Adiabatic and Non–Adiabatic 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 cross-over temperature, $T_c$, which is between 0.5 and 0.8 $T_m$, 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, eq. (20.1)). The last term is generally the smallest, but little is known about the size of this contributions except at very low temperatures. We therefore study the electron–phonon free energy, $F_{\text{ep}}$, 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 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, eq. (25.26). It is well known that electron–phonon interactions contribute to the low temperature electronic specific heat $C_{\text{el}}$, according to

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

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

The adiabatic approximation 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 wavefunctions do not see the nuclear motion, and depend only on the static nuclear positions. The case of lattice dynamics is treated by Born and Huang, p. 171. In the partition function, the same property is revealed by treating the operation of the nuclear kinetic energy on the electronic wavefunctions as a small effect. When this operation is neglected entirely, which is appropriate at high temperatures where the nuclear motion is classical, only the adiabatic part $F_{\text{ad}}$ survives in $F_{\text{ep}}$ (Wallace, p. 91–93). It is therefore seen that the electronic states are not mixed in the adiabatic part, and also that $F_{\text{ad}}$ is the dominant part at high temperatures. The nonadiabatic part $F_{\text{na}}^1 + F_{\text{na}}^2$ arises from mixing of electronic states by the nuclear kinetic energy, and becomes unimportant at high temperatures.

Allen and Heine 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 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. 11 is a nonadiabatic term which goes as $T^3 \ln T$. This has been studied extensively in the literature starting with Buckingham and Buckingham and Schafroth. See references 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\(^7\). We found the nonadiabatic part of this contribution, \(F_{1}^{\text{na}}\), to second order in the interaction. We calculated \(F_{2}^{\text{na}}\) 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 \(\rho\) to eliminate concern for the density dependence of phonon frequencies and electron–phonon interaction matrix elements. The density is that at the temperature \(T_{\mu}\) 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 groundstate 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 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, \(F_{ep} = F_{\text{ad}} + F_{1}^{\text{na}} + F_{2}^{\text{na}}\),

\[
\begin{align*}
\frac{F_{\text{ad}}}{N} &= \sum_{\vec{p} \vec{k} \vec{Q} \lambda} \frac{\hbar^2}{N^2 M} \left( n_{\vec{k} \lambda} + \frac{1}{2} \right) \left( f_{\vec{p}} - g_{\vec{p}} \right) \left\{ \left[ \vec{k} + \vec{Q} \right] \cdot \hat{\eta}_{\vec{k} \lambda} \right\}^2 \left[ \frac{U \left( \vec{k} + \vec{Q} \right)}{\epsilon_{\vec{p}} - \epsilon_{\vec{p} + \vec{Q}} + \hbar \omega_{\vec{k} \lambda}} \right]^2 - \left[ \vec{Q} \cdot \hat{\eta}_{\vec{k} \lambda} \right] \left[ \frac{U \left( \vec{Q} \right)}{\epsilon_{\vec{p}} - \epsilon_{\vec{p} + \vec{Q}} + \hbar \omega_{\vec{k} \lambda}} \right]^2
\end{align*}
\]

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

\[
\frac{F_{2}^{\text{na}}}{N} = \sum_{\vec{p} \vec{k} \vec{Q} \lambda} \frac{\hbar^2}{2N^2 M} f_{\vec{p}} \left( 1 - f_{\vec{p} + \vec{k} + \vec{Q}} \right) \left[ \left( \vec{k} + \vec{Q} \right) \cdot \hat{\eta}_{\vec{k} \lambda} \right] \left[ \frac{U \left( \vec{k} + \vec{Q} \right)}{\epsilon_{\vec{p}} - \epsilon_{\vec{p} + \vec{k} + \vec{Q}} + \hbar \omega_{\vec{k} \lambda}} \right]^2 - \left[ \hbar \omega_{\vec{k} \lambda} \right]^2
\]

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 \(\lambda\) 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.\(^7\)) a quick summary: Eq. 2, \(F_{\text{ad}}\), expresses the thermally averaged vibrational contributions to the excited electronic energies. Eqs. 3 and 4, \(F_{1}^{\text{na}}\), \(F_{2}^{\text{na}}\), describe the non–adiabatic 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 second order perturbation theory.\(^1,2,3,4,5,6,10,11,14,15\). For a general metal, the electrons are presumed to have band structure, and the energy denominators are band electron energies \(E_{\vec{p}}\). 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 \(\epsilon_{\vec{p}}\). 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 groundstate double counting. The potential for the nuclear motion, the “adiabatic potential”, is precisely the electronic groundstate energy as a function of static nuclear positions. Since this potential has been put into the phonon
Hamiltonian, the electronic groundstate energy has to be subtracted from the electron–phonon Hamiltonian. In this way the electronic statistical mechanics expresses only electronic excitations from the groundstate. The groundstate subtraction is an adiabatic effect, and is expressed by the term \((-g_p)\) 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.

B. Analytic temperature dependence

The temperature dependence of \(F_{\text{ad}}\), eq. (2), arises from the product of the Fermi–Dirac factor \((f_\beta - g_\beta)\) and the phonon factor \(\left(n_{\mathbf{k}\lambda} + 1/2\right)\). The value at \(T = 0\), i.e. the constant term in \(F_{\text{ad}}\), vanishes because \((f_\beta - g_\beta)\) vanishes at \(T = 0\). Using a Sommerfeld expansion (e.g. pp. 45 in Ashcroft and Mermin\(^\text{18}\)) of eq. (4), 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 \(1/2\) at very low temperatures, i.e. at \(k_BT \ll \langle h\omega \rangle\), so that the net dependence at very low temperatures is

\[
F_{\text{ad}} = B_2 (k_BT)^2. \tag{5}
\]

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

\[
\left(n_\mathbf{k} + \frac{1}{2}\right) = \frac{1}{\beta h\omega} + \frac{\beta h\omega}{12} + \frac{(\beta h\omega)^3}{720} + \cdots \tag{6}
\]

Hence the temperature dependence at \(k_BT \gtrsim \langle h\omega \rangle\) becomes

\[
F_{\text{ad}} = B_3 (k_BT)^3 + \cdots \tag{7}
\]

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

III. RESULTS

A. Phonon Model

When we calculated the non–adiabatic 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, \(\omega_E\), and that an Einstein model gives the correct temperature dependence. We reasoned that this insensitivity is due to the fact that the integrands of \(F_{1/2}^{\text{na}}\) are finite and well–behaved as a function of \(\omega_{E\lambda}\). 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 \(\omega_E\). 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 to find 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 \(\omega_E\) as shown in Fig. 1. Since in the case of \(F_{\text{ad}}\) the calculation using the full phonon dispersion is not prohibitive, we chose for this report to use a fully \(\mathbf{k}\)–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.\(^\text{18}\)).

B. Numerical Techniques

Eq. (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 \(|\mathbf{p}|\) is bounded by \((f_\beta - g_\beta)\) from above and below to \(|\mathbf{p}| \approx p_F\) to within a few \(k_BT\) makes it numerically more convenient for us to rewrite \(\sum_{\mathbf{p}}\) as an integral,

\[
\sum_{\mathbf{p}} = \frac{NV_A}{(2\pi)^3} \int d^3p. \tag{8}
\]

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

\begin{equation}
\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}{2NM} n_{\epsilon_{\vec{k}\lambda}} \frac{1}{\hbar\omega_{\epsilon_{\vec{k}\lambda}}} (f_{\vec{p}} - g_{\vec{p}}) \left\{ \left[ (\vec{k} + \vec{Q}) \cdot \hat{n}_{\epsilon_{\vec{k}\lambda}} \right]^2 \left[ U(\vec{k} + \vec{Q}) \right]^2 - \left[ \vec{Q} \cdot \hat{n}_{\epsilon_{\vec{k}\lambda}} \right]^2 \left[ U(\vec{Q}) \right]^2 \right\}
\end{equation}

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 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. 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
illustration purposes, the lengths $p_{1,2} = 1/2 |\vec{Q}_{1,2}|$ of the first two reciprocal lattice vectors are shown.

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 $(\epsilon_{\vec{p}_F} - \epsilon_{\vec{p}_F + \vec{Q}})^{-1}$ with $|\vec{p}|$ equal to the fictitious $p_F$ and with $\vec{Q}$ any reciprocal lattice vector. This integral diverges as the fictitious $p_F$ passes through $p_n = 1/2 Q_n$, 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 $p_n = 1/2 Q_n$. Fig. 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.

Our results for Na for $F^{ad}$ including our previous results for $F^{na}_2$ 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 $\approx 320$ K there is a cross–over 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 cross–over temperature is well between either one of these two temperatures.

Fig. 5 shows our results for K. We find the same qualitative behavior. The cross–over temperature is always well between the two reference temperatures. The same is seen for our results for Pb, shown in Fig. 6.

In the case of Al we repeated the calculation for both pseudopotential models. Our results are shown in Fig. 7.

The 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 $5 \times 10^{-5}$ eV. The net result of these two effects on the cross–over temperature (between the magnitudes of $F^{ad}$ and $F^{na}_2$) 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 cross–over temperatures are summarized in Table 1.

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

$$F_{el} = -\frac{1}{2} \Gamma_{bs} T^2.$$
thermodynamic relation was done on the entropy instead of the free energy. The responding values for $S$ 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.

D. Comparison with previous work

Previous work on the electron–phonon contribution was done on the entropy instead of the free energy. The thermodynamic relation

$$S = \frac{\partial F}{\partial T}$$  \hspace{1cm} (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 K 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.\textsuperscript{11} We found previously that for temperatures up to $T \leq 1.4 T_E$ the nonadiabatic contribution to the free energy is sufficient to achieve good agreement with Grimvall’s entropy calculation. We see now 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 $|S^{ad}| > |S^{na}|$. Grimvall’s conclusion that $S_{ep}(T \to \infty) = 0$ is therefore not correct. We also notice that, maybe not surprisingly, the cross–over temperature for the free energy is higher than the cross–over temperature for the entropy.

Allen and Hui\textsuperscript{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

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
structure & Na & K & Al & Pb \\
\hline
$\langle \hbar \omega \rangle$ [meV] & 10.53 & 6.42 & 25.79 & 5.90 \\
$T_{melit}$ [K] & 407 & 368 & 1234 & 722 \\
$T_{P=a0}$ [K] & 371.0 & 336.4 & 933.5 & 600.6 \\
$T_c$ [K] & 325 & 194 & 609 (A), 627 (H) & 563 \\
$F^{ad}/F_d(T_m)$ & -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 \\
\hline
\end{tabular}
\caption{Cross–Over temperatures and other quantities}
\end{table}
perturbation theory, part, 0 tions and phonons. This, of course, is not an error but a matter of choice. Nevertheless all 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. \ref{eq:3} for $F^{ad}$ and are therefore genuine electron–phonon interaction terms.

IV. CONCLUSIONS

A. Structure of the Free Energy

The exact free energy of a crystalline elemental metal can be expressed as

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

where $\Phi_0$ 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. \ref{eq:12}. In leading order thermodynamic perturbation theory, $F_{ep}$ is composed of a nonadiabatic part, $F^{na} = F^{na}_1 + F^{na}_2$, 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. $F^{na}_1$ is negligible compared to $F^{na}_2$ for $0 \leq T \leq T_m$.

2. $F^{na}_2$ is positive at all $T$. From a positive value at $T = 0$, $F^{na}_2$ decreases as $T^2$ at first, then decreases ever more slowly with increasing $T$ (Figs. 4, 6, 8, 9 of Bock et al.\textsuperscript{5}).

3. At very low temperatures, $F^{na}_2$ is the only significant contribution to $F_{ep}$, and has the form $F^{na}_2 = C_2 + A_2 T^2$, where $C_2 > 0$ and $A_2 < 0$. $C_2$ constitutes an entirely negligible contribution to the electronic groundstate energy. The temperature dependence is the same as $F_{el} = -(1/2)\gamma_b T^2$ at low temperatures, so that $F^{na}_2$ causes the well–known electron–phonon correction to the bare electronic specific heat. We have $C_{el} + C_{ep} = (\gamma_b - 2A_2) T$, where $|2A_2/\gamma_b|$ ranges from a few percent to around 2.

4. $F^{ad}$ can be of either sign. $F^{ad}$ is negligible compared to $F^{na}_2$ at low temperatures, but $|F^{ad}| > F^{na}_2$ at $T > T_c$. This is because of the strong temperature dependence of $F^{ad} = B_3 (k_B T)^3$ at $k_B T \gg \langle \hbar \omega \rangle$. Though $|F^{ad}/F^{na}_2|$ increases with temperature, $F^{na}_2$ it not always negligible at $T_m$ (Figs. 4 - 8). On the other hand, $S^{na}_2$ 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 1). The ratio $|S^{ad}/S_{el}|$ is larger, and $|C^{ad}/C_{el}|$ is larger still (Table 1), 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 $\epsilon_F$ or $\langle \hbar \omega \rangle$. From our calculations, $k_B T_c$ 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. 1 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). A good estimate can also be obtained from an Einstein approximation with $\omega E$ determined from $\hbar \omega E = \langle \hbar \omega \rangle$ (Bock et al.). As shown here (Sec. II 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). Based on a numerical evaluation for Pb to around 100 K, Grimvall concluded that $S_{sp}$ 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, shown in Fig. 10. Allen and Hui 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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References:
1. D. C. Wallace, *Statistical Physics of Crystals and Liquids* (World Scientific Publishing Co. Pte. Ltd., 2002).
2. G. M. Eliashberg, Sovet Phys. JETP 11, 696 (1960).
3. D. C. Wallace, *Thermodynamics of Crystals* (John Wiley & Sons, Inc., 1972).
4. P. B. Allen, Phys. Rev. B 36, 2920 (1987).
5. N. Bock, D. Coffey, and D. C. Wallace, Phys. Rev. B 72, 155120 (2005).
6. G. Grimvall, Physica Scripta 14, 63 (1976).
7. M. Born and R. Oppenheimer, Ann. Phys. 84, 457 (1927).
8. M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, 1956), 1st ed.
9. R. W. Zwanzig, Phys. Rev. 106, 13 (1957).
10. P. B. Allen and V. Heine, J. Phys. C 9, 2305 (1976).
11. P. B. Allen and J. C. K. Hui, Z. Physik B 37, 33 (1980).
12. M. J. Buckingham, Nature (London) 168, 281 (1951).
13. M. J. Buckingham and M. R. Schafroth, Proc. Phys. Soc. 67, 828 (1954).
14. M. Danino and A. W. Overhauser, Phys. Rev. B 26, 1569 (1982).
15. D. Coffey and C. J. Pethick, Phys. Rev. B 37, 442 (1988).
16. N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, 1976).
17. P. H. Dederichs, H. Schober, and D. J. Sellmyer, *Phonon States of Elements. Electron States and Fermi Surface of Alloys*, vol. Volume 13, Subvolume A (Springer–Verlag Berlin — Heidelberg — New York, 1981).
18. V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon Press, New York, 1978).
19. G. Grimvall, *The Electron–Phonon Interaction in Metals* (North–Holland Publishing Company, 1981).