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Temperature Dependence of the Electron-Phonon Mass Enhancement in Mercury

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A detailed analysis of critical-field data of mercury shows that they are in qualitative agreement with recent calculations of the temperature dependence of the electronic specific-heat effective mass.

The specific heat of a metal is usually written as the sum of two distinct parts, namely the contribution of the conduction electrons, C_e, and that of the lattice, C_1. In the normal state, the effect of the electron-phonon interaction on the electronic contribution, C_{en}, is described by the following relations[1] for $T \to 0$:

$$C_{en} = \gamma T \qquad \text{with } \gamma = \tfrac{2}{3}\pi^2 k_B^2 N(E_F)(1+\lambda) ,$$

where λ is the electron-phonon coupling constant, and $N(E_F)$ the density of states at the Fermi surface, including band-structure and Coulomb-interaction effects.

Although the electron-phonon enhancement is expected to be temperature dependent,[2-4] most low-temperature specific-heat data have been successfully analyzed in terms of a constant value of γ, showing that this temperature dependence is small. However, the analysis of the data is limited to the temperature range where the lattice contribution C_1 has a simple T^3 behavior and can therefore be separated easily.

A temperature shift of the cyclotron resonance frequency has been observed for zinc,[5] and the calculations of Allen and Cohen[6] have indicated that these data could be interpreted in terms of a variation of the electron-phonon enhancement factor $1+\lambda$. Similar results were later reported for lead[7] and mercury.[8]

Grimwall[9] has recently calculated the temperature dependence of the electronic specific-heat effective mass and suggested that it should be observable for mercury. However, presently available specific-heat data[10, 11] give no indication of such a temperature variation. C_{en} can also be calculated from critical-field data $H_c(T)$ at low temperatures; Finnemore and Mapother[12] have made precise measurements of $H_c(T)$ for mercury down to 0.3 °K. We show below that their results are consistent with the temperature dependence of γ calculated by Grimwall, and probably provide the first experimental evidence for such effects on the specific heat.

Assuming that the lattice entropy has the same value in the normal and superconducting states, and using the standard relation

$$S_n - S_s + \frac{VH_c}{4\pi}\frac{dH_c}{dT} = 0 , \tag{1}$$

where V is the molar volume, we obtain

$$\frac{4\pi S_{en}}{VT} - \frac{4\pi S_{es}}{VT} + \frac{dH_c^2}{d(T^2)} = 0 , \tag{2}$$

where S_{en} and S_{es} are the electronic entropies in the normal and superconducting states, respectively.

By integration we find

$$H_0^2 = H_c^2 + \frac{4\pi}{V}\int \frac{S_{en}}{T}\, dT^2 - \int \frac{4\pi S_{es}}{VT}\, dT^2 . \tag{3}$$

This relation gives the difference $H_0^2 - H_c^2$ in terms of S_{en} and S_{es}. If S_{es} is properly taken into account, the $H_c(T)$ data can be used to calculate S_{en} and therefore $\gamma(T)$. As the value of $S_{es}(T)$ is rather uncertain, we limit the present discussion to the temperature range where S_{es} is small.

S_{es} was calculated from C_{es}, the electronic specific heat in the superconducting state, assuming a constant energy gap $2\Delta = 4.8kT_c$,[12] where $T_c = 4.154$ °K for mercury; this should be a good approximation up to $T = 1.5$ °K.[13] We used the expression $C_{es} = 60\, e^{-8.17\,^\circ\mathrm{K}/T}$ (mJ/mole °K). The contribution of S_{es} to the difference $H_0^2 - H_c^2$, called $K(S_{es})$, is given by the second integral appearing in (3) and is shown by the full curve at the bottom of Fig. 1(b); it is negligible for $T \leqslant 1$ °K.

Using now the $H_c(T)$ data of Finnemore and Mapother (Table III of Ref. 12), we also plot in Fig. 1 (closed circles) the quantity K defined as follows:

$$\begin{aligned} K &= (4\pi/V)\int (S_{en}/T)\, dT^2 - 4\pi\gamma(0)T^2/V \\ &= H_0^2 - H_c^2 + \int (4\pi S_{es}/VT)\, dT^2 - 4\pi\gamma(0)\, T^2/V . \end{aligned}$$

Thus, K gives a measure of the deviation of S_{en}/T from $\gamma(0)$.

The values $H_0^2 = 168\,720$ (G)^2 and $\gamma(0) = 1.765$ mJ/mole (°K)^2 were used to calculate K. These values give a good fit to the low-temperature data, as shown by the fact that K is close to zero for $T^2 \leqslant 0.5$ (°K)^2. A temperature-independent γ would correspond to a linear relation between K and T^2, as can be seen in Fig. 1; this is not the case here.

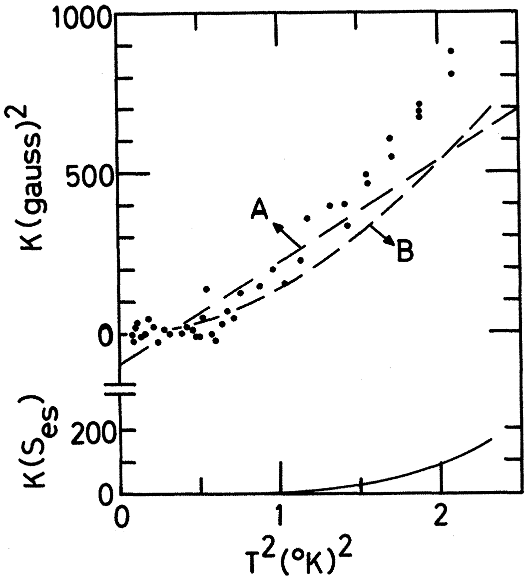

FIG. 1. Top: Critical-field data on mercury plotted as K (see text) vs T^2. Line A reproduces the fit of Finnemore and Mapother; curve B represents the calculations of Grimwall. Bottom: $K(S_{es})$ (see text) vs T^2. The units are $(\mathrm{G})^2$.

Finnemore and Mapother fitted their data with $\gamma = 1.809$ mJ/mole $(°\mathrm{K})^2$ and $H_0^2 = 168\,820\ \mathrm{G}^2$ (corresponding to dashed line A in Fig. 1) and ignored the deviations around the line.[14]

Mercury is a strong coupling superconductor and the electron-phonon coupling constant has been evaluated from tunneling experiments[15]: $\lambda = 1.6$. Using these data, Grimwall[9] has calculated the temperature variation of the electron-phonon enhancement of the electronic specific heat

$$C_{en} = [\gamma_0 + \gamma_1(T)]\, T = \gamma(T)\, T \ ,$$

γ_1 incorporates all electron-phonon effects and has a maximum value at 2 °K, where $\gamma_1(T)/\gamma_1(0) \simeq 1.18$. As previously mentioned, the contribution of S_{es} is too important at that temperature to permit an accurate correction. Below 1.3 °K, the calculation of Grimwall can be approximated[16] by $\gamma_1(T)/\gamma_1(0) = 1 + 0.08T^2$; combining with $\lambda = 1.6 = \gamma_1(0)/\gamma_0$,[17] and assuming $\gamma(0) = 1.765$ mJ/mole $(°\mathrm{K})^2$, we obtain $\gamma(T) = 1.765 + 0.087T^2$ mJ/mole $(°\mathrm{K})^2$. S_{en} and K are then readily calculated; the result is shown in Fig. 1 by the dashed curve B.

It should be emphasized at this point that the interpretation of the data is very sensitive to the choice of $\gamma(0)$: A higher value of $\gamma(0)$ will lead to a lower temperature dependence of γ. It is obvious however that the K vs T^2 data lie on a curve so that no constant value of γ will describe them properly over the temperature range considered. As the value $\gamma(0) = 1.765$ mJ/mole $(°\mathrm{K})^2$ gives a good fit at the lower temperatures, we feel it safe to conclude that there is a qualitative agreement with Grimwall's calculations. The K vs T^2 data can be fitted with a parabola; the corresponding temperature dependence of γ is given by

$$\gamma(T) = 1.765 + 0.125T^2\ \mathrm{mJ/mole}\ (°\mathrm{K})^2 \qquad (T \text{ in } °\mathrm{K})$$

One might eventually argue that the observed change of γ is due to some systematic error in the measurements. Finnemore and Mapother also measured the critical field of tin and indium with the same equipment.[12] No comparable effect is observed for these two elements; the electron-phonon coupling constant is here much smaller, and the increase of γ is expected to occur at higher temperatures, the electron-phonon interaction being more important at higher energies.[9, 18]

A confirmation of the temperature dependence of γ by direct specific-heat measurements seems difficult for mercury: The lattice contribution starts to deviate from a T^3 behavior above 0.7 °K and the analysis of the normal state data is further complicated by a nuclear contribution at low temperatures.[11] As mentioned previously, $\gamma(T)$ is expected to have a maximum value at 2 °K, but C_{en} is only 3.5% of the total specific heat at that temperature.

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the present purpose.

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Electronic Surface States of a Dielectric Film on a Metal Substrate*

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An electron near the surface of liquid or solid He, Ne, or H_2 is excluded from the interior of the medium because of a net repulsive interaction with the atoms or molecules composing it. If a layer of such a material is situated on a conductor these electrons may become localized near the insulator-vapor interface, bound there by polarization forces. We discuss the properties of these states and determine their lifetime prior to electron tunneling through the insulator to the metal.

I. INTRODUCTION

It has been known for several years[1,2] that the strongly repulsive interaction between an electron and certain closed-shell atoms or molecules (specifically He, Ne, and H_2) causes an effective exclusion of an excess electron from the interior of a condensed medium composed of such units. On the other hand, when outside the medium, the electron is pulled toward its surface by attractive polarization forces. In view of these considerations, Cohen and the author recently proposed[3,4] that there exist states of excess electrons localized near, but primarily external to, the surface of liquid and solid He, Ne, and H_2.

In this paper a related phenomenon is described. We consider a configuration of a dielectric layer, or film, lying on a metal substrate, as shown in Fig. 1. An electron in the vapor region will be attracted toward the dielectric surface. However, the polarization force will be enhanced relative to the case of an infinitely thick dielectric treated in I. Exclusion from the bulk of the dielectric will occur as it does in that problem. The net result is localization of the extra electron near the medium's surface, but with considerably larger binding energy than occurs in the absence of the metal. These electronic states, however, are not true eigenstates of the system in that the electrons can tunnel quantum mechanically through the insulator to the metal. The lifetime associated with this process must be calculated as well.

Section II utilizes the appropriate electrostatic potential, derived in Appendix A, to obtain the wave equation in a form similar to that of the author's previous treatment. In Sec. III, we discuss the eigenvalues of the most strongly bound states as well as the lifetimes for the tunneling process. Section IV provides further discussion and conclusions.

II. EFFECTIVE POTENTIAL AND RESULTING EIGENFUNCTION

Figure 1 illustrates the experimental configuration of interest. The previous studies of image-potential induced surface states[3,4] concern the case of an infinite dielectric to which the present problem reduces when t tends to infinity.

Experimental[2] and theoretical[1] evidence indicates that the insulators studied here have a negative electron affinity, owing to their filled, tightly bound electronic shells. The repulsive electron-medium interaction causes the conduction band minimum to lie at an energy V_0 which is positive with respect to the vacuum level, which we take to be zero. An energy $E < V_0$ lies in the energy gap so that an electron wave function at that energy decays exponentially with distance into the medium. Outside of the medium, the electron is attracted toward the insulator. At a distance x from the surface large enough for classical electrostatics to apply, the interaction between the electron and an infinite dielectric is[5]

$$V(x, t=\infty) = -\beta e^2/4x, \quad x > b > 0 \qquad \beta = (\epsilon - 1)/(\epsilon + 1), \tag{1}$$

where b is a cutoff parameter we employ because (1) loses its validity for close approach, and ϵ is the static dielectric constant of the insulator.

In Appendix A, we solve the classical electrostatic problem corresponding to the configuration of Fig. 1 and obtain a generalization of Eq. (1) that includes the influence of the metal. The resulting form for the potential in the vacuum region is a sum of (1) and an infinite series that converges uniformly since $\beta < 1$:

$$V(x, t) = \frac{-\beta e^2}{4x} + \frac{(1-\beta^2)e^2}{4\beta} \sum_{n=1}^{\infty} \frac{(-\beta)^n}{x + nt}, \qquad x \geq b > 0. \tag{2}$$