty of convergence in the above-mentioned sums in their calculations of F_3 and F_4 for Na and K. For example, Shukla and Taylor[7] found that F_3 converged reasonably well because it comes in as squared, but F_4 oscillated sometimes quite wildly; even when the summations were taken out to the 23rd shell, no convergence was found.

This difficulty of convergence of F_4 is a typical one in metals and is in fact one of the major problems in the anharmonic calculations in metals where the potential is a long-range and oscillatory type. For instance, both the Na and K potentials show an asymptotic behavior of the form[3,10] $V_{\text{asym}} = [\cos(2k_F r + \theta)]/r^5$, where k_F is the Fermi radius and θ is the phase factor. As mentioned before, since the anharmonic coefficients contain the derivatives of the potential function, the nth derivative of these potentials will also contain a term of the same form. Now for a given neighbor distance from the origin, r_n, the number of neighbors situated at this distance, is roughly proportional to r_n^2 for large r_n. Thus we can expect that for an anharmonic property which is directly proportional to these derivatives (such as F_4 and the quartic phonon frequency shift Δ_4), the corresponding contributions from the individual neighbor shells will show roughly an r_n^{-3} dependence, which of course gives rise to rather slow convergence. This dependence of F_4 and Δ_4 in some metals will be like $1/r$ if $V_{\text{asym}}=[\cos(2k_F r+\theta)]/r^3$. In such circumstances, a brute-force summation approach instead of the Ewald method of evaluating the anharmonic Fourier coefficients is bound to be unsatisfactory and not very reliable. This was clearly demonstrated by the F_4 calculations of Shukla and Taylor.[7]

The purpose of this paper is to calculate F_4 in metals by an alternative procedure where the anharmonic coefficient Fourier transforms can be calculated to any desired degree of accuracy and thus avoid the whole question of the truncation of sums mentioned previously. This necessitates another derivation of the expression for F_4. The expression for F_4 derived by Shukla and Taylor[7] is not suitable for the purposes of this paper.

The theory needed in the derivation of an alternative expression for F_4 is presented in Sec. II. The numerical method of calculating F_4 from the expression derived in Sec. II is presented in Sec. III. A discussion and comparison of the numerical results of F_4 for Na and K for different volumes, obtained by the present method, and the method used previously by Shukla and Taylor,[7] is presented in Sec. IV. The summary and conclusions of this work are contained in Sec. V.

II. THEORY

The quartic contribution to the Helmholtz free energy is given by[11-14]

$$F_4=\frac{\hbar^2}{32N}\sum_{\vec{q}_1 j_1}\sum_{\vec{q}_2 j_2}\Phi(\vec{q}_1 j_1,\vec{q}_2 j_2,-\vec{q}_1 j_1,-\vec{q}_2 j_2)\frac{N(\vec{q}_1 j_1)}{\omega(\vec{q}_1 j_1)}\,\frac{N(\vec{q}_2 j_2)}{\omega(\vec{q}_2 j_2)}\,, \tag{1}$$

where, in Eq. (1), $\omega(\vec{q}j)$ are the eigenvalues associated with the wave vector ($\vec{q}$) and branch-index (j) normal mode of vibration, N is the number of unit cells in the crystal, $\hbar$ is Planck's constant divided by 2π, $N(\vec{q}j)=\coth[\frac{1}{2}\beta\hbar\omega(\vec{q}j)]$, $\beta=[k_BT]^{-1}$, k_B is the Boltzmann constant, T is the absolute temperature, $\vec{q}_1 j_1$ and $\vec{q}_2 j_2$ denote the double Brillouin zone (BZ) and branch-index summations, and $\Phi(\vec{q}_1 j_1,\ \vec{q}_2 j_2,\ -\vec{q}_1 j_1,\ -\vec{q}_2 j_2)$ is the Fourier transform of the fourth-rank-tensor atomic force constant $\phi_{\alpha\beta\gamma\delta}(|\vec{r}^{\,l}|)$. It is defined by

$$\Phi(\vec{q}_1 j_1,\vec{q}_2 j_2,-\vec{q}_1 j_1,-\vec{q}_2 j_2)=\frac{2}{M^2}\sum_{\vec{l}}{}'\sum_{\alpha\beta\gamma\delta}\phi_{\alpha\beta\gamma\delta}(|\vec{r}^{\,l}|)e_\alpha(\vec{q}_1 j_1)e_\beta(\vec{q}_2 j_2)e_\gamma(\vec{q}_1 j_1)e_\delta(\vec{q}_2 j_2)$$
$$\times(1-\cos\vec{q}_1\cdot\vec{r}^{\,l})(1-\cos\vec{q}_2\cdot\vec{r}^{\,l})\,, \tag{2}$$

where, in Eq. (2), $\vec{r}^{\,l}=\frac{1}{2}a\vec{l}$, a is the lattice constant, $\vec{l}$ is the direct lattice vector with integer components which are either all odd or all even for a bcc lattice and whose sum is even for fcc lattice, the prime over the $\vec{l}$ summation sign indicates the omission of $\vec{l}=\vec{0}$ term from that sum, M is the atomic mass, $e_\alpha(\vec{q}j)$ is the αth component of the eigenvector $\vec{e}\cdot(\vec{q}j)$ corresponding to the mode $\vec{q}j$, and the $\alpha,\beta,\gamma,\delta$ indices are assigned the Cartesian values x,y,z, respectively which produces 81 components of the fourth-rank tensor $\phi_{\alpha\beta\gamma\delta}(|\vec{r}^{\,l}|)$.

Since it is impossible to obtain all the 81 components of $\phi_{\alpha\beta\gamma\delta}(|\vec{r}^{\,l}|)$ from some general force model, we obtain them from a two-body potential $\phi(|\vec{r}^{\,l}+\vec{u}|)$ by differentiating it with respect to the displacement vector $\vec{u}$ and setting $\vec{u}=\vec{0}$ after differentiation, i.e.,

$$\phi_{\alpha\beta\gamma\delta}(|\vec{r}^{\,l}|)=\left.\frac{\partial^4\phi(|\vec{r}^{\,l}+\vec{u}|)}{\partial u_\alpha\partial u_\beta\partial u_\gamma\partial u_\delta}\right|_{\vec{u}=\vec{0}} \tag{3}$$

In simple metals with small ion cores (Na, K, Al, etc.), the two-body potential $\phi(|\vec{r}^{\,l}|)$ is defined by[15]

$$\phi(r)=\frac{z^2e^2}{r}-\frac{4\pi e^2}{(2\pi)^3}\iiint\frac{G(|\vec{Q}|)}{|\vec{Q}|^2}\exp(i\vec{Q}\cdot\vec{r})d^3Q\,, \tag{4}$$

where, in Eq. (4), $G(|\vec{Q}|)$ is the electron-ion matrix element with the proper screening function including the exchange and correlation effects, z is the valence, and e is the charge of the electron.

Setting aside for a moment the derivation of F_4 from the potential given by Eq. (4), let us briefly see the cause of oscillation in F_4 mentioned previously in Sec. I. Substituting Eq. (2) into Eq. (1) and isolating the BZ and j sums, F_4 can be expressed as

$$F_4=\frac{\hbar^2}{16NM^2}\sum_{\vec{l}}{}'\sum_{\alpha\beta\gamma\delta}\phi_{\alpha\beta\gamma\delta}(|\vec{r}^{\,l}|)S_{\alpha\beta}(\vec{l})S_{\gamma\delta}(\vec{l})\,, \tag{5}$$

where

$$S_{\alpha\beta}(\vec{l})=\sum_{\vec{q}j}\frac{e_\alpha(\vec{q}j)e_\beta(\vec{q}j)}{\omega(\vec{q}j)}N(\vec{q}j)(1-\cos\vec{q}\cdot\vec{r}^{\,l}) \tag{6}$$

and a similar expression for $S_{\gamma\delta}(\vec{l})$.

Shukla and Taylor[7] used this approach in their calculations of F_4 for Na and K. With some algebraic manipulations and rearrangement of terms, it can be seen that Eqs. (5) and (6) yield Eq. (9) in their paper. We note here that in this approach of calculating F_4, where for a given direct lattice vector $\vec{r}^{\,l}$, the BZ and branch-index (j) summations in Eq. (6) are done first and the $\vec{l}$ summations in Eq. (5) last, F_4 is calculated as a function of $\vec{l}$. Since $\phi_{\alpha\beta\gamma\delta}(|\vec{r}^{\,l}|)$ contains a term of the type $|\vec{r}^{\,l}|^{-3}$ and $S_{\alpha\beta}(\vec{l})$ and $S_{\gamma\delta}(\vec{l})$ themselves oscillate, F_4 is found to be oscillatory and slowly convergent.

To avoid this oscillatory problem encountered by Shukla and Taylor[7] in the calculation of F_4, we can derive an alternative expression for F_4 in terms of the wave-vector-dependent fourth-rank-tensor functions $F_{\alpha\beta\gamma\delta}(\vec{q})$, where the $(\vec{l})$ summations can be performed first. This function is defined by

$$F_{\alpha\beta\gamma\delta}(\vec{q})=\sum_{\vec{l}}{}'\,\phi_{\alpha\beta\gamma\delta}(|\vec{r}^{\,l}|)\cos(\vec{q}\cdot\vec{r}^{\,l})\,. \tag{7}$$

Combining the two cosine functions in Eq. (2) and introducing the function defined by Eq. (7), F_4 can be written from Eq. (1) in the following alternative form:

$$F_4=\frac{\hbar^2}{16NM^2}\sum_{\vec{q}_1 j_1}\sum_{\vec{q}_2 j_2}\sum_{\alpha\beta\gamma\delta}\left[F_{\alpha\beta\gamma\delta}(\vec{0})-F_{\alpha\beta\gamma\delta}(\vec{q}_1)-F_{\alpha\beta\gamma\delta}(\vec{q}_2)+\tfrac{1}{2}F_{\alpha\beta\gamma\delta}(\vec{q}_1+\vec{q}_2)+\tfrac{1}{2}F_{\alpha\beta\gamma\delta}(\vec{q}_1-\vec{q}_2)\right]T_{\alpha\beta}(\vec{q}_1 j_1)T_{\gamma\delta}(\vec{q}_2 j_2)\,, \tag{8}$$

where

$$T_{\alpha\beta}(\vec{q}_1 j_1)=\frac{e_\alpha(\vec{q}_1 j_1)e_\beta(\vec{q}_1 j_1)}{\omega(\vec{q}_1 j_1)}\,N(\vec{q}_1 j_1) \tag{9}$$

and a similar expression for $T_{\gamma\delta}(\vec{q}_2 j_2)$. Since $\vec{q}_1$ and $\vec{q}_2$ are the whole Brillouin-zone sums in Eq. (8), which means for every $\vec{q}$ there is $-\vec{q}$ in the set, the last two terms in Eq. (8) are equal, and obviously with interchanging $\vec{q}_1 j_1$ and $\vec{q}_2 j_2$ the second and third terms in Eq. (8) are also equal. Thus the final expression for F_4 becomes

$$F_4=\frac{\hbar^2}{16NM^2}\sum_{\vec{q}_1 j_1}\sum_{\vec{q}_2 j_2}\sum_{\alpha\beta\gamma\delta}\left[F_{\alpha\beta\gamma\delta}(\vec{0})-2F_{\alpha\beta\gamma\delta}(\vec{q}_1)+F_{\alpha\beta\gamma\delta}(\vec{q}_1+\vec{q}_2)\right]T_{\alpha\beta}(\vec{q}_1 j_1)T_{\gamma\delta}(\vec{q}_2 j_2)\,. \tag{10}$$

The calculation of the quartic free energy from Eq. (10) requires the knowledge of the function $F_{\alpha\beta\gamma\delta}(\vec{q})$ which we now derive from the potential function defined in Eq. (4).

Since the two-body potential $\phi(r)$ defined by Eq. (4) consists of two terms, (a) Coulomb and (b) electron-ion, i.e.,

$$\phi(r)=\phi^{C}(r)+\phi^{E\text{-}I}(r)\,, \tag{11}$$

we can express $F_{\alpha\beta\gamma\delta}(\vec{q})$, from Eqs. (7), (3), and (4), as a sum of two contributions

$$F_{\alpha\beta\gamma\delta}(\vec{q})=F^{C}_{\alpha\beta\gamma\delta}(\vec{q})+F^{E\text{-}I}_{\alpha\beta\gamma\delta}(\vec{q})\,, \tag{12}$$

where $F^{C}_{\alpha\beta\gamma\delta}(\vec{q})$ and $F^{E\text{-}I}_{\alpha\beta\gamma\delta}(\vec{q})$ arise from the $\phi^{C}(r)$ and $\phi^{E\text{-}I}(r)$ terms of the potential function, respectively.

The derivation of $F^{E\text{-}I}_{\alpha\beta\gamma\delta}(\vec{q})$ is straightforward and can be carried out by substituting the second term in Eq. (4) into Eq. (3) and then the resulting expression into Eq. (7). We find

$$F^{E\text{-}I}_{\alpha\beta\gamma\delta}(\vec{q})=-\frac{4\pi e^2}{(2\pi)^3}\sum_{l}{}'\iiint\frac{G(|\vec{Q}|)}{|\vec{Q}|^2}\,\frac{\partial^4\exp[i\vec{Q}\cdot(\vec{r}^{\,l}+\vec{u})]}{\partial u_\alpha\,\partial u_\beta\,\partial u_\gamma\,\partial u_\delta}\times d^3Q\cos(\vec{q}\cdot\vec{r}^{\,l})\,. \tag{13}$$

Performing the necessary differentiations in Eq. (13), interchanging the order of summation and integration, and using the following transformation

$$\sum_{l}\exp(i\vec{q}\cdot\vec{r}^{\,l})=\frac{(2\pi)^3}{v}\sum_{\vec{\tau}}\delta(\vec{q}-\vec{\tau})\,, \tag{14}$$

where $\vec{\tau}$ is a vector of the reciprocal lattice and v is the unit-cell volume, the three-dimensional integration over $\vec{Q}$ in Eq. (13) involving the Dirac δ function can be trivially done, and the final result is

$$F^{E\text{-}I}_{\alpha\beta\gamma\delta}(\vec{q})=-\frac{4\pi e^2}{v}\sum_{\vec{\tau}}\frac{(\vec{q}+\vec{\tau})_\alpha(\vec{q}+\vec{\tau})_\beta(\vec{q}+\vec{\tau})_\gamma(\vec{q}+\vec{\tau})_\delta}{|\vec{q}+\vec{\tau}|^2}\times G(|\vec{q}+\vec{\tau}|)+D\,, \tag{15}$$

where D is a constant term independent of $\vec{q}$ arising from the $l\neq 0$ condition in Eq. (13). The constant term in Eq. (15) does not contribute to F_4, which can be easily verified by substituting Eq. (15) into Eq. (10).

The derivation of $F^{C}_{\alpha\beta\gamma\delta}(\vec{q})$ follows from the Ewald procedure as described in Born and Huang[16] or

Cohen and Keffer.[17] Here we will omit the details, but note the following: When each of the indices α, β, γ, and δ is assigned x, y, z values, a total of 81 terms is obtained, but only 15 of them are independent. Among those 15 terms, only four need be derived, viz., $F^{C}_{xxxx}(\vec{q})$, $F^{C}_{xxyy}(\vec{q})$, $F^{C}_{xxxy}(\vec{q})$, and $F^{C}_{xxyz}(\vec{q})$. The other 11 terms can be obtained from these four terms by a suitable change of indices. Furthermore, we can express these four terms in terms of certain other fourth-, second-, and zero-rank tensors as follows:

$$F^{C}_{xxxx}(\vec{q}) = 105e^2 S_{xxxx}(\vec{q}) - 90e^2 S_{xx}(\vec{q}) + 9e^2 S(\vec{q}) \,,$$

$$F^{C}_{xxyy}(\vec{q}) = 105e^2 S_{xxyy}(\vec{q}) \tag{16}$$

$$- 15e^2[S_{xx}(\vec{q}) + S_{yy}(\vec{q})] + 3e^2 S(\vec{q}) \,, \tag{17}$$

$$F^{C}_{xxxy}(\vec{q}) = 105e^2 S_{xxxy}(\vec{q}) - 45e^2 S_{xy}(\vec{q}) \,, \tag{18}$$

$$F^{C}_{xxyz}(\vec{q}) = 105e^2 S_{xxyz}(\vec{q}) - 15e^2 S_{yz}(\vec{q}) \,, \tag{19}$$

where

$$S_{xxxx}(\vec{q}) = \sum_{l}{}' \frac{x_l^4}{r_l^9} \cos(\vec{q}\cdot\vec{r}^{\,l}) \,, \tag{20}$$

$$S_{xxyy}(\vec{q}) = \sum_{l}{}' \frac{x_l^2 y_l^2}{r_l^9} \cos(\vec{q}\cdot\vec{r}^{\,l}) \,, \tag{21}$$

$$S_{xxxy}(\vec{q}) = \sum_{l}{}' \frac{x_l^3 y_l}{r_l^9} \cos(\vec{q}\cdot\vec{r}^{\,l}) \,, \tag{22}$$

$$S_{xxyz}(\vec{q}) = \sum_{l}{}' \frac{x_l^2 y_l z_l}{r_l^9} \cos(\vec{q}\cdot\vec{r}^{\,l}) \,, \tag{23}$$

$$S_{xx}(\vec{q}) = \sum_{l}{}' \frac{x_l^2}{r_l^7} \cos(\vec{q}\cdot\vec{r}^{\,l}) \,, \tag{24}$$

$$S_{xy}(\vec{q}) = \sum_{l}{}' \frac{x_l y_l}{r_l^7} \cos(\vec{q}\cdot\vec{r}^{\,l}) \,, \tag{25}$$

$$S(\vec{q}) \equiv S_5(\vec{q}) = \sum_{l}{}' \frac{\cos(\vec{q}\cdot\vec{r}^{\,l})}{r_l^5} \,, \tag{26}$$

and we note that $r_l = |\vec{r}^{\,l}|$. Here we have omitted writing the corresponding expressions for $S_{yy}(\vec{q})$ and $S_{yz}(\vec{q})$ as they can be obtained from $S_{xx}(\vec{q})$ and $S_{xy}(\vec{q})$, respectively, by a suitable change of indices.

The fourth- and second-rank tensors $S_{\alpha\beta\gamma\delta}(\vec{q})$ and $S_{\alpha\beta}(\vec{q})$ appearing in Eqs. (20)–(25) are obtained by repeated differentiations of $S_n(\vec{q})$ with respect to q_α, q_β, q_γ, and q_δ, using $n=9$ and 7, respectively. This basic function $S_n(\vec{q})$ is defined by

$$S_n(\vec{q}) = \sum_{l}{}' \frac{\cos(\vec{q}\cdot\vec{r}^{\,l})}{|\vec{r}^{\,l}|^n} . \tag{27}$$

Following the Ewald procedure, we obtain $S_n(\vec{q})$:

$$S_n(\vec{q}) = \frac{C^n}{\Gamma(\frac{1}{2}n)a^n} \sum_{\vec{l}}{}' \cos(\vec{q}\cdot\vec{r}^{\,l}) \int_1^\infty \xi^{n/2-1} \exp\left(\frac{-|\vec{l}|^2 C^2}{4}\,\xi\right) d\xi + \frac{2\pi^{3/2}C^{n-3}}{\Gamma(\frac{1}{2}n)a^n}\left[\sum_{\vec{\tau}} \int_1^\infty \xi^{-n/2+1/2} \exp\left(-\frac{|\vec{q}+\vec{\tau}|^2 a^2}{4C^2}\,\xi\right) d\xi - \frac{C^3}{\pi^{3/2}n}\right] . \tag{28}$$

Once again the last term in Eq. (28) arises from the $\vec{l}=0$ term which is excluded from the $\vec{l}$ summation in Eq. (27). Although there is no contribution from this term to F_4 it is needed for the verification of the sum rules (see Sec. III on numerical methods) where in Eq. (28), C is the Ewald parameter to be chosen in such a manner as to make the two sums over the direct-lattice vector ($\vec{l}$) and the reciprocal-lattice vector (τ) converge rather quickly, and $\Gamma(n/2)$ is the usual Γ function. In the calculations reported in this paper we have selected $C=\sqrt{\pi}$. For an fcc structure the quantity in the large square brackets in the second term in Eq. (28) should be multiplied by 2 and the constant term changes into $C^3/(2\pi^{3/2}n)$.

III. NUMERICAL METHOD

The numerical method of calculating F_4, from Eq. (5), as a function of the number of neighbors or shells, has been given before in Shukla and Taylor[7] and more recently in MacDonald *et al.*[8] The method of performing Brillouin-zone (BZ) and branch-index ($\vec{q}$ and $\vec{j}$) summations, required in the calculation of $S_{\alpha\beta}(\vec{l})$, has been given before by Shukla and Wilk.[18] The number of points needed in the BZ sum for a satisfactory convergence of $S_{\alpha\beta}(\vec{l})$, for $\vec{l}$ as large as the vector of the 23rd shell, have been discussed before.[7] In the present calculations we have used the same number of points in the whole zone (viz., 16 000 points) in the calculation of $S_{\alpha\beta}(\vec{l})$. The fourth-rank tensors $\phi_{\alpha\beta\gamma\delta}(|\vec{r}^{\,l}|)$ appearing in the expression for F_4 [Eq. (5)] were evaluated from the same potential as that used by Shukla and Taylor.[7] Following these procedures we have calculated F_4 for Na and K for the same set of volumes at which the earlier calculations were performed by Shukla and Taylor.[7] The F_4 results for five volumes in Na and four volumes in K, calculated to 23 shells, are presented in Fig. 1. For 23 shells, and all the volumes, we also present in Tables I and II the numerical values of F_4 for Na and K, respectively.

Now we turn our attention to the calculation of

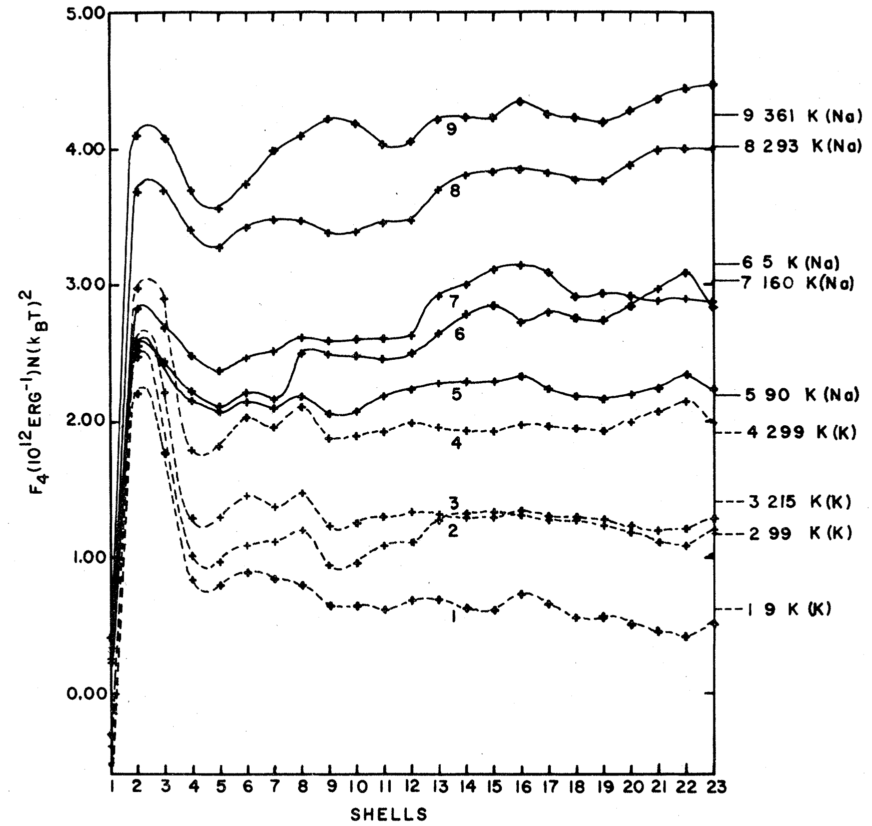

FIG. 1. Quartic contribution to the Helmholtz free energy (F_4): The solid curves labeled 5, 6, 7, 8, and 9 refer to Na at volumes (zero pressure) corresponding to temperatures 90, 5, 160, 293, and 361 K, respectively. The dashed curves 1, 2, 3, and 4 refer to K at volumes (zero pressure) corresponding to temperatures 9, 99, 215, and 299 K, respectively. The F_4(Ewald) numbers for Na and K are shown on the vertical axis on the right-hand side of the graph.

F_4 by the alternative expression given by Eq. (10). For a given wave vector $\vec{q}$ the electron-ion contribution to $F_{\alpha\beta\gamma\delta}(\vec{q})$, arising in Eq. (10), was calculated from Eq. (15). As described previously in Sec. II, all the Coulomb contributions to $F_{\alpha\beta\gamma\delta}(\vec{q})$ were obtained from Eqs. (16)–(19). The total $F_{\alpha\beta\gamma\delta}(\vec{q})$ is then given by the sum of these two contributions.

Since the tensors $F^{C}_{\alpha\beta\gamma\delta}(\vec{q})$ and $F^{E\text{-}I}_{\alpha\beta\gamma\delta}(\vec{q})$ are the important ingredients in the present method of the calculation of F_4, it is important to devise some method of checking their numerical accuracy. We have derived the following relations among these fourth-rank tensors which have proved extremely useful in providing checks on our numerical calculations. We present these relations separately for the Coulomb and the electron-ion contributions.

(a) Relations among $F^{E\text{-}I}_{\alpha\beta\gamma\delta}(\vec{q})$. Substituting the values of $\alpha, \beta, \gamma, \delta$ in terms of x, y, z, we find from Eq. (15) the following relations:

$$F^{E\text{-}I}_{xxxx}(\vec{q}) + F^{E\text{-}I}_{yyyy}(\vec{q}) + F^{E\text{-}I}_{zzzz}(\vec{q}) + 2[F^{E\text{-}I}_{xxyy}(\vec{q}) + F^{E\text{-}I}_{xxzz}(\vec{q}) + F^{E\text{-}I}_{yyzz}(\vec{q})] = \frac{-4\pi e^2}{v}\sum_{\vec{\tau}} |\vec{q}+\vec{\tau}|^2 G(|\vec{q}+\vec{\tau}|) + 8D, \tag{29}$$

$$F^{E\text{-}I}_{xxxy}(\vec{q}) + F^{E\text{-}I}_{yyxy}(\vec{q}) + F^{E\text{-}I}_{zzxy}(\vec{q}) = \frac{-4\pi e^2}{v}\sum_{\vec{\tau}} (\vec{q}+\vec{\tau})_x(\vec{q}+\vec{\tau})_y G(|\vec{q}+\vec{\tau}|) + 3D, \tag{30}$$

$$F^{E\text{-}I}_{xxxz}(\vec{q}) + F^{E\text{-}I}_{yyxz}(\vec{q}) + F^{E\text{-}I}_{zzxz}(\vec{q}) = \frac{-4\pi e^2}{v}\sum_{\vec{\tau}} (\vec{q}+\vec{\tau})_x(\vec{q}+\vec{\tau})_z G(|\vec{q}+\vec{\tau}|) + 3D, \tag{31}$$

$$F^{E\text{-}I}_{yyyz}(\vec{q}) + F^{E\text{-}I}_{zzyz}(\vec{q}) + F^{E\text{-}I}_{xxyz}(\vec{q}) = \frac{-4\pi e^2}{v}\sum_{\vec{\tau}} (\vec{q}+\vec{\tau})_y(\vec{q}+\vec{\tau})_z G(|\vec{q}+\vec{\tau}|) + 3D. \tag{32}$$

TABLE I. Sodium: quartic contribution to free energy F_4 for all shells up to and including the shell indicated in units of $10^{12}N(k_BT)^2$ erg^{-1}. Lattice parameters are zero-pressure values.

		Temperature and lattice parameter				
Shells	Coordinates	4.2247 Å (T = 5 K)	4.234 Å (T = 190 K)	4.251 Å (T = 160 K)	4.288 Å (T = 293 K)	4.309 Å (T = 361 K)
1	111	0.222 82	0.259 61	0.319 31	0.315 38	0.415 04
2	200	2.572 21	2.567 81	2.826 59	3.704 13	4.101 19
3	220	2.426 37	2.443 74	2.702 48	3.714 02	4.086 32
4	311	2.178 58	2.237 41	2.491 31	3.412 66	3.694 10
5	222	2.091 28	2.122 45	2.375 96	3.297 39	3.565 88
6	400	2.215 25	2.150 31	2.472 35	3.426 19	3.750 61
7	331	2.178 79	2.096 33	2.510 35	3.460 96	3.985 78
8	420	2.499 23	2.189 86	2.618 28	3.476 48	4.098 48
9	422	2.504 21	2.068 37	2.592 35	3.390 00	4.216 42
10	333	2.497 20	2.087 48	2.598 19	3.401 35	4.186 96
11	511	2.463 41	2.186 89	2.634 55	3.465 59	4.039 26
12	440	2.503 32	2.239 04	2.633 49	3.488 08	4.052 18
13	531	2.644 88	2.280 29	2.929 34	3.707 11	4.204 47
14	442	2.799 43	2.290 32	3.085 06	3.803 62	4.228 29
15	600	2.853 81	2.293 45	3.136 80	3.836 28	4.236 20
16	620	2.727 77	2.338 90	3.151 54	3.846 30	4.349 31
17	533	2.804 86	2.248 70	3.103 13	3.825 25	4.260 27
18	622	2.761 61	2.190 78	2.926 98	3.787 50	4.229 72
19	444	2.753 27	2.172 92	2.943 93	3.779 77	4.203 81
20	551	2.851 57	2.204 51	2.917 71	3.887 75	4.280 95
21	711	2.975 61	2.244 03	2.886 48	4.020 00	4.377 70
22	640	3.088 00	2.354 52	2.901 97	4.016 10	4.451 35
23	642	2.849 37	2.255 65	2.867 68	4.126 14	4.464 74

TABLE II. Potassium: quartic contribution to free energy F_4 for all shells up to and including the shell indicated in units of $10^{12}N(k_BT)^2$ erg^{-1}. Lattice parameters are zero-pressure values.

		Temperature and lattice parameter			
Shells	Coordinates	5.233 Å (T = 9 K)	5.261 Å (T = 99 K)	5.305 Å (T = 215 K)	5.343 Å (T = 299 K)
1	111	−0.528 67	−0.523 71	−0.372 34	−0.303 43
2	200	2.212 57	2.484 80	2.601 75	2.992 97
3	220	1.991 20	2.231 87	2.449 69	2.907 91
4	311	0.839 20	1.030 21	1.305 45	1.812 88
5	322	0.803 64	0.998 31	1.300 91	1.829 93
6	400	0.894 86	1.108 19	1.458 51	2.033 83
7	331	0.859 87	1.131 31	1.382 24	1.976 68
8	420	0.800 47	1.205 92	1.479 76	2.123 95
9	422	0.664 39	0.955 14	1.245 42	1.884 72
10	333	0.659 37	0.978 61	1.252 29	1.892 61
11	511	0.636 94	1.093 40	1.285 89	1.930 87
12	440	0.685 09	1.113 75	1.332 95	1.994 98
13	531	0.692 68	1.295 20	1.323 65	1.964 88
14	442	0.638 99	1.321 58	1.314 73	1.943 77
15	600	0.622 14	1.329 83	1.311 88	1.936 78
16	620	0.739 24	1.320 56	1.348 74	1.980 23
17	533	0.669 98	1.294 02	1.304 74	1.972 57
18	622	0.569 73	1.298 79	1.285 05	1.956 79
19	444	0.577 97	1.291 84	1.269 56	1.934 42
20	551	0.527 40	1.217 01	1.237 48	2.001 87
21	711	0.469 60	1.129 95	1.200 90	2.083 23
22	640	0.417 04	1.100 01	1.221 86	2.175 22
23	642	0.517 96	1.194 07	1.293 34	2.005 47

(b) Relations among $F^C_{\alpha\beta\gamma\delta}(\vec{q})$. $F^C_{\alpha\beta\gamma\delta}(\vec{q})$ has been expressed in terms of $S_{\alpha\beta\gamma\delta}(\vec{q})$, $S_{\alpha\beta}(\vec{q})$, and $S(\vec{q})$ in Eqs. (16)–(19). Therefore, instead of finding the relations among the tensors $F^C_{\alpha\beta\gamma\delta}(\vec{q})$, we find it is sufficient for our purposes to find relations among the tensors $S_{\alpha\beta\gamma\delta}(\vec{q})$, $S_{\alpha\beta}(\vec{q})$, and $S(\vec{q})$. From Eqs. (20)–(26) and the other expressions generated from them by interchange of indices, such as $S_{yyyx}(\vec{q})$, etc., we obtain the following relations:

$$S_{xxxx}(\vec{q})+S_{yyyy}(\vec{q})+S_{zzzz}(\vec{q}) + 2[S_{xxyy}(\vec{q})+S_{xxzz}(\vec{q})+S_{yyzz}(\vec{q})]=S(\vec{q})\,, \tag{33}$$

$$S_{xxxy}(\vec{q})+S_{yyxy}(\vec{q})+S_{zzxy}(\vec{q})=S_{xy}(\vec{q})\,, \tag{34}$$

$$S_{xxxz}(\vec{q})+S_{yyxz}(\vec{q})+S_{zzxz}(\vec{q})=S_{xz}(\vec{q})\,, \tag{35}$$

$$S_{yyyz}(\vec{q})+S_{zzyz}(\vec{q})+S_{xxyz}(\vec{q})=S_{yz}(\vec{q})\,, \tag{36}$$

$$S_{xx}(\vec{q})+S_{yy}(\vec{q})+S_{zz}(\vec{q})=S(\vec{q})\,. \tag{37}$$

Once again using the same step length ($Z=20$), as in the first method of the calculation of F_4, which gives 500 wave vectors in the irreducible sector of the BZ (IrSBZ) and 16 000 vectors in the whole zone, the above sum rules for the electron-ion and the Coulomb parts of the potential function are satisfied to better than 1 part in 10^6 for each wave vector. Once we have assured ourselves of the numerical accuracy of the tensors $F_{\alpha\beta\gamma\delta}(\vec{q})$, F_4 was calculated from Eq. (10) by performing the double whole BZ and branch-index summations in a straightforward manner. We note here that although $\vec{e}(\vec{q}j)$ and $F_{\alpha\beta\gamma\delta}(\vec{q})$ are obtained for the IrSBZ, they can be easily obtained for the whole zone from their rotational transformation properties.

Another useful check on the final results of F_4 is given by the calculation of F_4 in the Einstein approximation (F_4^E). In this approximation all the phonon frequencies $\omega(\vec{q}j)$ are replaced by the average Einstein phonon frequency ω_E. The j sums in Eq. (10) are exactly done from the orthonormal property of the eigenvectors viz.,

$$\sum_{j_1} e_\alpha(\vec{q}_1 j_1)e_\beta(\vec{q}_1 j_1)=\delta_{\alpha\beta}\,,$$

where $\delta_{\alpha\beta}$ is the usual Kronecker delta symbol.

Similarly from the j_2 sum we have another Kronecker delta, $\delta_{\gamma\delta}$. Taking into account the property $\delta_{\alpha\beta}=1$ if $\alpha=\beta$ and zero otherwise, j_1 and j_2 summations in Eq. (10) are eliminated. Thus we obtain

$$F_4^E=\frac{\hbar^2}{16NM^2\omega_E^4}\sum_{\vec{q}_1,\vec{q}_2}\sum_{\alpha,\gamma}[F_{\alpha\alpha\gamma\gamma}(0)-2F_{\alpha\alpha\gamma\gamma}(\vec{q}_1) + F_{\alpha\alpha\gamma\gamma}(\vec{q}_1+\vec{q}_2)]\,. \tag{38}$$

Now for a given wave vector $\vec{q}$ we have the following sum for the Coulomb contribution:

$$\sum_{\alpha,\gamma} F^C_{\alpha\alpha\gamma\gamma}(\vec{q})=F^C_{xxxx}(\vec{q})+F^C_{yyyy}(\vec{q})+F^C_{zzzz}(\vec{q}) + 2[F^C_{xxyy}(\vec{q})+F^C_{xxzz}(\vec{q})+F^C_{yyzz}(\vec{q})]\,. \tag{39}$$

Substituting for the first three and the last three terms in Eq. (39) from Eqs. (16) and (17) and the equations obtained from them by interchanging the indices, and making use of the sum rules given by Eqs. (33) and (37), we obtain

$$\sum_{\alpha,\gamma} F^C_{\alpha\alpha\gamma\gamma}(\vec{q})=105e^2S(\vec{q})-150e^2S(\vec{q})+45e^2S(\vec{q})=0\,.$$

Therefore, in the Einstein approximation, the contribution to F_4 comes only from the electron-ion term of the potential function. This contribution can be easily evaluated from Eqs. (38) and (29). We find

$$F_4^E=F_4^E(E-I) =\left(\frac{-4\pi e^2}{v}\right)\left(\frac{\hbar^2}{16NM^2\omega_E^4}\right)\sum_{\vec{q}_1,\vec{q}_2}\sum_{\vec{\tau}}[|\vec{\tau}|^2G(|\vec{\tau}|)-2|\vec{q}_1+\vec{\tau}|^2G(|\vec{q}_1+\vec{\tau}|)+|\vec{q}_1+\vec{q}_2+\vec{\tau}|^2G(|\vec{q}_1+\vec{q}_2+\vec{\tau}|)]\,,$$

which can be evaluated in a straightforward manner.

IV. DISCUSSION

In order to make a direct comparison of the magnitude of F_4 calculated by the two methods presented in Sec. III, we have chosen to calculate F_4 from the same Na and K potential functions used in the earlier calculations of Shukla and Taylor.[7] The details concerning these potential functions and the choice of screening function can be found in their paper. It was shown in their work that the Geldart-Taylor[19] and Vashista-Singwi[20] screening functions gave essentially the same results for F_4. Thus we have carried out all the calculations in this paper with the Geldart-Taylor screening function. To simplify the comparison of F_4 by the two methods we introduce the following notation: When F_4 is calculated from Eq. (5), we denote it by $F_4(s)$, where s is the shell index at which the $\vec{l}$ summation is truncated in Eq. (5). The calculated value of F_4 from Eq. (10) is represented by F_4 (Ewald).

Before we compare $F_4(s)$ and F_4(Ewald) we note the following striking differences among the results of $F_4(s)$ for Na and K. For all the volumes at which we have carried out our calculations in Na and K, the nearest-neighbor contribution to F_4 is small. It is negative in K but positive in Na. The second neighbors make a large positive contribution in both Na and K. In absolute magnitude, this is a factor of 10 larger than the nearest-neighbor contribution.

It is interesting to note that for the five different volumes at which we have performed our calculations in Na, $F_4(2)$ and $F_4(23)$ differ by less than 2% at the 160-K volume, whereas they differ by 14% at the 90-K volume. For the other three volumes, $F_4(2)$ and $F_4(23)$ differ at the most by 10%.

In K, $F_4(2)$ is four times larger than $F_4(23)$ at 9-K volume, whereas at 99- and 215-K volumes, $F_4(2)$ is approximately twice as large as $F_4(23)$. At 299-K volume $F_4(2)$ is 50% larger than $F_4(23)$.

We have chosen to compare $F_4(2)$ and $F_4(23)$ in detail because Copley[4] has used in his calculations of Δ, Γ, F_3, and F_4 for Rb only two neighbors in the anharmonic interaction. If the trend in K is any indication of the behavior of $F_4(s)$ in heavier alkali metals (i.e., Rb and Cs), his calculations on Rb cannot be reliable due to the cutoff of anharmonic interactions at the second-neighbor distance.

Quite recently, MacDonald *et al.*[8] have examined the behavior of the high-temperature specific heat of Rb. Since I have participated in this work, the following remarks on $F_4(s)$ for Rb are in order. The nearest-neighbor contribution is indeed negative, the second-neighbor contribution is a factor of 10 larger in absolute magnitude than the nearest-neighbor contribution, and $F_4(2)$ is about 50% larger than $F_4(6)$, at which the sums were truncated in Ref. 8.

In light of the above remarks about the nearest-neighbor contributions to F_4 being negative or very small, the validity of another recent calculation of F_3 and F_4 on alkali metals by Trivedi *et al.*[21] is highly questionable. This is partly due to the use of the nearest-neighbor model in the anharmonic interactions and the leading-term approximation in their calculations. The latter introduces 40% error[18] in the calculation of F_4. The worst part of the calculation seems to be in misleading the readership again on the issue of the sign of anharmonic contribution to C_v. Although Cowley[22] has clarified this point before, what Trivedi *et al.* call a new method of calculating C_v is in fact the calculation of C_p (which is always positive), yet Trivedi *et al.*[21] insist on using the same wrong arguments. For a further detailed discussion of this point we refer the reader to a forthcoming publication.[23]

Comparing now $F_4(s)$ and F_4(Ewald) in Na and K, we observe some correspondence between the results of these two methods of calculating F_4. For example, in Na, F_4(Ewald) agrees exactly with $F_4(s)$, where $s = 18$, at the 90-K volume. The agreement between the two is almost exact at 160- and 361-K volumes with $s = 17$ and 10, respectively. At the other two volumes referred to, $T = 5$ and 293 K, F_4(Ewald) and $F_4(s)$ differ by about 1% where for the two volumes $s = 22$ and 21, respectively.

In K, F_4(Ewald) and $F_4(s)$ differ by less than 1% in each case for the three volumes corresponding to temperatures 9, 215, and 299 K, where for each of these volumes $s = 15$, 7, and 10, respectively. The largest disagreement between F_4 (Ewald) and $F_4(s)$ $(s = 7)$ arises for the volume at 99 K. In this case they differ by 3%. It is clear from the above discussion that F_4 (Ewald) and $F_4(s)$ are in agreement with each other for "some" shell indix s, but s changes with volume. Thus without *a priori* knowledge of an exact value of F_4, such as the one obtained by Ewald procedure, one cannot decide the shell index (s) at which the summation in Eq. (5) should be truncated to obtain a correct answer for F_4.

Since we have examined in detail the accuracy of the two-neighbor model by comparing $F_4(2)$ and $F_4(23)$, it would be interesting to compare $F_4(2)$ with F_4(Ewald) for all the volumes at which we have carried out our calculations of F_4 for Na and K. We find from this comparison that $F_4(2)$ and F_4(Ewald) are in good agreement in Na; they agree to within 2% at 361-K volume and differ by 18% at 5-K volume. However, in K the agreement between the two is very poor at all the volumes. The percentage differences between $F_4(2)$ and F_4(Ewald) range from 56 to 254 corresponding to the volumes at 299 and 9 K, respectively.

The good agreement between $F_4(2)$ and F_4(Ewald) in Na at 361-K volume is probably a sheer coincidence because of the lack of similar agreements either for the other volumes in Na or for any volume in K at which we have performed our calculations. Once again we find a two-neighbor model not very reliable.

Finally we note here in passing that for Al Koehler *et al.*[1] have compared their eighth-neighbor anharmonic interaction real-space calculations of Δ and Γ with the reciprocal-space calculations of Δ and Γ by Högberg and Sandström.[24] They have found some disagreements between the numerical values of Δ and Γ obtained by the two calculations. However, the potential employed in the two calculations is different and thus the comparison is not very meaningful.

V. CONCLUSION

We have derived an alternative expression for the quartic term of the Helmoltz free energy (F_4) in terms of the fourth-rank wave-vector-dependent tensors. This expression is more appropriate for the calculation of F_4 in metals. The numerical values of F_4 for a range of volumes from almost 0 K to the melting temperature in Na and K obtained by the present method and the shell-summation method, used previously by Shukla and Taylor,[7] are compared.

The numerical results of the two methods show some correspondence with each other. However, the shell index, where the sums can be truncated in the previous method[7] in order to obtain the agreement with the present method, is found to be different for different volumes. This shows the arbitrariness of the shell-summation method in anharmonic calculations, because the present method gives converged answers for F_4 for different volumes. The two-neighbor anharmonic interaction employed in a previous calculation[4] is shown to be unreliable.

We have also derived several sum rules for the wave-vector-dependent fourth-rank tensors required in the calculation of F_4. These sum rules and the calculation in the Einstein approximation provide some useful checks on the numerical results of F_4. We have shown in the Einstein approximation, the Coulomb term of the potential function makes no contribution to F_4. Thus F_4 is entirely determined by the electron-ion term, which can be easily calculated from a relatively simple expression. The numerical results of this latter independent calculation can be checked against the computer program for the complete expression given by Eq. (10) by setting all $\omega(\vec{q}j) = \omega_E$.

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