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Anharmonic free energy and specific heat at constant volume of sodium and potassium

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The lowest-order cubic (F_3) and quartic (F_4) anharmonic contributions to the Helmholtz free energy have been calculated at several temperatures and lattice spacings for sodium and potassium using interionic potentials developed by Taylor and co-workers. The effect of using either the Geldart-Taylor or Vashishta-Singwi screening on these calculations has been examined. F_3 and F_4 are not sensitive to the choice of screening. A method of calculating F_3 has been developed which is more suited to long-range potentials. At all temperatures the anharmonic specific heat at constant volume (C_V^A) is found to be positive for potassium. For sodium, C_V^A is positive for $T < 293$ °K at which temperature F_3 and F_4 appear to cancel each other; the sign of C_V^A becomes negative at $T = 361$ °K.

I. INTRODUCTION

In two recent publications Glyde and Taylor[1] and Duesbery *et al.*[2] have calculated anharmonic-phonon frequency shifts and widths as functions of temperature in Na and K. In both cases self-consistent phonon theory was used with the cubic anharmonic term treated as a perturbation. However, it was also concluded[1] that straightforward use of perturbation theory gives similar results. Hence, we felt that it would be both useful and interesting to use perturbation theory to calculate the Helmholtz free energy for these metals.

In this paper we present the perturbation-theory calculations of the two lowest-order terms in the Helmholtz free energy F_3 and F_4 and the resulting anharmonic contribution to the specific heat C_V^A for Na and K. In Sec. II we describe the model used to calculate the interionic potentials which are the same ones that were used by Glyde and Taylor[1] and Duesbery *et al.*[2] Since this model depends on the use of electron-gas screening, it contains long-range oscillations arising from the well-known logarithmic singularity in the slope of the screening function. This means that calculations of F_3 and F_4, the cubic and quartic contributions to the free energy, must be extended to many neighbors. This can be very time consuming unless maximum use of symmetry is made. In Sec. III we outline the method used to reduce F_3 and F_4 to a form which enables their calculation in a reasonable amount of time even on a medium-size computer, such as the 28K word Burroughs 5500, where our calculations were performed.

In Sec. IV we present the calculations of F_3 and F_4. To calculate the potentials we used the Geldart and Taylor[3] screeing function in both Na and K. However, there are a number of other calculations of electron-gas screening available[4,5] and to test the significance of the choice of screening we repeated the Na calculations at two temperatures using the Vashishta and Singwi[5] version of screening. Both of these screening functions satisfy the compressibility theorem but differ somewhat for $q \sim k_F$. Fortunately, though, the two sets of F_3 and F_4 were quite similar and therefore the choice of screening does not appear to be very critical. A more detailed discussion of this and the significance of the data is given in Sec. V.

II. THE INTERIONIC POTENTIAL

Calculations of F_3 and F_4 necessarily rely heavily on the use of models developed for the theory of lattice dynamics in metals. Now the lattice dynamics of Na and K have attracted a great deal of attention in recent years. Prompted by the publication of a number of accurate experimental measurements of phonon dispersion curves,[6-9] elastic constants,[10-12] liquid structure factors,[13] and specific heats[14] a vast number of calculations based on a wide variety of models has appeared in the literature. If we exclude those models which are essentially parametrization schemes to fit experimental data, we find that the rest of the calculations rely on the use of a two-body effective interionic potential which is constructed in the following manner. First, the Coulomb repulsion between the ions is introduced. This is then screened by the conduction electrons interacting with the ions via the electron-ion interaction. The bare electron-ion interaction is usually calculated using a pseudopotential model, which is then screened by some form of screening function based on electron-gas theory. Finally some workers have introduced a Born-Mayer-type of repulsive interaction to take into account any possible overlap between neighboring ion cores. Vosko[15] has shown that the core-core overlap interaction in Na is negligibly small and a similar result is to be expected in any material, such as K, which has a tightly bound core. Hence, the Born-Mayer interaction should not be used in these materials.

Geldart *et al.*[16] were the first people to provide a fundamental calculation in Na which gave good agreement with the experimental phonon dispersion curves of Woods *et al.*[6] without resorting to the Born-Mayer interaction. To describe their model let us note that in a material such as Na or K, where nonlocal effects are small,[17] the interionic potential may be written in the form

$$V(r)=(Z'e)^2/r-[2(Z'e)^2/\pi]\int_0^\infty F(q)\sin qr/qr\,dq\ , \tag{1}$$

$$F(q)=1/Z'^2 M(q)^2\{Q(q)/[q^2+Q(q)]\}\ . \tag{2}$$

$M(q)$ is the bare electron-ion matrix element, Z' is the valence, and $Q(q)$ is the static electron gas screening function related to the dielectric functions by the equation

$$\epsilon(q)=1+Q(q)/q^2\ . \tag{3}$$

To calculate $M(q)$ a single orthogonalized-plane-wave (OPW) model was used to represent the conduction electron state and the nonlocal terms were averaged over the Fermi sphere. In this approximation $M(q)$ takes the form[16,18]

$$M(q)=G(qr_0)-\xi q^2\,\overline{U}_0(q), \tag{4}$$

where

$$G(x)=3(\sin x-x\cos x)/x^3, \tag{5}$$

$$\xi=\Omega_0/8\pi Z'a_0, \tag{6}$$

Ω_0 being the volume per ion, a_0 the Bohr radius, and $\overline{U}_0(q)$ is basically a pseudopotential arising from the non-plane-wave-like component of the OPW. $\overline{U}_0(q)$ must be expressed in rydbergs.

To calculate $\overline{U}_0(q)$ the Prokofjew[19] potential was used to represent the Na$^+$ ion and a similar type of potential constructed by Duesbery *et al.*[2] was used to represent the K$^+$ ion. The calculations were performed at five values of the lattice parameter a in Na and four values of a in K. For sodium at 90 °K, lattice parameter ($a=4.234$ Å) values of $\overline{U}_0(q)$ can be obtained from Geldart, Taylor, and Varshni.[16] Similarly for sodium and potassium $\overline{U}_0(q)$ can be obtained at other lattice parameters and is available upon request from the authors.

For the screening function $Q(q)$, the Geldart and Taylor[3] calculation was used.

The choice of model for our calculations is precisely the same as was used by Glyde and Taylor[1] and by Duesbery *et al.*[2] This model has already been used very successfully to calculate phonon frequencies,[1,2,16] elastic constant,[1,2,20] and the Na liquid structure factor.[21] Hence, we feel that we can use it confidently for the extensive calculations required to determine F_3 and F_4.

III. EXPRESSIONS FOR F_3 AND F_4

The formal expressions for the cubic (F_3) and quartic (F_4) terms of the Helmholtz free energy, valid for all temperatures, have been derived by many authors[22-25] after Ludwig's original derivation and we shall only state the results.

A. Quartic term (F_4)

The finite temperature expression for the quartic term is given by

$$F_4=\frac{\hbar^2}{32N}\sum_{\vec{k}_1,\vec{k}_2}\ \sum_{j_1,j_2}\Phi(\vec{k}_1j_1,\vec{k}_2j_2,-\vec{k}_1j_1,-\vec{k}_2j_2)$$
$$\times(2n_1+1)/\omega_1(2n_2+1)/\omega_2\ , \tag{7}$$

where $\omega_i\equiv\omega(\vec{k}_ij_i)$ is the eigenvalue associated with the $\vec{k}_ij_i$ normal mode of vibration, N is the number of unit cells in crystal, $\beta\equiv1/k_BT$, $n_i\equiv n(\vec{k}_ij_i)=1/(e^{\beta\hbar\omega_i}-1)$, and $\Phi(\vec{k}_1j_1,\vec{k}_2j_2;\vec{k}_3j_3;\vec{k}_4j_4)$ ($\equiv\phi$) is the Fourier transform of the fourth-order atomic force constant defined by

$$\Phi(\vec{k}_1j_1;\vec{k}_2j_2;\vec{k}_3j_3;\vec{k}_4j_4)=\frac{1}{2M^2}\sum_{\vec{n}}{}'\bigg(\frac{C(r_n)}{|\vec{n}|^4}(\vec{n}\cdot\vec{e}_1)(\vec{n}\cdot\vec{e}_2)(\vec{n}\cdot\vec{e}_3)(\vec{n}\cdot\vec{e}_4)+\frac{2B(r_n)}{a|\vec{n}|^3}$$
$$\times[(\vec{n}\cdot\vec{e}_1)(\vec{n}\cdot\vec{e}_2)(\vec{e}_3\cdot\vec{e}_4)+(\vec{n}\cdot\vec{e}_2)(\vec{n}\cdot\vec{e}_3)(\vec{e}_4\cdot\vec{e}_1)+(\vec{n}\cdot\vec{e}_3)(\vec{n}\cdot\vec{e}_4)(\vec{e}_1\cdot\vec{e}_2)$$
$$+(\vec{n}\cdot\vec{e}_4)(\vec{n}\cdot\vec{e}_1)(\vec{e}_2\cdot\vec{e}_3)+(\vec{n}\cdot\vec{e}_2)(\vec{n}\cdot\vec{e}_4)(\vec{e}_1\cdot\vec{e}_3)+(\vec{n}\cdot\vec{e}_1)(\vec{n}\cdot\vec{e}_3)(\vec{e}_2\cdot\vec{e}_4)]+\frac{4A(r_n)}{a^2|\vec{n}|^2}$$
$$\times[(\vec{e}_1\cdot\vec{e}_2)(\vec{e}_3\cdot\vec{e}_4)+(\vec{e}_2\cdot\vec{e}_3)(\vec{e}_4\cdot\vec{e}_1)+(\vec{e}_1\cdot\vec{e}_3)(\vec{e}_2\cdot\vec{e}_4)]\bigg)\prod_{j=1}^{4}(1-e^{-\pi ia\vec{k}_j\cdot\vec{n}})\ , \tag{8}$$

where $r_n\equiv|\vec{r}_n|\equiv\frac{1}{2}|a\vec{n}|$, a is the lattice constant, $\vec{n}$ is a vector with integer components determined by the lattice geometry, M is the atomic mass, and $\vec{e}_i\equiv\vec{e}(\vec{k}_ij_i)$ is the eigenvector corresponding to the mode $\vec{k}_ij_i$. Substituting for ϕ in Eq. (7) we find

$$F_4=\frac{\hbar^2}{16NM^2}\sum_n{}'[S_{4a}(\vec{n})+S_{4b}(\vec{n})+S_{4c}(\vec{n})]\ , \tag{9}$$

where

$$S_{4a}(\vec{n})=[C(r_n)/|\vec{n}|^4]f^2(\vec{n})\ ,$$

$$S_{4b}(\vec{n})=\frac{2B(r_n)}{a|\vec{n}|^3}\left(4\sum_{\alpha}g_{\alpha}^2(\vec{n})+2f(\vec{n})h(\vec{n})\right)\ ,$$

$$S_{4c}(\vec{n})=\frac{4A(r_n)}{a^2|\vec{n}|^2}\left(2\sum_{\alpha}I_{\alpha}^2(\vec{n})+4\sum_{\alpha}J_{\alpha\beta}^2(\vec{n})+h^2(\vec{n})\right)$$

$$f(\vec{n})=\sum_{\vec{k}j}[\vec{n}\cdot\vec{e}(\vec{k}j)]^2c(\vec{k}j,\vec{n})\ ,$$

$$g_{\alpha}(\vec{n})=\sum_{\vec{k}j}[\vec{n}\cdot\vec{e}(\vec{k}j)]e_{\alpha}(\vec{k}j)c(\vec{k}j,\vec{n})\ ,$$

$$h(\vec{n})=\sum_{\vec{k}j}[\vec{e}(\vec{k}j)\cdot\vec{e}(\vec{k}j)]c(\vec{k}j,\vec{n})\ ,$$

$$I_{\alpha}(\vec{n})=\sum_{\vec{k}j}e_{\alpha}^2(\vec{k}j)c(\vec{k}j,\vec{n})\ ,$$

$$J_{\alpha\beta}(\vec{n})=\sum_{\vec{k}j}e_{\alpha}(\vec{k}j)e_{\beta}(\vec{k}j)c(\vec{k}j,\vec{n})\ ,$$

$$c(\vec{k}j,\vec{n})=[1-\cos(2\pi a\vec{k}\cdot\vec{n})][2n(\vec{k}j)+1]/\omega(\vec{k}j)\ ,$$

and $\alpha\in[x,y,z]$ and $\beta=\alpha+1$ (i.e., if α is x, β is y, etc.). $A(r_n)$, $B(r_n)$, and $C(r_n)$ are defined by

$$A(r_n)=[\phi''(r)-(1/r)\phi'(r)]_{r=r_n}\ ,$$

$$B(r_n)=[\phi'''(r)-(3/r)\phi''(r)+(3/r^2)\phi'(r)]_{r=rn}\ ,$$

$$C(r_n)=[\phi^{iv}(r)-(6/r)\phi'''(r)+(15/r^2)\phi''(r)$$
$$-(15/r^3)\phi'(r)]_{r=rn}\ ,$$

where $\phi'(r)$, $\phi''(r)$, ... etc. denote the various derivatives of $\phi(r)$ with respect to r evaluated at $r=r_n$ and a is the lattice constant.

B. Cubic term (F_3)

The full expression for F_3 is given by

$$F_3=-\frac{\hbar^2}{48N}\sum_{k_1k_2k_3}\sum_{j_1j_2j_3}\Delta(\vec{k}_1+\vec{k}_2+\vec{k}_3)$$

$$\times|\Phi(k_1j_1,k_2j_2,k_3j_3)|^2f(1,2,3),\qquad(10)$$

where

$$f(1,2,3)=\frac{1}{\omega_1\omega_2\omega_3}\left[\frac{n_1n_2+n_2n_3+n_3n_1+n_1+n_2+1}{(\omega_1+\omega_2+\omega_3)}+3\,\frac{n_2n_3+n_3n_1-n_1n_2+n_3}{(\omega_1+\omega_2-\omega_3)}\right]$$

and $\Delta(\vec{k}_1+\vec{k}_2+\vec{k}_3)$ is unity if $\vec{k}_1+\vec{k}_2+\vec{k}_3$ is zero or $2\pi\tau$, where τ is a vector of the reciprocal lattice, and zero otherwise. $\Phi(k_1j_1,k_2j_2,k_3j_3)$ is the Fourier transform of the third-order atomic force constant and other symbols appearing in Eq. (10) have been defined before in connection with F_4. Using the restriction of Δ function on the three wave vectors $\vec{k}_1$, $\vec{k}_2$, and $\vec{k}_3$, $\Phi(k_1j_1,k_2j_2,k_3j_3)$ can be written as

$$\phi(k_1j_1,k_2j_2,k_3j_3)$$
$$=\frac{i}{M^{3/2}}\sum_{\vec{n}}\sum_{\alpha\beta\gamma}e_{\alpha}(\vec{k}_1j_1)e_{\beta}(\vec{k}_2j_2)e_{\gamma}(\vec{k}_3j_3)$$
$$\times\Phi_{\alpha\beta\gamma}(\vec{n})[s_1+s_2+s_3]\ ,\qquad(11)$$

where $s_i=\sin(\pi a\vec{k}_i\cdot\vec{n})$ and α, β, γ each take the value xyz in summation. The summation over $\vec{n}$ implies the sum over neighbors considered in the anharmonic interaction. When the summation is carried out over α, β, γ, in Eq. (11) the resulting 27 terms can be grouped into 10 terms by using the symmetry properties of $\phi_{\alpha\beta\gamma}$ (the third-order tensor derivative) and we find

$$\Phi(1,2,3)=\frac{i}{M^{3/2}}\sum_{\vec{n}}[\phi_{xxx}(n)e_{1x}e_{2x}e_{3x}+\phi_{yyy}(n)e_{1y}e_{2y}e_{3y}+\phi_{zzz}(n)e_{1z}e_{2z}e_{3z}$$
$$+\phi_{xyx}(n)(e_{1x}e_{2y}e_{3x}+e_{1y}e_{2x}e_{3x}+e_{1x}e_{2x}e_{3y})+\phi_{xzx}(n)(e_{1x}e_{2z}e_{3x}+e_{1z}e_{2x}e_{3x}+e_{1x}e_{2x}e_{3z})$$
$$+\phi_{yxy}(n)(e_{1y}e_{2x}e_{3y}+e_{1x}e_{2y}e_{3y}+e_{1y}e_{2y}e_{3x})+\phi_{yzy}(n)(e_{1y}e_{2z}e_{3y}+e_{1z}e_{2y}e_{3y}+e_{1y}e_{2y}e_{3z})$$
$$+\phi_{zxz}(n)(e_{1z}e_{2x}e_{3z}+e_{1x}e_{2z}e_{3z}+e_{1z}e_{2z}e_{3x})+\phi_{zyz}(n)(e_{1z}e_{2y}e_{3z}+e_{1y}e_{2z}e_{3z}+e_{1z}e_{2z}e_{3y})$$
$$+\phi_{xyz}(n)(e_{1x}e_{2y}e_{3z}+e_{2x}e_{3y}e_{1z}+e_{3x}e_{1y}e_{2z}+e_{1x}e_{2z}e_{3y}+e_{1z}e_{2y}e_{3x}+e_{1y}e_{2x}e_{3z})]$$
$$\times[s_1(n)+s_2(n)+s_3(n)]\}\ .\qquad(12)$$

Now for a given wave vector $\vec{k}$ the summation over neighbors would involve sums of the type

$$D_{xyz}(\vec{k})=\sum_{\vec{n}}\phi_{xyz}(\vec{n})\sin(\pi a\vec{k}\cdot\vec{n})\ .\qquad(13)$$

This sum can be easily carried out for a nth lattice point in the sth shell having n^s lattice points with coordinates $\frac{1}{2}a[n_x^s,n_y^s,n_z^s]$, where n_x^s, n_y^s, n_z^s are three non-negative integers with $n_x^s\geq n_y^s\geq n_z^s$.

The final result is

$$D_{xyz}(\vec{k})=-\sum_{s}n^s/6\,\phi_{xyz}(n^s)$$
$$\times[s_{xx}(s_{yy}s_{zz}+s_{yz}s_{zy})+s_{xy}(s_{yz}s_{zx}+s_{yx}s_{zx})$$
$$+s_{xz}(s_{yx}s_{zy}+s_{yy}s_{zx})]\ ,\qquad(14)$$

where $s_{\alpha\beta}=\sin(\pi ak_{\alpha}n_{\beta}^s)$. Due to the invariant nature of the summand, the right-hand side is to be evaluated for one representative point only in a given shell. The sum over s implies the summation over shells. Similarly other sums of the type

$$D_{xxx}(k)=\sum_{\vec{n}}\phi_{xxx}(n)\sin(\pi a\vec{k}\cdot\vec{n}),$$

etc., can be evaluated.

IV. NUMERICAL RESULTS

When evaluating F_3 and F_4 one has to decide (a) how many neighbors over which to perform the sums and (b) what mesh size to use for the sums over the $\vec{k}$ vectors. Let us discuss (a) first. We have carried out the calculation of both F_3 and F_4 for as many as 23 neighbor shells in both materials and at all temperatures. In each case, F_3 converged very nicely and it was almost certainly not necessary to sum over so many neighbors. On the other hand, as each neighbor contribution was added in to F_4 it tended to oscillate, sometimes quite wildly, and by the time the 23rd neighbor was reached, it still had not converged. However, it was possible to estimate what the final number would be within certain confidence limits and these estimates are the numbers that are listed in this paper.

The reason for the slow oscillatory convergence is easy to understand. Both the Na and K potentials show an asymptotic behavior of the form[2,20] $r^{-5}\cos(2k_F r+\theta)$. Therefore, 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 the distance is roughly proportional to r_n^2 for large r_n. Thus we can expect that contributions to F_4 from individual neighbor shells will show roughly an r_n^{-3} dependence, which of course gives rise to rather slow convergence. Exactly the same problem has been encountered in the calculation of elastic constants.[20] The more rapid convergence of F_3 is attributable to the fact that this term contains essentially the square of the potential and its derivatives, and thus the individual neighbor contributions show an r_n^{-6} dependence, which rapidly became negligibly small as r_n increases.

An important consequence of the slow convergence of F_4 is the fact that it can be extremely hazardous to terminate the sums at a small number of neighbors when using an oscillatory potential. For example, if we had terminated our sums at the second-neighbor shell we would have obtained values of F_4 which differed from the final numbers in Na by about 15% or so. However, in K, the same procedure would have yielded values of F_4 which were typically 100% too large.

Turning our attention to the mesh size for the sums over k vectors, we have used a simple cubic mesh of wave vectors ($\vec{k}=\vec{p}/L$) and boundaries of the first Brillouin zone defined by $p_x+p_y\leq L$, $p_y+p_z\leq L$, $p_z+p_x\leq L$, and $L\geq p_x\geq p_y\geq p_z\geq 0$, where p_x, p_y, p_z, and L are integers. This yields $2L^3$ points in the whole zone. We find that for $L=6$, F_3 converges to two significant figures. For $L=7$, the computing time involved becomes prodigious and does not seem to justify the slight improvement in accuracy. For F_4, $L\sim 20$ seems to be necessary to get good convergence but the computer time is no problem in this case since F_4 is a much simpler quantity to calculate. Hence, the numbers for F_4 quoted in this paper are for $L=20$.

V. DISCUSSION

The experimental specific-heat data for all the alkali metals in the solid phase have been analyzed by Martin[14] from the viewpoint of extracting the anharmonic contribution to the specific heat at constant volume (C_V^A). In each case he has presented the results in the form

$$C_V^A=3NA(V)k_BT\ , \tag{15}$$

where the coefficient A refers to the 0 °K volume. Thus, we can make a meaningful comparison of our results of $A(V)$ with experiment only at low-temperature volumes.

For potassium we find that A is positive over the entire temperature range. At $T=9$ °K our value of A is within 75% of the value given in Table VII of Martin's paper, which can certainly be regarded as reasonable agreement for this type of calculation.

For sodium the situation is not so simple. Our values of A, although positive over most of the temperature range, becomes ~0 at 293 °K and ac-

TABLE I. F_3, F_4, and the coefficient A in C_V^A for sodium and potassium. F_3 and F_4 are in units of $10^{12}N(KT)^2$ erg^{-1} and A in units of 10^{-4}.

Lattice parameter	F_3	F_4	$F=F_3+F_4$	A ($C_V^A=3NAKT$)
		Sodium		
4.2247 Å ($T=5$ °K)	−2.56	2.10±0.20	−0.46±0.20	0.42±0.2
4.234 Å ($T=90$ °K)	−2.47	1.42±0.10	−1.05±0.10	0.97±0.1
4.251 Å ($T=160$ °K)	−2.58	1.95±0.05	−0.63±0.05	0.58±0.05
4.288 Å ($T=293$ °K)	−3.01	2.90±0.2	−0.11±0.2	0.10±0.2
4.309 Å ($T=361$ °K)	−3.08	3.10±0.15	+0.02±0.15	0.02±0.14
		Potassium		
5.233 Å ($T=9$ °K)	−1.66	0.70±0.15	−0.96±0.15	0.88±0.14
5.261 Å ($T=99$ °K)	−1.91	1.30±0.10	−0.61±0.10	0.56±0.1
5.305 Å ($T=215$ °K)	−2.01	1.10±0.05	−0.91±0.05	0.84±0.05
5.343 Å ($T=299$ °K)	−2.28	1.70±0.10	−0.58±0.10	0.53+0.1

tually turn out to be negative at $T=361$ °K. This situation arises because of the strong cancellation between F_3 and F_4. Our low-temperature value differs from Martin's result by a factor of 4 which is still not unreasonable, although it is not as satisfactory as for K.

As mentioned in the Introduction we felt that it was of interest to check the influence of the choice of electron gas screening on the final results. Hence, we recalculated the Na potential at two values of the lattice parameter using Vashishta and Singwi[5] (VS) screening instead of Geldart and Taylor[3] (GT) screening. These two screening functions both satisfy the compressibility theorem, but differ somewhat for $q \sim k_F$. The values of F_3 and F_4 resulting from VS screening differ slightly from the GT values but the difference does not seem to be significant. For example, at $a=4.234$ Å, VS screening gives $F_3=-2.525$, $F_4=1.55\pm0.10$ in units of $10^{12}N(k_BT)^2\,\mathrm{erg}^{-1}$ as compared to the GT results of $F_3=-2.468$ and $F_4=1.42\pm0.10$ in the same units. Quite clearly then the choice of screening for the type of calculations in this paper is not critical.

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