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Adiabatic and nonadiabatic contributions to the free energy from the electron-phonon interaction for Na, K, Al, and Pb

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We calculate the adiabatic contributions to the free energy due to the electron-phonon interaction at intermediate temperatures $0 \leq k_B T < \epsilon_F$ for the elemental metals Na, K, Al, and Pb. Using our previously published results for the nonadiabatic contributions we show that the adiabatic contribution, which is proportional to T^2 at low temperatures and goes as T^3 at high temperatures, dominates the nonadiabatic contribution for temperatures above a crossover temperature, T_c, which is between $0.5T_m$ and $0.8T_m$, where T_m is the melting temperature of the metal. The nonadiabatic contribution falls as T^{-1} for temperatures roughly above the average phonon frequency.

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I. INTRODUCTION

The crystal free energy consists of contributions from the static-lattice potential, the phonons, the electronic excitations, phonon-phonon interactions, and electron-phonon interactions [Wallace,[1] Eq. (20.1)]. The last term is generally the smallest, but little is known about the size of this contribution except at very low temperatures. We, therefore, study the electron-phonon free energy F_{ep} in order to assess its contribution to the thermodynamic properties of metals at all temperatures to melting.

The total electron-phonon free energy was derived by Eliashberg[2] in a paper on superconductivity. In this formulation, the electron-phonon interaction in the crystal ground state is double counted. The ground state subtraction, which corrects for the ground state double counting, was derived in Wallace,[3] Eq. (25.26). It is well known that electron-phonon interactions contribute to the low-temperature electronic specific heat C_{el}, according to

$$C_{el} = \Gamma_{bs}(1+\lambda)T. \tag{1}$$

The bare electron contribution is $\Gamma_{bs}T$, where Γ_{bs} is proportional to the electronic density of states at the Fermi level determined by band structure. The nonadiabatic electron-phonon contribution gives the term in λ, and can be quite large, e.g., $\lambda \approx 1.5$ for lead.[4,5] In earlier years, many theoretical calculations of λ were carried out for the simple metals, showing rather good agreement between theory and experiment. These results were reviewed by Grimvall,[6] Tables III–VI; see also Wallace,[3] Tables 27 and 28. Grimvall[6] evaluated the Eliashberg formula for lead, and concluded that F_{ep} vanishes at temperatures above the phonon characteristic temperature. This conclusion will be revised in the present paper.

The adiabatic approximation[7] rests on the expansion of the coupled nuclear-electron Hamiltonian in powers of m/M, the ratio of electron to nuclear mass. When terms of order m/M are neglected, the electronic wave functions do not see the nuclear motion, and depend only on the static nuclear positions.[7] The case of lattice dynamics is treated by Born and Huang,[8] p. 171. In the partition function, the same property is revealed by treating the operation of the nuclear kinetic energy on the electronic wave functions as a small effect.[9] When this operation is neglected entirely, which is appropriate at high temperatures where the nuclear motion is classical, only the adiabatic part F^{ad} survives in F_{ep} (Wallace,[1] pp. 91–93). It is, therefore, seen that the electronic states are not mixed in the adiabatic part, and also that F^{ad} is the dominant part at high temperatures. The nonadiabatic part $F_1^{na}+F_2^{na}$ arises from the mixing of electronic states by the nuclear kinetic energy, and becomes unimportant at high temperatures.

Allen and Heine[10] separated electron-phonon effects into adiabatic and nonadiabatic contributions, and studied the adiabatic part of the electron energy shifts. For the Eliashberg formulation, Allen and Hui[11] studied the adiabatic contribution to the high-temperature specific heat. Present results will be compared with Allen and Hui in Sec. III. The leading correction to the linear temperature dependence in the specific heat given in Eq. (1) is a nonadiabatic term which goes as $T^3 \ln T$. This has been studied extensively in the literature starting with Buckingham[12] and Buckingham and Schafroth.[13] See Refs. 14 and 15, and references therein for more recent work.

We have previously addressed the problem of calculating the contribution to the free energy from the electron-phonon interaction.[5] We found the nonadiabatic part of this contribution, F_2^{na}, to second order in the interaction. We calculated F_2^{na} for four nearly-free-electron metals, Na, K, Al, and Pb, for temperatures between zero and roughly 1.5 times the melting temperature.

As in the calculation of the nonadiabatic contribution, our calculations are done for a constant density ρ to eliminate concern for the density dependence of phonon frequencies and electron-phonon interaction matrix elements. The density is that at the temperature T_ρ, where the phonon frequencies are measured. The melting temperature at this density is higher than the customary zero-pressure melting temperature. Our calculations cover the range from $T=0$ to above T_m.

The paper is organized as follows. In Sec. II we present the expression for the adiabatic and nonadiabatic parts of F_{ep}, and we discuss the formulation for metals in general, the simplification for the nearly-free-electron metals studied here, and the ground state subtraction. Asymptotic temperature dependences are derived for the adiabatic part. In Sec. III our results are presented with a detailed discussion of the numerical methods used, the adiabatic and nonadiabatic parts are compared, and our results are compared with previous work. Our conclusions are summarized in Sec. IV.

II. ADIABATIC CONTRIBUTION TO THE ELECTRON-PHONON FREE ENERGY

A. Analytic form of the free energy

The electron-phonon contribution to the free energy can be written in three pieces, $F_{ep}=F^{ad}+F_1^{na}+F_2^{na}$,

$$\frac{F^{ad}}{N}=\sum_{\vec{p}\vec{k}\vec{Q}\lambda}\frac{\hbar^2}{N^2M}\frac{n_{\vec{k}\lambda}+\frac{1}{2}}{\hbar\omega_{\vec{k}\lambda}}(f_{\vec{p}}-g_{\vec{p}})\times\left\{\frac{[(\vec{k}+\vec{Q})\cdot\hat{\eta}_{\vec{k}\lambda}]^2[U(\vec{k}+\vec{Q})]^2}{\epsilon_{\vec{p}}-\epsilon_{\vec{p}+\vec{k}+\vec{Q}}}-\frac{[\vec{Q}\cdot\hat{\eta}_{\vec{k}\lambda}]^2[U(\vec{Q})]^2}{\epsilon_{\vec{p}}-\epsilon_{\vec{p}+\vec{Q}}}\right\}, \tag{2}$$

$$\frac{F_1^{na}}{N}=\sum_{\vec{p}\vec{k}\vec{Q}\lambda}\frac{\hbar^2}{N^2M}\hbar\omega_{\vec{k}\lambda}\left(n_{\vec{k}\lambda}+\frac{1}{2}\right)\times\frac{f_{\vec{p}}}{\epsilon_{\vec{p}}-\epsilon_{\vec{p}+\vec{k}+\vec{Q}}}\frac{[(\vec{k}+\vec{Q})\cdot\hat{\eta}_{\vec{k}\lambda}]^2[U(\vec{k}+\vec{Q})]^2}{[\epsilon_{\vec{p}}-\epsilon_{\vec{p}+\vec{k}+\vec{Q}}]^2-[\hbar\omega_{\vec{k}\lambda}]^2}, \tag{3}$$

$$\frac{F_2^{na}}{N}=\sum_{\vec{p}\vec{k}\vec{Q}\lambda}\frac{\hbar^2}{2N^2M}f_{\vec{p}}(1-f_{\vec{p}+\vec{k}+\vec{Q}})\frac{[(\vec{k}+\vec{Q})\cdot\hat{\eta}_{\vec{k}\lambda}]^2[U(\vec{k}+\vec{Q})]^2}{[\epsilon_{\vec{p}}-\epsilon_{\vec{p}+\vec{k}+\vec{Q}}]^2-[\hbar\omega_{\vec{k}\lambda}]^2}. \tag{4}$$

Our results are calculated and quoted per atom. Throughout this paper we will use the following nomenclature: $f_{\vec{p}}$ is the Fermi-Dirac distribution function at finite temperature and $g_{\vec{p}}$ is the same at $T=0$. $n_{\vec{k}\lambda}$ is the Bose-Einstein distribution function at finite temperature and $\hat{\eta}_{\vec{k}\lambda}$ is the polarization vector of the phonon branch λ for wave vector $\vec{k}$ which is inside the Brillouin zone. $\vec{Q}$ is a reciprocal lattice vector and $\omega_{\vec{k}\lambda}$ is the frequency of a phonon mode. $U(\vec{k}+\vec{Q})$ is the Fourier transform of the pseudopotential for momentum transfer $\vec{k}+\vec{Q}$.

To remind the reader of the physical meaning of the three terms in Eqs. (2)–(4) (a more detailed discussion can be found in Bock *et al.*[5]) a quick summary: Eq. (2), F^{ad}, expresses the thermally averaged vibrational contributions to the excited electronic energies. Equations (3) and (4), $F_{1,2}^{na}$, describe the nonadiabatic corrections to all electronic energy levels and take into account the mixing of electron states due to the ion motion.

In the free energy formulation, the electron-phonon interaction is treated in a second order perturbation theory.[1–6,10,11,14,15] For a general metal, the electrons are presumed to have band structure, and the energy denominators are band electron energies $E_{\vec{k}}$. For nearly-free-electron metals, band structure effects may be treated in pseudopotential perturbation theory, where in zeroth order the electron energies are the free-electron energies $\epsilon_{\vec{k}}$. This is why free-electron energies appear in the denominator of Eqs. (2)–(4). In these equations, the band structure effects, to second order in the pseudopotential, are contained in the last term in brackets in Eq. (2). Pseudopotential perturbation theory has been extensively developed over many years, and pseudopotential parameters have been calibrated to experimental data such as equilibrium density and bulk modulus. We use these calibrated pseudopotentials here, so that our models have no free parameters.

Finally, we need to clarify the problem of ground state double counting. The potential for the nuclear motion, the "adiabatic potential," is precisely the electronic ground state energy as a function of static nuclear positions. Since this potential has been put into the phonon Hamiltonian, the electronic ground state energy has to be subtracted from the electron-phonon Hamiltonian. In this way the electronic statistical mechanics expresses only electronic excitations from the ground state. The ground state subtraction is an adiabatic effect, and is expressed by the term $(-g_{\vec{p}})$ in Eq. (2). The decomposition of the total Hamiltonian for a metal crystal, and derivation of the corresponding free energy, including Eqs. (2)–(4), is given in Wallace.[1]

B. Analytic temperature dependence

The temperature dependence of F^{ad}, Eq. (2), arises from the product of the Fermi-Dirac factor $(f_{\vec{p}}-g_{\vec{p}})$ and the phonon factor $(n_{\vec{k}\lambda}+\frac{1}{2})$. The value at $T=0$, i.e., the constant term in F^{ad}, vanishes because $(f_{\vec{p}}-g_{\vec{p}})$ vanishes at $T=0$. Using a Sommerfeld expansion (e.g., p. 45 in Ashcroft and Mermin[16]) of Eq. (2), the Fermi-Dirac factor gives a quadratic temperature dependence in leading order, plus higher order terms which are of relative order $(k_BT/\epsilon_F)^2$ and so can be neglected at temperatures to well above T_m. The phonon factor reduces to the constant $\frac{1}{2}$ at very low temperatures, i.e., at $k_BT \ll$ the mean phonon energy $\langle\hbar\omega\rangle$, so that the net dependence at very low temperatures is

$$F^{ad}=B_2(k_BT)^2. \tag{5}$$

At higher temperatures, i.e., at $k_BT \gtrsim \langle\hbar\omega\rangle$, each phonon factor can be expanded as

$$\left(n_{\vec{k}}+\frac{1}{2}\right)=\frac{1}{\beta\hbar\omega}+\frac{\beta\hbar\omega}{12}+\frac{(\beta\hbar\omega)^3}{720}+\cdots . \tag{6}$$

Hence the temperature dependence at $k_BT \gtrsim \langle\hbar\omega\rangle$ becomes

$$F^{ad}=B_3(k_BT)^3+\cdots . \tag{7}$$

As we will show in a later section, our numerical results confirm this analytic temperature dependence.

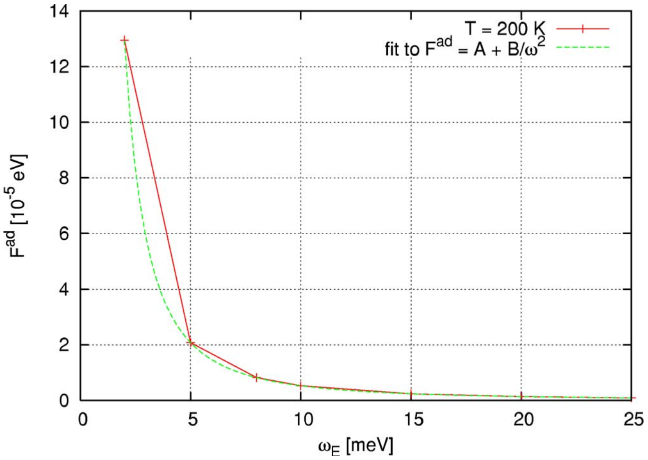

FIG. 1. (Color online) ω_E dependence of F^{ad} for Na at $T=200$ K.

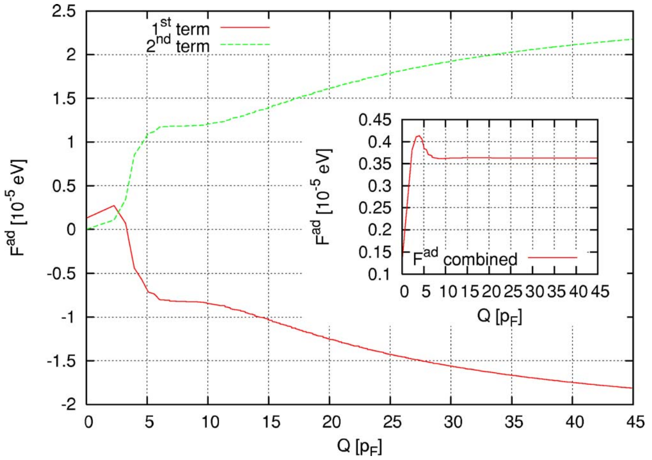

FIG. 2. (Color online) Convergence behavior of F^{ad} for Na at $T=200$ K. The inset shows the combined terms.

III. RESULTS

A. Phonon model

When we calculated the nonadiabatic contributions we found that we could replace the phonon dispersion with a constant frequency with high accuracy which simplified our numerical evaluation. In fact, we found that the result of our calculation was not sensitive to the value of this frequency, ω_E, and that an Einstein model gives the correct temperature dependence. We reasoned that this insensitivity is due to the fact that the integrands of $F^{na}_{1,2}$ are finite and well-behaved as a function of $\omega_{\vec{k}\lambda}$. The adiabatic contribution, on the other hand, diverges as $\omega_E \to 0$ as illustrated in Fig. 1 and is, therefore, very sensitive to the choice of ω_E. Although the Einstein model will give the correct temperature dependence at low and high temperatures, as listed in Eqs. (5) and (7), we have no way of finding the Einstein frequency which will give us the correct magnitude without doing a calculation with the full phonon dispersion. This is a serious problem as can be seen from the extreme dependence on ω_E as shown in Fig. 1. Since in the case of F^{ad} the calculation using the full phonon dispersion is not prohibitive, we chose for this paper to use a fully $\vec{k}$-dependent phonon dispersion.

In the following we calculated the phonon dispersion and eigenvectors from Born–von Kármán force constants to get a more realistic representation of the real phonon spectrum with its three branches (the force constants were taken from Dederichs *et al.*[17]).

B. Numerical techniques

Equation (2) is written in terms of sums over the electron and phonon momenta. We are using a free-electron dispersion spectrum which is isotropic in the electron momentum. This combined with the fact that $|\vec{p}|$ is bounded by $(f_{\vec{p}}-g_{\vec{p}})$ from above and below to $|\vec{p}|\approx p_F$ to within a few k_BT makes it numerically more convenient for us to rewrite $\Sigma_{\vec{p}}$ as an integral,

$$\sum_{\vec{p}} = \frac{NV_A}{(2\pi)^3}\int d^3p. \tag{8}$$

The sum over phonon momenta however is evaluated more conveniently as a sum because of the two terms in the curly brackets in F^{ad}. The momentum transfer $\vec{k}+\vec{Q}$ enters the second term only with the reciprocal lattice vector $\vec{Q}$. Were we to integrate over the final electron momentum $\vec{p}\,'=\vec{p}+\vec{k}+\vec{Q}$, the second term would introduce discrete steps into the integrand as we change $\vec{p}\,'$. This is very difficult to handle numerically. Summing over $\vec{k}$ and $\vec{Q}$ instead converges much faster. The expression we evaluated is given by

$$\frac{F^{ad}}{N} = \frac{V_A}{(2\pi)^3}\mathcal{P}\int d\vec{p}\sum_{\vec{k}\vec{Q}\lambda}\frac{\hbar^2}{NM}\frac{n_{\vec{k}\lambda}+\frac{1}{2}}{\hbar\omega_{\vec{k}\lambda}}(f_{\vec{p}}-g_{\vec{p}}) \times\left\{\frac{[(\vec{k}+\vec{Q})\cdot\hat{\eta}_{\vec{k}\lambda}]^2[U(\vec{k}+\vec{Q})]^2}{\epsilon_{\vec{p}}-\epsilon_{\vec{p}+\vec{k}+\vec{Q}}}-\frac{[\vec{Q}\cdot\hat{\eta}_{\vec{k}\lambda}]^2[U(\vec{Q})]^2}{\epsilon_{\vec{p}}-\epsilon_{\vec{p}+\vec{Q}}}\right\}, \tag{9}$$

where $\mathcal{P}$ denotes the Cauchy principal value.

At this point we would like to address the question of convergence in our calculation since the sum on $\vec{k}+\vec{Q}$ is not obviously bounded by an upper limit. We had found for the two nonadiabatic parts strong convergence as a function of $\vec{p}\,'$ due to a combination of the pseudopotential factor and the energy denominator. In the case of the adiabatic contribution, however, this is not quite so obvious. The energy denominator is only linear in the energy difference and we, therefore, expect the convergence of the two single terms in F^{ad} to go as Q^{-2}, which is quite weak. We do suspect, however, that the two terms in the curly brackets will exhibit cancellation to some degree and might improve the convergence behavior of F^{ad}. In Fig. 2 we plot the two terms separately and combined as a function of magnitude of $\vec{Q}$. Despite the slow convergence behavior of the terms by themselves, their combination converges strongly.

C. Comparing the adiabatic with the nonadiabatic results

As mentioned earlier, we calculated F^{ad} using force constant models for the phonon dispersion for the elemental metals Na, K, Al, and Pb. Our result for Na is shown in Fig.

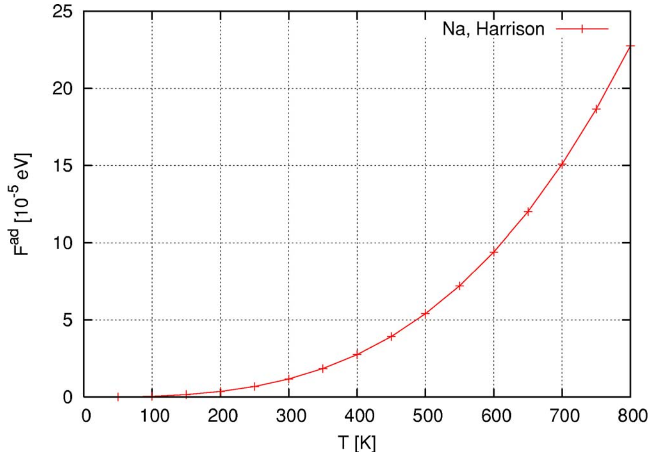

FIG. 3. (Color online) F^{ad} for Na using full phonons.

3. A polynomial fit of the temperature dependence in the low- and high-temperature regime shows that our initial analysis was correct and $F^{ad} \propto T^2$ for low temperatures and that it turns into $\propto T^3$ for higher temperatures.

The sign of F^{ad} for all metals studied here except Al is positive. It is not obvious from Eq. (9) why this is the case. We can speculate that the sign is determined by the relative magnitudes of the two terms in parentheses in F^{ad} since we know from our convergence study (Fig. 2) that the two terms are roughly of equal strength but of opposite sign. The difference between the two terms is the scattering momentum which is the full phonon momentum in the first term $(\vec{k}+\vec{Q})$ and the reciprocal lattice vector only in the second term $(\vec{Q})$.

The Fermi-Dirac factor $(f_{\vec{p}}-g_{\vec{p}})$ ensures that the first electron momentum, $\vec{p}$, is essentially confined to the Fermi surface, p_F. For the denominators to be small, the second electron momentum, $(\vec{p}+\vec{k}+\vec{Q})$ and $(\vec{p}+\vec{Q})$, has to, therefore, lie close to the Fermi surface. Although the exact shape of the Fermi surface can be quite complicated we would like to restrict this argument to a spherical Fermi surface since we are using the pseudopotential formalism in this calculation and do not take separate bands into account. In this case it is plausible to speculate that a change of the radius of the Fermi surface might be able to effect an overall sign change in F^{ad}.

We explore this possibility by means of a "simplified F^{ad}," given by Eq. (9) with the pseudopotential set to a constant and with a "fictitious p_F" that is allowed to vary. This amounts to pretending that we can change the number of free electrons, hence change the size of the Fermi surface, without changing anything else. In this case the essential part of the second term in Eq. (9) is the $\vec{p}$-angle average of $(\epsilon_{\vec{p}}-\epsilon_{\vec{p}+\vec{Q}})^{-1}$ with $|\vec{p}|$ equal to the fictitious p_F and with Q any reciprocal lattice vector. This integral diverges as the fictitious p_F passes through $p_n = \frac{1}{2}Q_n$, where Q_1 is the magnitude of the first reciprocal lattice vector, and so on for Q_2, etc. At the same time, the first term in Eq. (9) is well behaved as a function of the fictitious p_F. Numerical evaluation of the simplified F^{ad} is shown in Fig. 4 for Na and Al, and reveals the expected logarithmic discontinuities at $p_n = \frac{1}{2}Q_n$. Figure 4 supports the view that the sign of F^{ad} depends directly on the size of the Fermi surface relative to the Brillouin zone surface.

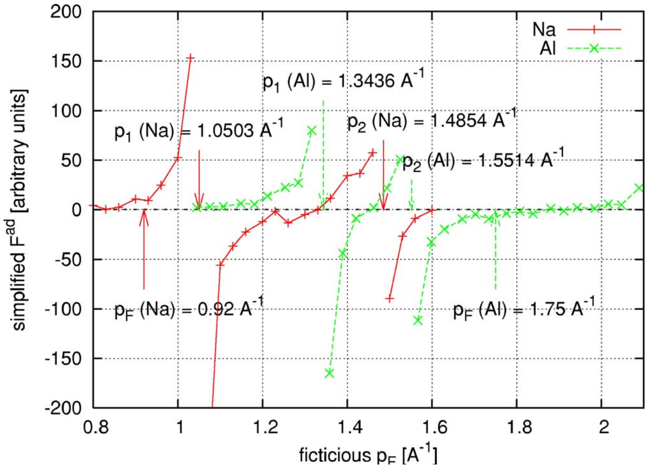

FIG. 4. (Color online) Dependence of the sign of F^{ad} as a function of p_F for Na at $T=200$ K and for Al at $T=500$ K. For illustration purposes, the lengths $p_{1,2} = \frac{1}{2}|\vec{Q}_{1,2}|$ of the first two reciprocal lattice vectors are shown.

Our results for Na for F^{ad} including our previous results for F_2^{na} are shown in Fig. 5. At low temperatures, the adiabatic contribution vanishes and the nonadiabatic contribution approaches a constant. In the low-temperature regime, the free energy is dominated by the nonadiabatic contribution. In the high-temperature regime, the adiabatic contribution increases as T^3 and the nonadiabatic contribution slowly vanishes. The adiabatic contribution dominates in this temperature regime. At about ≈320 K there is a crossover between the two contributions. For reference we included the temperature of an average phonon frequency and the melting temperature of Na in the graph. The crossover temperature is well between either one of these two temperatures.

Figure 6 shows our results for K. We find the same qualitative behavior. The crossover temperature is always well between the two reference temperatures. The same is seen for our results for Pb, shown in Fig. 7.

In the case of Al we repeated the calculation for both pseudopotential models. Our results are shown in Fig. 8. The

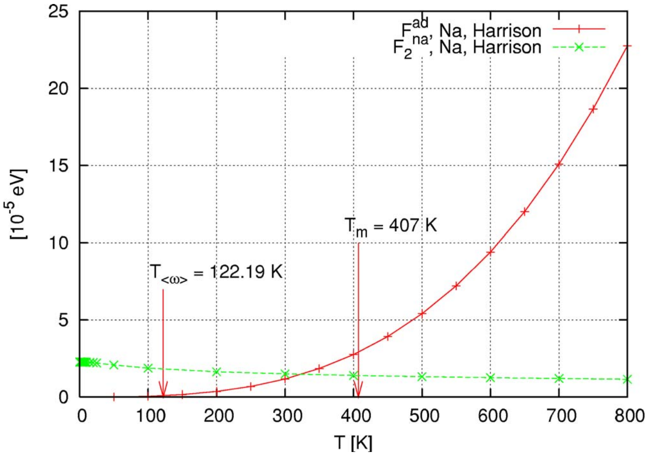

FIG. 5. (Color online) F^{ad} and F_2^{na} for Na. The crossover temperature is shown.

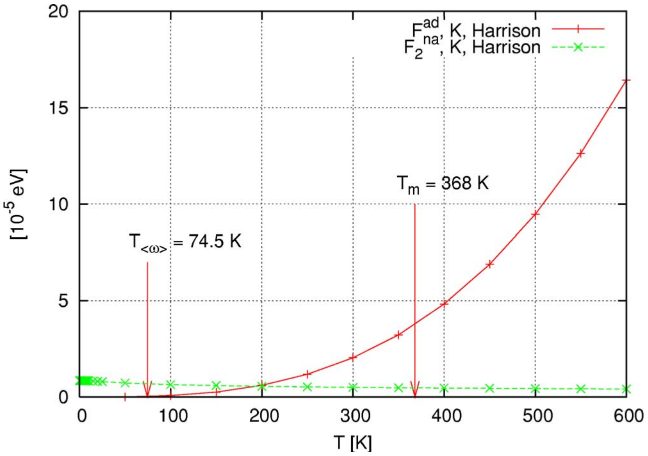

FIG. 6. (Color online) F^{ad} and F_2^{na} for K. The crossover temperature is shown.

different pseudopotentials effect a slightly different curvature of the temperature dependence in the adiabatic contribution. As we found previously, the nonadiabatic contribution is shifted in energy by about 5×10^{-5} eV. The net result of these two effects on the crossover temperature (between the magnitudes of F^{ad} and F_2^{na}) is to shift this temperature by only roughly 20 K. The difference between the two pseudopotential models is presumable well within the accuracy of the pseudopotential method and our calculation itself. It does not make any difference which model is chosen.

All of the crossover temperatures are summarized in Table I.

In order to assess the overall importance of the adiabatic electron-phonon free energy at high temperatures, we compare it with the bare electron free energy F_{el}. The leading order Sommerfeld expansion of F_{el}, which is quite accurate to T_m for the nearly-free-electron metals, is

$$F_{el} = -\tfrac{1}{2}\Gamma_{bs}T^2. \tag{10}$$

Since F^{ad} increases approximately as T^3 at high T, the ratio F^{ad}/F_{el} has its maximum magnitude at T_m. This ratio is listed in Table I, based on our calculations and the electronic density of states of Moruzzi *et al.*[18] Our corresponding values for S^{ad}/S_{el} at T_m, and C^{ad}/C_{el} at T_m, are also listed in Table I. These results allow us to make estimates for nearly-free-electron metals, of whether or not the adiabatic electron-phonon contribution is significant in a given property of a given metal.

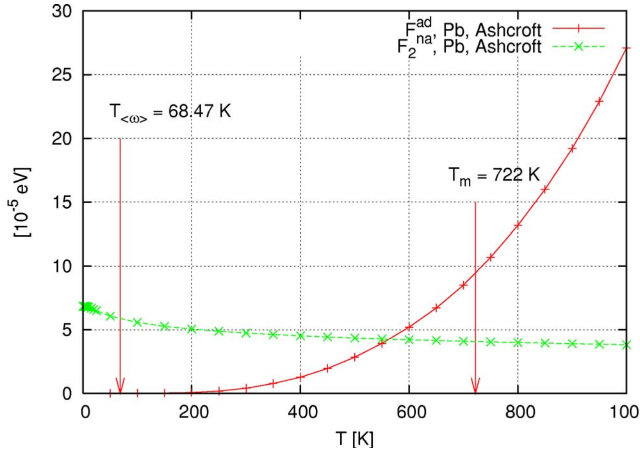

FIG. 7. (Color online) F^{ad} and F_2^{na} for Pb The crossover temperature is shown.

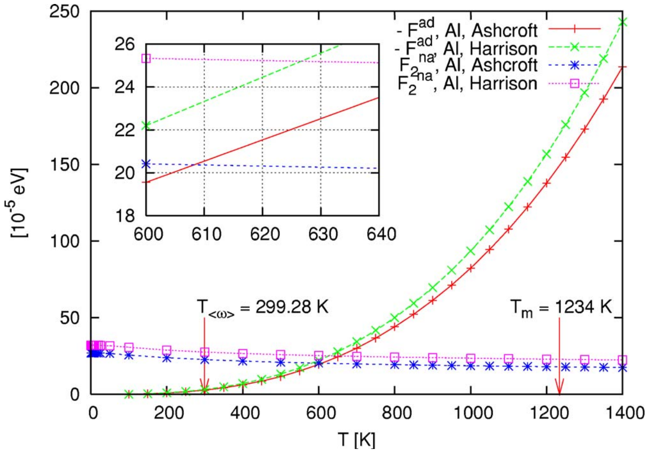

FIG. 8. (Color online) F^{ad} and F_2^{na} for Al. Note that F^{ad} is negative but drawn here as $-F^{ad}$. The crossover temperature is shown. Both pseudopotentials are used. The inset shows the crossover region. The data sets are labeled as in the larger plot.

D. Comparison with previous work

Previous work on the electron-phonon contribution was done on the entropy instead of the free energy (see Fig. 9). The thermodynamic relation

$$S = -\frac{\partial F}{\partial T} \tag{11}$$

relates the two quantities. In order to see how our result for the free energy affects the entropy, we took the derivative of the adiabatic and nonadiabatic contributions and plotted the entropy for temperatures between 100 and 1000 K for lead in Fig. 10. The nonadiabatic entropy slowly vanishes with increasing temperature, whereas the adiabatic contribution increases. The electron-phonon contribution to the entropy in lead was calculated by Grimvall.[19] We found previously that

TABLE I. Crossover temperatures and other quantities.

	Na	K	Al	Pb
Structure	bcc	bcc	fcc	fcc
$\langle\hbar\omega\rangle$ [meV]	10.53	6.42	25.79	5.90
T_{melt} [K]	407	368	1234	722
$T_{melt}^{P=0}$ [K]	371.0	336.4	933.5	600.6
T_c [K]	325	194	609 (A), 627 (H)	563
$F^{ad}/F_{el}(T_m)$	−0.03	−0.03	0.19 (A), 0.22 (H)	−0.13
$S^{ad}/S_{el}(T_m)$	−0.045	−0.045	0.26 (A), 0.30 (H)	−0.20
$C^{ad}/C_{el}(T_m)$	−0.09	−0.09	0.45 (A), 0.50 (H)	−0.39

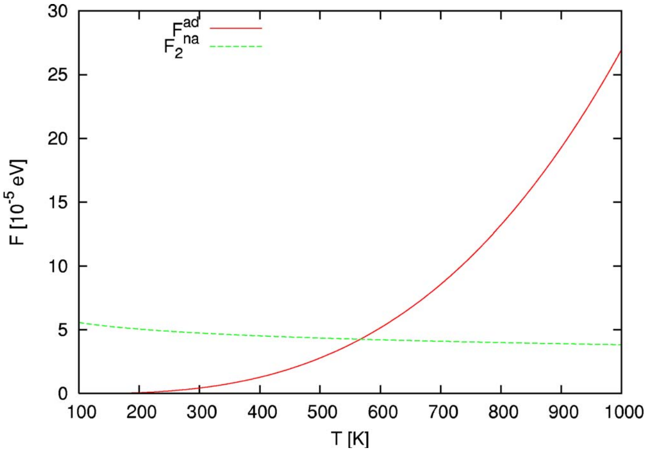

FIG. 9. (Color online) The free energy contributions F^{ad} and F_2^{na} for Pb.

for temperatures up to $T \leqslant 1.4 T_E$ the nonadiabatic contribution to the free energy is sufficient to achieve good agreement with Grimvall's entropy calculation. We now see why. The adiabatic contribution is too small to contribute noticeably to the total entropy. At higher temperatures, however, this will not be the case anymore and the adiabatic contribution will become important. As we see from Fig. 10, S^{ad} increases with temperature and at around $T = 240$ K $|S^{ad}| > |S_2^{na}|$. Grimvall's conclusion that $S_{ep}(T \to \infty) = 0$ is therefore not correct. We also notice that, maybe not surprisingly, the crossover temperature for the free energy is higher than the crossover temperature for the entropy.

Allen and Hui[11] studied the adiabatic electron-phonon specific heat as derived from the Eliashberg free energy. They argued that for A15 metals, which have narrow peaks in the electronic density of states, the adiabatic contribution can be as large as the bare electronic specific heat at high temperatures. Our results in Table I are not inconsistent with this possibility. Differences in our procedure and theirs prevent a further comparison of results. First, their electron-phonon free energy does not contain the ground state subtraction. We note, however, that while the ground state subtraction contributes to the free energy and entropy at all temperatures, its contribution to the specific heat vanishes at high temperatures. Second, our adiabatic specific heat is $C^{ad} = -T(\partial^2 F^{ad} / \partial T^2)_V$, while Allen and Hui remove certain terms from this C^{ad}, to be placed in the bare phonon and bare electron specific heats. This, of course, is not an error but a matter of choice. Nevertheless all the terms in question arise from Eq. (2) for F^{ad} and are, therefore, genuine electron-phonon interaction terms.

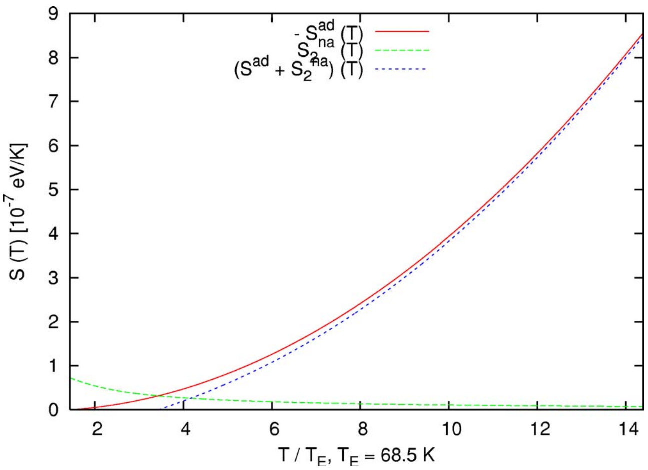

FIG. 10. (Color online) The entropy contributions S^{ad} and S_2^{na} for Pb. The free energy is shown for comparison in Fig. 9.

IV. CONCLUSIONS

A. Structure of the free energy

The exact free energy of a crystalline elemental metal can be expressed as[1,5]

$$F = \Phi_0(V) + F_{el}(V,T) + F_{ep}(V,T) + F_{ph}(V,T) + F_{anh}(V,T), \tag{12}$$

where Φ_0 is the static-lattice potential, F_{ph} represents quasiharmonic phonons, F_{anh} represents phonon-phonon interactions, F_{el} represents static-lattice electronic excitations, and F_{ep} is the remainder of the free energy expressed in terms of interactions between electronic excitations and phonons. F_{ep} is the smallest and most complicated term in Eq. (12). In the leading order thermodynamic perturbation theory, F_{ep} is composed of a nonadiabatic part, $F^{na} = F_1^{na} + F_2^{na}$, and an adiabatic part, F^{ad}. The nonadiabatic part arises from the mixing of electronic states due to the motion of the ions, and strongly affects the lowest electronic excitations. Hence F^{na} dominates F_{ep} at low temperatures. The adiabatic part, F^{ad} expresses the averaging over the thermal motion of the ions of each electronic excited state, and is formally the leading contribution to F_{ep} at high temperatures, where the ion motion is classical. Hence there exists a crossover temperature T_c, below which the major contribution to F_{ep} is F^{na}, and above which it is F^{ad}.

B. Sign and magnitude estimates

The following properties are characteristic of our results for Na, K, Al, and Pb. We suppose these properties are common but not without exception among metals, in general.

(1) F_1^{na} is negligible compared to F_2^{na} for $0 \leqslant T \leqslant T_m$.

(2) F_2^{na} is positive at all T. From a positive value at $T = 0$, F_2^{na} decreases as T^2 at first, then decreases ever more slowly with increasing T (Figs. 4, 6, 8, and 9 of Bock *et al.*[5]).

(3) At very low temperatures, F_2^{na} is the only significant contribution to F_{ep}, and has the form $F_2^{na} = C_2 + A_2 T^2$, where $C_2 > 0$ and $A_2 < 0$. C_2 constitutes an entirely negligible contribution to the electronic ground state energy. The temperature dependence is the same as $F_{el} = -\left(\frac{1}{2}\right)\Gamma_{bs} T^2$ at low temperatures, so that F_2^{na} causes the well-known electron-phonon correction to the bare electronic specific heat. We have $C_{el} + C_{ep} = (\Gamma_{bs} - 2A_2)T$, where $|2A_2 / \Gamma_{bs}|$ ranges from a few percent to around 2.

(4) F^{ad} can be of either sign. F^{ad} is negligible compared to F_2^{na} at low temperatures, but $|F^{ad}| > F_2^{na}$ at $T > T_c$. This is because of the strong temperature dependence of F^{ad}

$=B_3(k_BT)^3$ at $k_BT \gtrsim \langle \hbar\omega \rangle$. Though $|F^{ad}/F_2^{na}|$ increases with temperature, F_2^{na} it not always negligible at T_m (Figs. 5–8). On the other hand, S_2^{na} is negligible compared to $|S^{ad}|$ at high temperatures (Fig. 10).

(5) The ratio $|F^{ad}/F_{el}|$ reaches its maximum at T_m, where it ranges from a few percent to 0.2 (Table I). The ratio $|S^{ad}/S_{el}|$ is larger, and $|C^{ad}/C_{el}|$ is larger still (Table I), so that the adiabatic contribution to the specific heat can become important at high temperatures.

(6) The theory is a complex mixture of electronic excitations and phonons, hence the crossover temperature T_c does not scale with either ϵ_F or $\langle \hbar\omega \rangle$. From our calculations, k_BT_c is well above $\langle \hbar\omega \rangle$, and T_c/T_m is in the range 0.5–0.8.

(7) Based on our results shown in Fig. 4, we expect to see a significant dependence of F^{ad} on the concentrations of the constituents in a real system in which the number of electrons in the conduction band can be controlled, as in an intermetallic compound, for instance.

It is possible to carry out an accurate numerical calculation of the low-temperature nonadiabatic coefficient A_2 [see, e.g., Eq. (25.83) of Wallace[3]]. A good estimate can also be obtained from an Einstein approximation with ω_E determined from $\hbar\omega_E=\langle \hbar\omega \rangle$ (Bock *et al.*[5]). As shown here (Sec. III A), an accurate calculation of F^{ad} requires the use of realistic phonon frequencies and eigenvectors. While an Einstein model does give the correct temperature dependence of F^{ad}, it does not give a reliable magnitude [Eqs. (28.44) and (28.52) and line 3 of Table 27 of Wallace[3]]. Based on a numerical evaluation for Pb to around 100 K, Grimvall[6] concluded that S_{ep} is negligible for temperatures above the mean phonon energy. Our results show that this is not the case, however, since at higher temperatures the adiabatic contribution starts to dominate and the total entropy rises, as shown in Fig. 10. Allen and Hui[11] argued that C^{ad} can become as large as C_{el} for certain metals at high temperatures. Our results for nearly-free-electron metals are not inconsistent with such behavior.

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