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Corrections to the Electronic Heat Capacity of Metals Due to Finite Lifetimes of the Conduction Electrons

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The electron–phonon interaction is well known to enhance the low-temperature electronic heat capacity of metals, $C_{\rm el}$. At high temperatures this enhancement vanishes, but the electron–phonon interaction gives the electrons a finite lifetime. That means a broadened density of states, which affects the high-temperature $C_{\rm el}$. Starting from a many-body theory expression for the entropy, this paper presents an analytical calculation of the correction to $C_{\rm el}$ and a numerical calculation of $C_{\rm el}$ from a realistic density-of-states function, $N(\varepsilon)$. The effect arising from the broadening of $N(\varepsilon)$ may have any sign and typically alters the heat capacity by 10% or less in transition metals.

KEY WORDS: electronic heat capacity; electron–phonon interaction; electronic density of states; electronic entropy; heat capacity; metals; solid-state physics.

1. INTRODUCTION

It is the purpose of this paper to discuss corrections to the Sommerfeld model for the electronic heat capacity of metals, $C_{\rm el}$, arising from the electron–phonon interactions at high temperatures. The Sommerfeld theory leads to the well-known result [1]

$$C_{\rm el} = \frac{2\pi^2}{3} k_{\rm B}^2 T N(\varepsilon_{\rm F}) \tag{1}$$

$N(\varepsilon_{\rm F})$ is the electronic density of states for one spin direction at the Fermi

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level. Electron–phonon many-body interactions will modify Eq. (1) at low temperatures. We can write [2]

$$C_{\text{el}} = C_{\text{band}}(T)(1 + \lambda_{\text{el}-\text{ph}}) \tag{2}$$

where $\lambda_{\text{el}-\text{ph}}$ is the electron-phonon mass enhancement parameter and $C_{\text{band}}(T)$ is the heat capacity in the Sommerfeld model. If $N(\varepsilon)$ can not be regarded as a constant, one may expand it as

$$N(\varepsilon) = N^0 + (\varepsilon - \varepsilon_{\text{F}})\, N' + \tfrac{1}{2}(\varepsilon - \varepsilon_{\text{F}})^2 N'' \tag{3}$$

Here $N^0 = N(\varepsilon_{\text{F}})$, $N' = dN(\varepsilon)/d\varepsilon$, and $N'' = d^2N(\varepsilon)/d\varepsilon^2$ are evaluated at $\varepsilon = \varepsilon_{\text{F}}$. This expansion, together with the Sommerfeld model, gives to the order T^3 [1],

$$C_{\text{band}} = \frac{2\pi^2}{3} k_{\text{B}}^2 T N(\varepsilon_{\text{F}}) \left\{ 1 + \frac{(\pi k_{\text{B}} T)^2}{2} \left[\frac{7}{5} \frac{N''}{N^0} - \left(\frac{N'}{N^0} \right)^2 \right] \right\} \tag{4}$$

The corrections involving N' and N'' in Eq. (4) may become important at high temperatures. Since $\lambda_{\text{el-ph}}$ goes to zero rapidly for $T \geqslant \theta_{\text{D}}/4$, where θ_{D} is the Debye temperature, Eq. (4) might then be expected to give a good account of the electronic heat capacity. However, at the same time that $\lambda_{\text{el-ph}}$ tends to zero, the electron–phonon interaction gives the band electrons a finite lifetime. This affects $N(\varepsilon)$ and hence implies a correction to the high temperature form of C_{el}. We shall see that the finite lifetime affects C_{el}, but only if the energy dependence of $N(\varepsilon)$ near ε_{F} is significant. We may remark that the effect of a varying $N(\varepsilon)$ has recently been studied in connection with other electronic properties. For instance, Mitrović and Carbotte [3] considered the effects of a nonconstant $N(\varepsilon)$, together with electron-phonon interactions, on the tunneling conductance in superconductors. Picket [4] discussed the effect of the electron–phonon interaction on the electronic distribution function at finite temperatures, with an applications to the spin susceptibility. The mass enhancement parameters, $\lambda_{\text{el-ph}}$, for A15 compounds with sharp structures in $N(\varepsilon)$, were calculated by Klein et al. [5]. In this paper, I have studied the effect of the electron–phonon interaction (the finite electron lifetime) on the electronic heat capacity, C_{el}, at high temperatures. Preliminary work on this problem has been presented by Grimvall [6] in a paper on titanium.

2. GENERAL THEORY

It is convenient to start from an entropy expression given by Grimvall [7]:

$$S_{\text{el}} = \frac{V}{(2\pi)^3} \frac{1}{i\pi T} \int d^3k \int_{-\infty}^{\infty} \omega \left(-\frac{\partial f}{\partial \omega} \right) [\ln G_{\text{R}}(\omega, k; T) - \ln G_{\text{A}}(\omega, k; T)] \, d\omega \tag{5}$$

where V is the specimen volume, $f(\omega)$ is the Fermi factor, and G_{R} and G_{A} denote retarded and advanced Green functions. G_{R} is defined as

$$G_{\text{R}}(\omega, k; T) = [\omega - \varepsilon(k) - \text{Re}\, M(\omega, k; T) - i \,\text{Im}\, M(\omega, k; T)]^{-1} \tag{6}$$

G_{A} is the complex conjugate of G_{R}. Further, $\varepsilon(k)$ is the electron band energy for a state of wave vector k, and $M(\omega, k; T)$ is the contribution to the electron self-energy from the electron–phonon interaction. All energies are counted relative to the chemical potential, $\mu = 0$.

We now express Eq. (5) as an integral containing $N(\varepsilon)$. We assume that the system is isotropic and use the formula

$$\frac{V}{(2\pi)^3} \int d^3k(\ldots) = \int_{-\infty}^{\infty} d\varepsilon \, N(\varepsilon)(\ldots) \tag{7}$$

to rewrite Eq. (5) as

$$S_{\text{el}} = \frac{1}{i\pi T} \int_{-\infty}^{\infty} d\varepsilon \, N(\varepsilon) \int_{-\infty}^{\infty} \omega \left(\frac{\partial f}{\partial \omega} \right) [\ln G_{\text{R}} - \ln G_{\text{A}}] \, d\omega \tag{8}$$

At high temperatures, we have $\text{Re}\, M = 0$, $\text{Im}\, M = \Gamma$, where $\Gamma = \Gamma(T) = \pi \lambda_{\text{el-ph}} k_{\text{B}} T$ [2]. The relation $\ln z = \ln|z| + i \arg z$, used in Eq. (8), gives

$$S_{\text{el}} = \frac{2}{\pi T} \int_{-\infty}^{\infty} d\varepsilon \, N(\varepsilon) \int_{-\infty}^{\infty} \omega \left(\frac{\partial f}{\partial \omega} \right) \Phi(\omega, \varepsilon) \, d\omega \tag{9}$$

Here

$$\Phi(\omega, \varepsilon) = \int_{-\infty}^{\omega} dE \frac{\Gamma}{(E - \varepsilon)^2 + \Gamma^2} = \begin{cases} -\arctan \dfrac{\Gamma}{\omega - \varepsilon}, & \omega < \varepsilon \\ \pi - \arctan \dfrac{\Gamma}{\omega - \varepsilon}, & \omega > \varepsilon \end{cases} \tag{10}$$

Integration of Eq. (9) with respect to ω yields

$$S_{\mathrm{el}} = -\frac{2k_{\mathrm{B}}}{\pi}\int_{-\infty}^{\infty} dE\, g(E) \int_{-\infty}^{\infty} d\varepsilon \frac{N(\varepsilon)\,\Gamma}{(E-\varepsilon)^2+\Gamma^2} \tag{11}$$

where

$$g(E) = f(E)\ln f(E) + [1-f(E)]\ln[1-f(E)] \tag{12}$$

3. TWO ANALYTICAL MODEL CALCULATIONS

One part of the integrand in Eq. (11) is

$$I(E) = \frac{1}{\pi}\int_{-\infty}^{\infty} d\varepsilon \frac{N(\varepsilon)\,\Gamma}{(E-\varepsilon)^2+\Gamma^2} \tag{13}$$

We now consider two analytical expressions for $N(\varepsilon)$. With

$$N(\varepsilon) = N^0 + N'\varepsilon \tag{14}$$

we easily obtain the entropy as

$$S_{\mathrm{el}} = \frac{2\pi^2}{3} k_{\mathrm{B}}^2 T N^0 \tag{15}$$

Hence the finite Γ has no effect in this case. The same result is obtained if

$$N(\varepsilon) = N^0 + N_{\mathrm{odd}}(\varepsilon) \tag{16}$$

where $N_{\mathrm{odd}}(\varepsilon)$ is an odd function in ε; $N_{\mathrm{odd}}(-\varepsilon) = -N_{\mathrm{odd}}(\varepsilon)$.

Next, we take

$$N(\varepsilon) = \frac{N^0}{1+(\varepsilon/a)^2} \tag{17}$$

Then Eq. (11) can be written as

$$S_{\mathrm{el}} = -2k_{\mathrm{B}}N^0 a \int_{-\infty}^{\infty} dE\, g(E) \frac{\Gamma+a}{(\Gamma+a)^2+E^2} \tag{18}$$

This integral cannot be solved exactly, but in the limit $k_{\mathrm{B}}T/(\Gamma+a) \ll 1$, one finds, with $C_{\mathrm{el}} = T(\partial S_{\mathrm{el}}/\partial T)$,

$$\begin{aligned} C_{\mathrm{el}} &= \frac{2\pi^2}{3} k_{\mathrm{B}}^2 T N^0 \left(\frac{a}{\Gamma+a}\right)^2 \left[1 - \frac{7}{5}\left(\frac{\pi k_{\mathrm{B}} T}{\Gamma+a}\right)^2\right] \\ &= C_0(1+\gamma_a+\gamma_\Gamma) \end{aligned} \tag{19}$$

C_0 is the heat capacity given by Eq. (1), γ_a is the correction factor due to varying $N(\varepsilon)$ when $\Gamma \to 0$,

$$\gamma_a = -\frac{7}{5}\left(\frac{\pi k_B T}{a}\right)^2 \tag{20}$$

and γ_Γ denotes the correction factor due to electron–phonon interaction:

$$\gamma_\Gamma = -\left[1-\left(\frac{a}{\Gamma+a}\right)^2\right]+\frac{7}{5}\left(\frac{\pi k_B T}{a}\right)^2\left[1-\left(\frac{a}{\Gamma+a}\right)^4\right] \tag{21}$$

If $\Gamma \ll a$,

$$\gamma_\Gamma = -\frac{2\Gamma}{a}+\frac{7}{5}\left(\frac{\pi k_B T}{a}\right)^2\frac{4\Gamma}{a} \tag{22}$$

The quantity γ_Γ arises because of the finite Γ, but it also contains effects of a nonconstant $N(\varepsilon)$ through the parameter a.

4. A NUMERICAL CALCULATION

In most realistic cases, $N(\varepsilon)$ is not of such a form that one can apply the analytical results given in Sect. 3. Then it is necessary to perform a full numerical integration. I have made a model calculation for $N(\varepsilon)$ having the shape of rectangular double wells:

$$N(\varepsilon) = \begin{cases} N_0, & |\varepsilon| < \varepsilon_1 \\ N_0/2, & \varepsilon_1 \leqslant |\varepsilon| < 3\varepsilon_1 \\ N_0, & |\varepsilon| \geqslant 3\varepsilon_1 \end{cases} \tag{23}$$

I choose $\varepsilon_1 = 0.1$ eV. Equation (11) has then been used, together with $C_{el} = T(\partial S_{el}/\partial T)$. Curve A in Fig. 1 shows C_{el} with $\Gamma = 1.5\, k_B T$. In curve B, Γ is equal to zero. In curve C, C_{el} according to Eq. (1) is shown. The most characteristic feature of C_{el} in Fig. 1 perhaps is the fact that curves A and B cross. The following gives a crude argument for that effect. The entropy in Eq. (11) weights the effective density of states $I(E)$, Eq. (13), by a weight function $g(E)$. The heat capacity C_{el} has a term which weights $I(E)$ by the function $W(E) = (E/k_B T)^2\,(-\partial f/\partial E)$. $W(E)$ has two peaks, centered at $E = \pm 2.4 k_B T$. Crudely, C_{el} is therefore proportional to the effective densities of states $I(\pm 2.4 k_B T)$. Now $I(E)$ for the unbroadened potential well, Eq. (23), is higher than $I(E)$ of the broadened case when $|E| < \varepsilon_1$ but lower when E falls within the square well. This accounts qualitatively for the crossover of the curves A and B in Fig. 1.

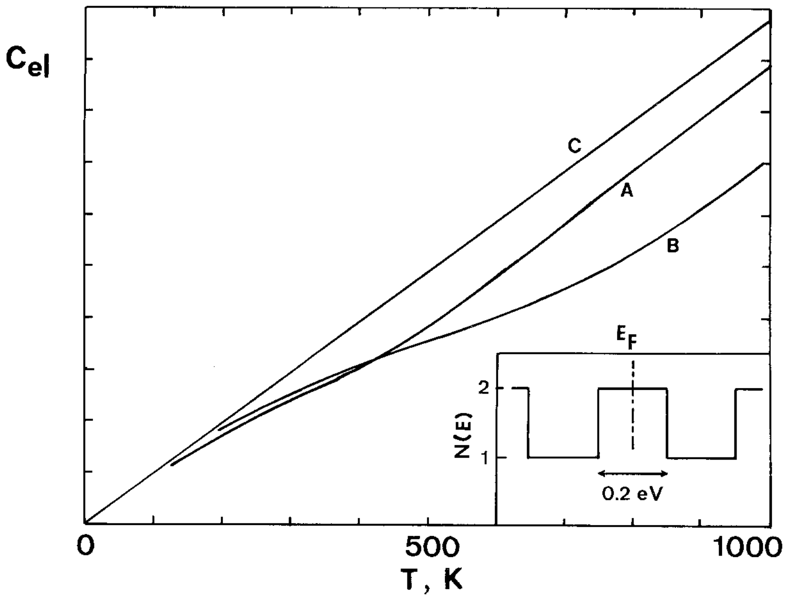

Fig. 1. The electronic heat capacity C_{el} (in arbitrary units) as a function of temperature, based on a model density of states, $N(\varepsilon)$. Here $N(\varepsilon)$ is given in the inset. Curve A is a full numerical calculation based on $N(\varepsilon)$, including finite electron lifetime effects due to electron–phonon interactions. In curve B these effects are neglected. Curve C is the standard result, $(2\pi^2/3)\,k_{\mathrm{B}}^2TN(\varepsilon_{\mathrm{F}})$.

5. NUMERICAL EXAMPLES FOR REAL METALS

The electronic heat capacity has been calculated for a realistic $N(\varepsilon)$ of a transition metal, starting from Eq. (11) for the entropy and with a numerical evaluation of the temperature-dependent chemical potential, $\mu(T)$. I have chosen $N(\varepsilon)$ of vanadium [8], given in the inset in Fig. 2, and $\lambda_{\mathrm{el\text{-}ph}} = 1.0$. Curve A in Fig. 2 shows C_{el} with $\Gamma = 3.14\,k_{\mathrm{B}}T$. In curve B, Γ is equal to zero, and in curve C, C_{el} according to Eq. (1) is shown.

I have repeated calculations, like those above for V, with $N(\varepsilon)$ for Sc, Y, Zr, Ti, Nb, Mo, Tc, Pd, Rh, and Ru, taken from Ref. 8. In some of these cases (Y, Zr, Ti, Mo, Tc), C_{el} for the broadened density of states is larger than for the unbroadened case, while Nb shows the opposite behavior. For Rh and Sc, C_{el} values of the broadened and unbroadened cases cross, in analogy to the result given in Fig. 1. In none of the investigated metals do C_{el} values of the broadened and unbroadened cases differ by more than 12% for temperatures below 1500 K. It should be noted that the electronic density of states, as calculated by two different authors, may be quite dif-

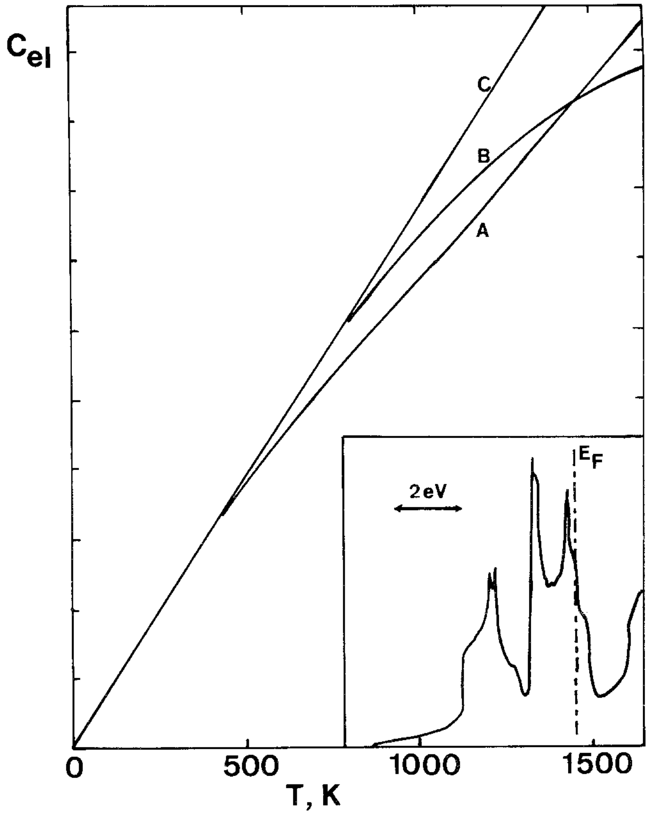

Fig. 2. The electronic heat capacity C_{el} (in arbitrary units) as a function of temperature, based on a realistic electronic density of states for vanadium, $N(\varepsilon)$. Curve A is a full numerical calculation based on $N(\varepsilon)$, including finite electron lifetime effects due to electron–phonon interactions. In curve B these effects are neglected. Curve C is the standard result, $(2\pi^2/3)\,k_B^2 TN(\varepsilon_F)$. The inset gives the actual shape of $N(\varepsilon)$ [8].

ferent in the details of importance here. Therefore my numerical results should be considered more to give a general trend than to be precise results for specific elements.

6. DISCUSSION AND CONCLUSIONS

Many physical properties depend on the electronic density of states, $N(\varepsilon)$, at the Fermi level. For a slowly varying $N(\varepsilon)$, it may be sufficient to consider the Fermi-level value, $N(\varepsilon_F)$. When $N(\varepsilon)$ is strongly varying with ε within the range of energies probed by a certain physical property, it is necessary to consider the detailed shape of $N(\varepsilon)$. The electron–phonon interaction leads to a finite lifetime for the conduction electrons, i.e., each electron state has a certain energy width. This smoothens the density of states obtained by a band structure calculations. In this paper, it is investigated how the broadening of the electron states affects the high-temperature electronic heat capacity C_{el}. Using realistic density-of-states curves for transition metals, it is found that the correction in C_{el}, relative to the result of an unbroadened density of states, usually is less than 12%. The correction may have any sign, and it may change sign as a function of temperature.

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