

## Calculation of the Temperature Dependence of the Electron-Phonon Mass Enhancement\*

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Theoretical calculations are presented of the temperature dependence of the electron-phonon mass enhancement for 16 nontransition metals. The results are in good agreement with low-temperature measurements on zinc as reported by Sabo in the preceding paper. A pseudopotential model of the electron-phonon coupling was used, with a modified form of the single-orthogonalized-plane-wave approximation. These calculations agree well with calculations based on data obtained from superconducting tunneling experiments.

### I. INTRODUCTION

RECENTLY, Grimvall<sup>1</sup> pointed out that the electron-mass renormalization arising from electron-phonon interactions has an interesting temperature dependence which could in principle be observed in low-temperature experiments such as cyclotron resonance and the de Haas-van Alphen effect. In the preceding paper,<sup>2</sup> Sabo has reported the observation of temperature shifts of the cyclotron-resonance frequency in zinc for several orbits. In this paper, we present calculations of temperature dependence of the mass enhancement which agree well in magnitude with the effects observed in zinc.

In Sec. II, the theory of the temperature dependence mass enhancement is reviewed and formulated in terms of the function  $\alpha^2F$  which is in principle experimentally accessible through superconducting tunneling. In Sec. III, model calculations and pseudopotential calculations of the temperature shift of the mass enhancement in nontransition metals are presented and discussed. It is shown that failures of the one-orthogonalized-plane-wave (OPW) model near zone boundaries give a severe distortion of the temperature shift, although they do not significantly alter the zero-temperature mass enhancement. A simple phenomenological alteration of the OPW model is proposed to overcome this difficulty. This modified one OPW method is then used to calculate the temperature shift of the electron-phonon mass enhancement for 16 nontransition metals.

### II. THEORY

In cyclotron-resonance experiments, an electron mass  $m_c(O_k)$  characteristic of an orbit  $O_k$  in  $\mathbf{k}$  space is measured. In the absence of electron-electron and electron-phonon interactions, the mass can be expressed in terms of the band structure  $\epsilon_k$ ,

$$m_c(O_k) = \frac{\hbar^2}{2\pi} \oint_{O_k} \frac{dl}{\hat{n}_k \cdot \nabla_k \epsilon_k}, \quad (1)$$

where  $\hat{n}_k$  is a unit vector at  $\mathbf{k}$  normal to the orbit in the

plane of the orbit,  $dl$  is an element of path length in  $\mathbf{k}$  space, and the integral is evaluated around the orbit  $O_k$  on the Fermi surface. The presence of coulomb interactions between electrons modifies the energy spectrum  $\epsilon_k$  of single-particle excitations. Although these effects are not amenable to exact calculations, recent theoretical estimates by Rice<sup>3</sup> indicate that coulomb shifts in  $\epsilon_k$  are small and nearly constant near the Fermi surface, yielding a mass change of the order of 5% or less. We, therefore, assume that Coulomb effects are negligible.

The presence of electron-phonon interactions also modifies the energy spectrum. In this case, the wave-vector- and frequency-dependent self energy  $\Sigma(\mathbf{k}, \omega)$  can be accurately calculated. The modified spectrum  $E_k$  is then given by

$$E_k = \epsilon_k + \Sigma(\mathbf{k}, E_k), \quad (2)$$

and this shift is known to yield important changes in the measured electron mass. The renormalized cyclotron mass is

$$m_c^*(O_k) = \frac{\hbar^2}{2\pi} \oint_{O_k} \frac{dl}{\hat{n}_k \cdot \nabla_k E_k}, \quad (3)$$

$$m_c^*(O_k) \equiv [1 + \lambda(O_k)] m_c(O_k). \quad (4)$$

Equation (4) defines  $\lambda(O_k)$ , the renormalization characteristic of the orbit  $O_k$ . Combining Eqs. (1)–(3), we find

$$\lambda(O_k) = \oint_{O_k} \frac{\lambda_k dl}{\hat{n}_k \cdot \nabla_k \epsilon_k} \left( \oint_{O_k} \frac{dl}{\hat{n}_k \cdot \nabla_k \epsilon_k} \right)^{-1}, \quad (5)$$

where  $\lambda_k$  is defined as

$$\lambda_k \equiv - \left. \frac{\partial \Sigma(\mathbf{k}, \omega)}{\partial \omega} \right|_{\omega=E_k=0}. \quad (6)$$

We have assumed that the  $\mathbf{k}$  dependence of  $\Sigma$  is negligible, and taken the zero of energy to be the Fermi energy. The physical significance of  $\lambda_k$  is that it measures the renormalization of the mass of the specific electronic state  $\mathbf{k}$ . For those parts of the Fermi surface where limiting-point cyclotron resonance is observable,  $\lambda_k$  is

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<sup>1</sup> G. Grimvall, *J. Phys. Chem. Solids* **29**, 1221 (1968).

<sup>2</sup> J. J. Sabo, Jr., preceding paper, *Phys. Rev. B* **1**, 1325 (1969).

<sup>3</sup> T. M. Rice, *Phys. Rev.* **175**, 858 (1968).

the appropriate renormalization. In typical experiments such as ordinary Azbel-Kaner resonance or measurements of the temperature dependence of de Haas-van Alphen signals, the measured renormalization  $\lambda_k$  is averaged over an orbit. When  $\lambda_k$  is averaged over the entire Fermi surface, the result, denoted as  $\lambda$ , gives the renormalization of the specific heat coefficient<sup>4</sup>  $\gamma$  and the coupling parameter in the McMillan equation<sup>5</sup> for the superconducting transition temperature.<sup>6-8</sup>

The electron-phonon self-energy  $\Sigma$  can be written as

$$\Sigma(\mathbf{k}, \omega) = \int_0^\infty d\omega' \sum_{\mathbf{k}'} |M_{\mathbf{k} \rightarrow \mathbf{k}'}|^2 B(\mathbf{q}, \omega') \times \left\{ \frac{1+N'-f'}{\omega-E_{\mathbf{k}'}-\omega'} + \frac{f'+N'}{\omega-E_{\mathbf{k}'}+\omega'} \right\}, \quad (7)$$

where  $f'$  and  $N'$  are, respectively, the Fermi function at energy  $E_{\mathbf{k}'}$  and the Bose function at energy  $\omega'$ . The term  $M_{\mathbf{k} \rightarrow \mathbf{k}'}$  is the matrix element for an electron in a state  $\mathbf{k}$  to scatter to a state  $\mathbf{k}'$  by emitting a phonon of mode  $(-\mathbf{q}, \nu)$  or absorbing a phonon of mode  $(\mathbf{q}, \nu)$ , where  $\mathbf{q}$  is the momentum transfer  $\mathbf{k}' - \mathbf{k}$  reduced to the first Brillouin zone and  $\nu$  is the mode index which is suppressed in our equations. The factor  $B(\mathbf{q}, \omega)$  is the phonon-spectral weight function, which is strongly peaked at  $\omega$  equal to the frequency  $\omega_{\mathbf{q}\nu}$  of the  $(\mathbf{q}, \omega)$  phonon. If  $B(\mathbf{q}, \omega)$  is approximated by the Dirac  $\delta$  function  $\delta(\omega - \omega_{\mathbf{q}\nu})$ , Eq. (7) reduces to an expression given by many authors.<sup>1,9</sup>

Because we are interested in  $\Sigma$  for states  $(\mathbf{k}, \omega)$  near the Fermi surface and because the denominators in (7) strongly weight values of  $E_{\mathbf{k}'}$  nearly equal to  $\omega$  which is at the Fermi surface, the  $\sum_{\mathbf{k}'}$  sum in (10) can be approximated as follows:

$$\sum_{\mathbf{k}'} A_{\mathbf{k}, \mathbf{k}'} \sim \frac{N(0)}{2} \int_{-\infty}^\infty dE_{\mathbf{k}'} \langle A_{\mathbf{k}, \mathbf{k}'} \rangle, \quad (8)$$

where  $N(0)$  is the density of electronic states (unrenormalized) at the Fermi surface and the brackets  $\langle \rangle$  denote averaging of the intermediate state  $\mathbf{k}'$  over the Fermi surface (FS).

$$\langle A_{\mathbf{k}, \mathbf{k}'} \rangle = \int_{\text{FS}} \frac{dS_{\mathbf{k}'}}{v_{\mathbf{k}'}} A_{\mathbf{k}, \mathbf{k}'} \left( \int_{\text{FS}} \frac{dS_{\mathbf{k}'}}{v_{\mathbf{k}'}} \right)^{-1}, \quad (9)$$

and  $v_{\mathbf{k}'}$  is the magnitude of the velocity of the state  $\mathbf{k}'$ .

<sup>4</sup> This is strictly true only at  $T=0$ . At finite temperatures, the temperature dependence of the specific-heat renormalization differs from that of the mass renormalization. See Grimvall, Ref. 1.

<sup>5</sup> W. L. McMillan, Phys. Rev. **167**, 331 (1968).

<sup>6</sup> P. B. Allen, M. L. Cohen, L. M. Falicov, and R. V. Kasowski, Phys. Rev. Letters **21**, 1794 (1968).

<sup>7</sup> P. B. Allen and M. L. Cohen, Solid State Commun. **7**, 677 (1969).

<sup>8</sup> P. B. Allen and M. L. Cohen, Phys. Rev. **187**, 525 (1969).

<sup>9</sup> J. R. Schrieffer, *Theory of Superconductivity* (W. A. Benjamin, Inc., New York, 1964), pp. 196-200.

We then have

$$\Sigma(\mathbf{k}, \omega) = \int_0^\infty d\omega' \int dE_{\mathbf{k}'} \alpha_{\mathbf{k}}^2(\omega') F_{\mathbf{k}}(\omega') \times \left\{ \frac{1+N'-f'}{\omega-E_{\mathbf{k}'}-\omega'} + \frac{f'+N'}{\omega-E_{\mathbf{k}'}+\omega'} \right\}. \quad (10)$$

The function  $\alpha_{\mathbf{k}}^2 F_{\mathbf{k}}$  is defined as<sup>10</sup>

$$\alpha_{\mathbf{k}}^2(\omega) F_{\mathbf{k}}(\omega) \equiv \frac{1}{2} N(0) \langle |M_{\mathbf{k} \rightarrow \mathbf{k}'}|^2 B(\mathbf{q}, \omega) \rangle. \quad (11)$$

We also define a function  $\alpha^2 F$ :

$$\alpha^2(\omega) F(\omega) \equiv \frac{1}{2} N(0) \langle \langle |M_{\mathbf{k} \rightarrow \mathbf{k}'}|^2 B(\mathbf{q}, \omega) \rangle \rangle, \quad (12)$$

where the double brackets  $\langle \langle \rangle \rangle$  denote averaging both the initial state  $\mathbf{k}$  and the intermediate state  $\mathbf{k}'$  over the Fermi surface in the manner of Eq. (9). The latter function  $\alpha^2 F$  is well known from studies of superconductivity,<sup>11</sup> and can in fact be extracted from superconducting tunneling data for superconductors where the coupling is strong enough that phonon structure can be observed.<sup>12</sup>

The integrals in (10) are to be evaluated as principal parts. Only terms which contain a Fermi function  $f'$  survive the  $E'$  integration. We can then rewrite (10) as

$$\Sigma(\mathbf{k}, \omega) = - \int_0^\infty d\omega' \int_{-\infty}^\infty dE_{\mathbf{k}'} \alpha_{\mathbf{k}}^2(\omega') \times F_{\mathbf{k}}(\omega') \frac{2\omega'}{E^2 - \omega'^2} f(E + \omega). \quad (13)$$

Finally, using (6), we get

$$\lambda_{\mathbf{k}}(T) = 2 \int_0^\infty d\omega \frac{\alpha_{\mathbf{k}}^2(\omega) F_{\mathbf{k}}(\omega)}{\omega} G\left(\frac{\omega}{T}\right), \quad (14)$$

where  $G(\omega/T)$  is a temperature-dependent function first discussed by Grimvall,<sup>1</sup>

$$G\left(\frac{\omega}{T}\right) = \int_{-\infty}^\infty dE \frac{\partial f(E)}{\partial E} \frac{\omega^2}{E^2 - \omega^2} = \frac{a^2}{2} \int_{-\infty}^\infty dx \frac{1}{\cosh^2 x} \frac{1}{a^2 - x^2}. \quad (15)$$

The function  $G$  depends only on the variable  $a = \hbar\omega/2k_B T$  and has the limiting values

$$G(\omega/T) \approx 1 + (\pi^2/3)(k_B T/\hbar\omega)^2, \quad \text{if } \hbar\omega \gg k_B T \quad (16a)$$

$$\approx \frac{7\zeta(3)}{2\pi^2} \left( \frac{\hbar\omega}{k_B T} \right)^2, \quad \text{if } \hbar\omega \ll k_B T \quad (16b)$$

<sup>10</sup> D. J. Scalapino, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, Inc., New York, 1969).

<sup>11</sup> D. J. Scalapino, J. R. Schrieffer, and J. W. Wilkins, Phys. Rev. **148**, 263 (1966).

<sup>12</sup> W. L. McMillan and J. M. Rowell, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, Inc., New York, 1969).

where  $\zeta(x)$  is the Riemann zeta function. The result (16a) enables us to recover the well-known formula for  $\lambda$  at zero temperature

$$\lambda = 2 \int_0^\infty \frac{\alpha^2(\omega) F(\omega)}{\omega} d\omega. \quad (17)$$

A plot of  $G(\omega/T)$  and a useful series expansion are given by Grimwall.<sup>1</sup> As a function of temperature for fixed frequency,  $G$  rises from its zero-temperature value of 1, reaching a peak value around 1.205 at  $k_B T/\hbar\omega \approx 0.26$ . At high temperatures,  $G$  approaches zero as an inverse square. Thus, we expect the renormalization  $\lambda_k$  or  $\lambda$  to rise with temperature initially, reaching a peak value less than 20% higher than its zero-temperature value, at a temperature around  $\frac{1}{4}$  the value of the most important group of phonons and decaying to zero at higher temperatures. This temperature dependence is not easy to observe experimentally. The preceding paper reports a small but significant increase in cyclotron-resonance masses with temperature for zinc, and we believe that this is the first experimental evidence for this effect.

The physical origin of this temperature dependence is not easy to visualize. The mathematical origin is in the broadening of the Fermi distribution. At low temperatures, this allows scattering to intermediate states  $\mathbf{k}'$  that lie off the Fermi surface by an amount  $\sim k_B T$ . This can lead to enhanced self-energies: The energy of an electron above the Fermi sea is lowered an additional amount by the presence of a few unoccupied states below the Fermi surface which it can scatter into, and the energy of an electron below the Fermi surface is raised an additional amount by having a few intermediate states above the Fermi surface blocked. The importance of these finite temperature processes arises from the fact that they can be more nearly resonant in energy than the corresponding zero-temperature processes. At still higher temperatures, however, when there is nearly constant occupancy of states above and below the Fermi surface on the scale of phonon energies, then all states are shifted in energy nearly the same amount, and the mass enhancement goes to zero.

### III. CALCULATIONS

The experimental results of Sabo<sup>2</sup> for zinc show a significant variation of  $\lambda(T)$  from orbit to orbit. This is not too surprising in the light of previous experiments which have indicated that  $\lambda(O_k)$  varies from orbit to orbit.<sup>13</sup> A detailed comparison of theory and experiment for the mass renormalization must take band-structure effects into account in order to explain variations between different orbits. To our knowledge, no one has undertaken an analysis of this type. The existence

of measurements of masses over a finite range of temperatures provides additional useful data and, thus, possibly additional incentive for such a calculation.

In the present paper, we shall be content with treating only the average mass enhancement and its temperature dependence. The average mass enhancement  $\lambda$  is easier to calculate. In a previous paper,<sup>8</sup> we have reviewed a considerable body of evidence showing that  $\lambda$  can be calculated using a spherical approximation to the Fermi-surface and single-OPW wave functions; i.e., omitting all band-structure effects except for an accurate empirical pseudopotential.

In addition, we will make the approximation that the lattice parameters, phonon frequencies, pseudopotential, and density of states are all independent of temperature. At higher temperatures, this will introduce some errors, particularly for materials like zinc and cadmium where the band structure and density of states are apparently quite temperature-dependent.<sup>14</sup> However, we are most interested in temperatures considerably smaller than the Debye temperature where these approximations introduce negligible errors.

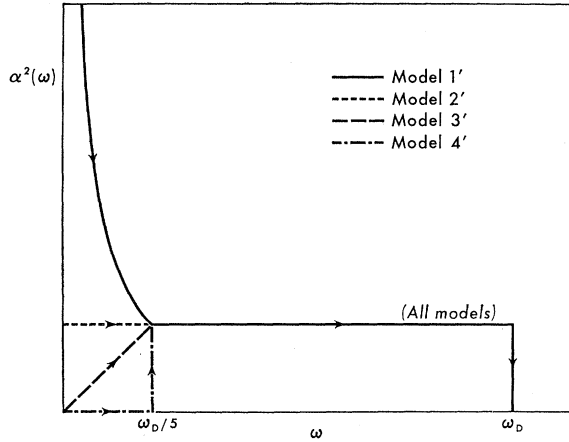
The problem is now reduced to the calculation of  $\alpha^2 F$ , from which the temperature dependence of  $\lambda$  is easily derived. For the case of a strong coupling superconductor like lead, the function  $\alpha^2 F$  is known from superconducting tunneling measurements,<sup>12,15</sup> and  $\lambda(T)$  can be directly obtained from experimental quantities. Unfortunately, superconducting tunneling is not sensitive enough to reveal the structure of  $\alpha^2 F$  for zinc, which is a weak-coupling superconductor. However, it is known from extensive work on materials like lead that the function  $\alpha^2 F$  is similar in structure to the phonon density of states  $F(\omega)$ . For a first approximation, it is reasonable to assume that  $\alpha^2(\omega)$  is a constant. The phonon density of states  $F(\omega)$  has been calculated for zinc by Young and Koppel<sup>16</sup> who used a force-constant fit to the dispersion relations measured by neutron scattering. The magnitude of  $\alpha^2$  can be adjusted to yield the correct zero-temperature value of  $\lambda$ , which is known from the superconducting transition temperature, the observed enhancement of the specific-heat coefficient  $\gamma$  above its unrenormalized band-structure value, and from previous calculations.<sup>6-8</sup> The results are shown in Fig. 3 of the previous paper for zinc, and compared with the experimental results. (This is also shown later, in Fig. 4 of this paper.) There is excellent agreement between theory and experiment considering that the electron-phonon coupling  $\alpha^2$  has been treated simply as a constant. The behavior of  $\lambda(T) - \lambda(0)$  for low temperatures is sensitive to the behavior of  $\alpha^2 F$  in the low-frequency region, i.e., to the manner in which electrons couple to long-wavelength acoustic phonons.

<sup>14</sup> R. V. Kasowski and L. M. Falicov, Phys. Rev. Letters **22**, 1001 (1969).

<sup>15</sup> W. L. McMillan and J. M. Rowell, Phys. Rev. Letters **14**, 108 (1965).

<sup>16</sup> J. A. Young and J. U. Koppel, Phys. Rev. **134**, A1476 (1964).

<sup>13</sup> See, for example, work on magnesium by J. C. Kimball, R. W. Stark, and F. M. Mueller, Phys. Rev. **162**, 600 (1967).

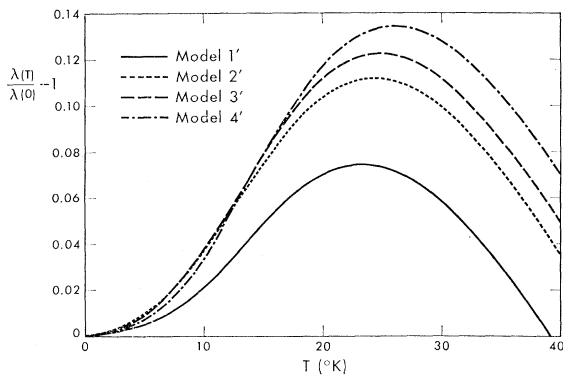
FIG. 1. Models of the electron-phonon coupling  $\alpha^2(\omega)$ .

To illustrate some of the possibilities, it is useful to explore several models of the phonon coupling. We first rewrite Eq. (14):

$$\lambda(T) - \lambda(0) = \int_0^{\omega_D} \frac{d\omega}{\omega} \alpha^2(\omega) F(\omega) \times \int_{-\infty}^{\infty} \frac{dx}{\cosh^2 x} \frac{x^2}{(\hbar\omega/2k_B T)^2 - x^2}. \quad (18)$$

This equation can be integrated to yield the limiting behavior for small temperature assuming a particular model for  $\alpha^2 F$ .

We have considered 4 models, and the results are summarized in Table I. The first 3 models assume that  $F(\omega)$  is of the Debye type, scaling as a quadratic function of  $\omega$ . The coupling  $\alpha^2$  is then assumed to go as  $\omega^n$ , where the values  $n = -1, 0, 1$  are chosen. The choice  $n = 0$  corresponds to coupling to longitudinal acoustic phonons and give a  $T^2 \log T$  increase of  $\lambda$  with  $T$ . The choice  $n = 1$  may be realistic for transverse-acoustic modes. The essential point we wish to make is

FIG. 2. The mass renormalization as a function of temperature calculated using the models of Fig. 1 for  $\alpha^2$  and the phonon density of states of zinc for  $F(\omega)$ .

that a variety of types of behavior are possible, including a somewhat surprising decrease with temperature for the  $n = -1$  model. The reason for this is that phonons with  $\hbar\omega < 2.27k_B T$  have a diminished contribution to  $\lambda(T)$  (arising from the shape of the Grimvall function  $G$ ). The  $n = -1$  model strongly emphasizes the effect of small  $\omega$  phonons and leads to values of  $\lambda$  decreasing with  $T$ . The fourth model treats  $\alpha^2 F$  as a constant in the range  $\omega_0 < \omega < \omega_D$  and zero outside this range, where  $\omega_D$  is the Debye frequency and  $\omega_0$  is some low-frequency cutoff. This model gives a fourth power increase in  $\lambda$  with  $T$  for  $k_B T \ll \hbar\omega_0$ .

We have also explored four more realistic models where  $F(\omega)$  is the actual phonon density of states of zinc and  $\alpha^2(\omega)$  is a constant for  $\frac{1}{5}\omega_D < \omega < \omega_D$  and behaves for  $\omega < \frac{1}{5}\omega_D$  as in the previous set of models. The new models for  $\alpha^2$  are shown in Fig. 1, and the computed values of  $\lambda(T)$  are shown in Fig. 2. It is interesting to note that, in spite of the diversity of possible low-temperature behaviors shown in Table I, the realistic models 2', 3', and 4' give very similar results for  $\lambda(T)$  in the region below 15°K. Model 1', however, with its extra emphasis

TABLE I. Low-temperature behavior of  $\lambda(T) - \lambda(0)$  for various models of  $\alpha^2 F$ .

	Behavior of $\alpha^2$	Behavior of $\alpha^2 F$	Behavior of $\lambda(T) - \lambda(0)$ for small $T$
1	$1/\omega$	$(\omega/\omega_D)^1$	$-(k_B T/\hbar\omega_D)^2$
2	const	$(\omega/\omega_D)^2$	$(k_B T/\hbar\omega_D)^2 \log(\hbar\omega_D/k_B T)$
3	$\omega$	$(\omega/\omega_D)^3$	$+(k_B T/\hbar\omega_D)^2$
4	...	const if $\omega_0 < \omega < \omega_D$ 0 otherwise	$+(k_B T/\hbar\omega_0)^4$

on the small-frequency phonons, gives a weaker temperature shift than the more physical models.

To calculate  $\alpha^2 F$  accurately, we need models of the phonon spectrum, the Fermi surface, and the electron-phonon coupling.<sup>17</sup> For the sake of simplicity, we will assume a single atom in the unit cell and 3 acoustic-phonon modes. We approximate the phonon spectral weight function  $B_\nu(q, \omega)$  by a  $\delta$  function  $\delta(\omega - \omega_{q\nu})$  at the observed frequency  $\omega_{q\nu}$  of the  $(q\nu)$  phonon. Then, if we assume a spherically symmetric phonon spectrum and Fermi surface, we get

$$\alpha^2(\omega) F(\omega) = \sum_{\nu=1}^3 \alpha_\nu^2(\omega) F_\nu(\omega),$$

$$\alpha_\nu^2(\omega) = \frac{m_b}{4m\epsilon_F} \sum_{\mathbf{G}} \int \frac{d\Omega_{\mathbf{q}}}{4\pi} \times \frac{|M_{\mathbf{k} \rightarrow \mathbf{k} + \mathbf{q} + \mathbf{G}}|^2 \theta(2k_F - |\mathbf{q} + \mathbf{G}|)}{|\mathbf{q} + \mathbf{G}|/2k_F} \bigg|_{q=q_\nu(\omega)}, \quad (19)$$

<sup>17</sup> Single-OPW calculations of  $\alpha^2 F$  have been discussed previously by J. P. Carbotte and R. C. Dynes, Phys. Rev. **172**, 476 (1968); J. P. Carbotte, R. C. Dynes, and P. N. Trofimenkoff, Can. J. Phys. **47**, 1107 (1969); also see Ref. 10.

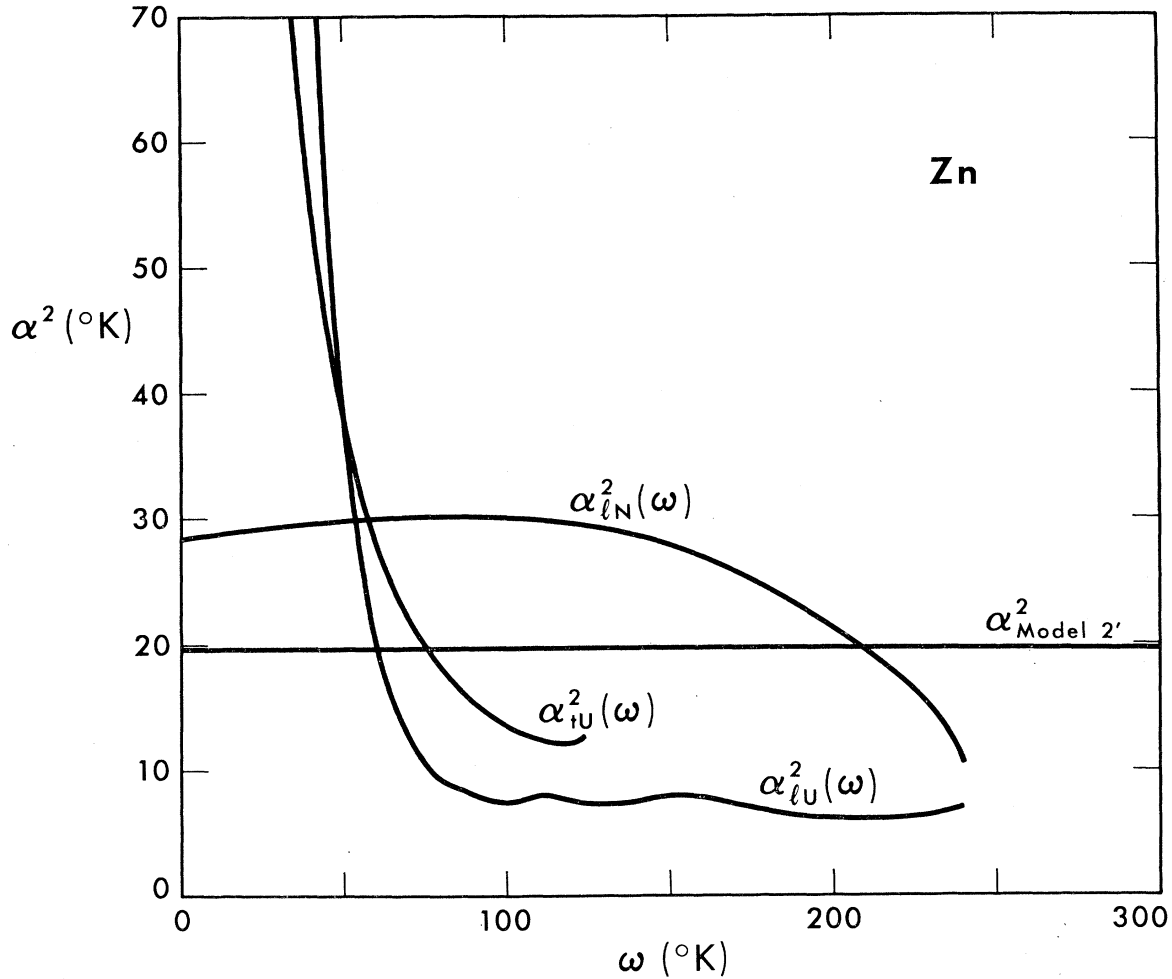


FIG. 3. The electron-phonon coupling  $\alpha^2(\omega)$  for zinc calculated in the single-OPW approximation using the Stark-Falicov pseudopotential.

where  $\epsilon_F$  is the free-electron Fermi energy,  $m_b/m$  is the ratio of the band-structure density of states at the Fermi surface to the corresponding free-electron value,  $q_\nu(\omega)$  is the wavevector of the phonon of mode  $\nu$  and frequency  $\omega$ , the integration is over angles, the summation is over reciprocal lattice vectors, and the  $\theta$  function assures that the states  $\mathbf{k}$  and  $\mathbf{k}+\mathbf{q}+\mathbf{G}$  are both on the Fermi surface.

The matrix element in a one-OPW model is

$$M_{\mathbf{k} \rightarrow \mathbf{k}+\mathbf{q}+\mathbf{G}} = \left( \frac{\hbar}{2M\omega_{\mathbf{q}\nu}} \right)^{1/2} \hat{\epsilon}_{\mathbf{q}\nu} \cdot (\mathbf{q}+\mathbf{G}) V(\mathbf{q}+\mathbf{G}), \quad (20)$$

where  $M$  is the ionic mass,  $\hat{\epsilon}_{\mathbf{q}\nu}$  is the polarization vector, and  $V(\mathbf{q})$  is the empirical pseudopotential, evaluated on the Fermi surface in a nonlocal model. To evaluate  $\alpha_\nu^2(\omega)$  for zinc and cadmium, we must make adjustments to take account of the fact that there are two atoms in a cell and optical phonons as well as acoustic. These modifications have been described previously,<sup>8</sup>

and consist of replacing the six phonon modes by three acoustic modes in an extended Brillouin zone. Then Eqs. (19) and (20) are correct, provided the pseudopotential in Eq. (20) is supplemented by a structure factor  $S(\mathbf{G})$  normalized such that  $S(0)=1$ . The phonon density of states  $F_\nu(\omega)$  is also normalized to unity. A quadratic model described previously<sup>8</sup> is used for the phonon-dispersion relation and density of states with polarizations taken to be pure longitudinal or pure transverse. The results are shown in Fig. 3 for zinc using the empirical pseudopotential of Stark and Falicov<sup>18</sup> and other parameters as listed in Ref. 8. For comparison, the function  $\alpha^2$  of model 2' is also shown; both models yield  $\lambda(0)=0.42$ . The  $\mathbf{G}=0$  (normal or  $N$  part) and the  $\mathbf{G} \neq 0$  (umklapp or  $U$  part) of  $\alpha_\nu^2$  are shown separately in Fig. 3. The transverse phonons do not couple to electrons by  $N$  processes within our model, so  $\alpha_{tN}^2$  is zero. Both umklapp parts,  $\alpha_{tU}^2$  and  $\alpha_{lU}^2$ ,

<sup>18</sup> R. W. Stark and L. M. Falicov, Phys. Rev. Letters **19**, 795 (1967).

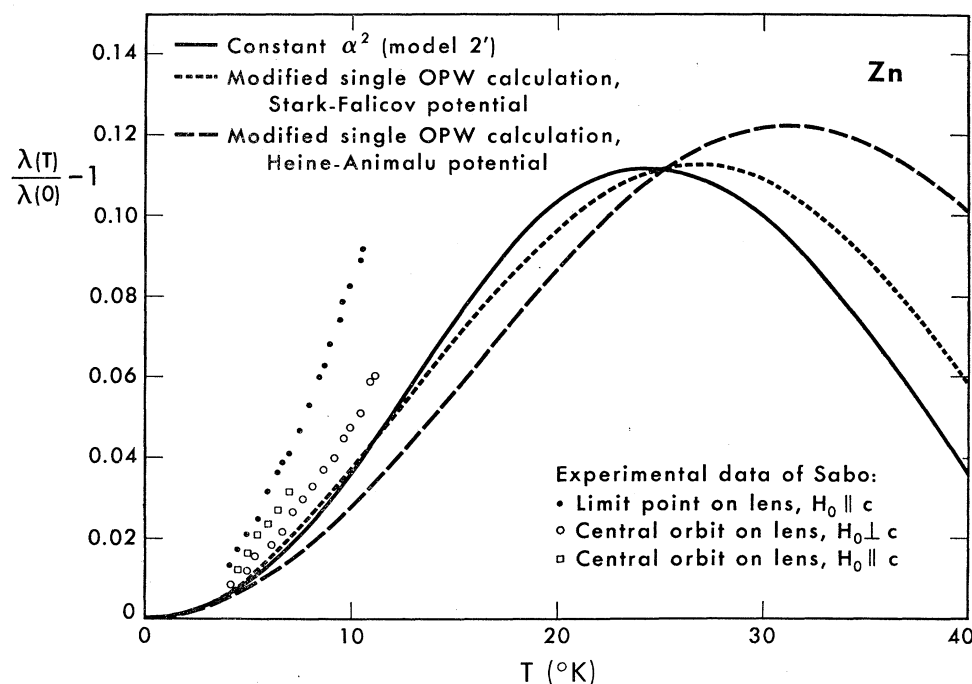


FIG. 4. Theoretical and experimental values of the mass renormalization as a function of temperature in zinc. The experimental points are  $[m^*(T) - m^*(0)]/[m^*(0) - m_b]$ , where  $m^*$  is the measured mass and  $m_b$  is an estimated band mass for the orbit. Uncertainties in the masses  $m_b$  could lead to small scale factor changes in the experimental points, and might change the ordering of the temperature shifts of various orbits.

diverge as  $1/\omega$  for small frequencies in the single-OPW approximation. This behavior is radically altered if band-structure effects are properly included. The reason is that only electrons that lie on the intersection of the Fermi surface and a zone boundary can couple to long-wavelength phonons by an umklapp process. But for these electrons, the single-OPW approximation breaks down completely. If more than one OPW is taken into account, the matrix element  $M_{k \rightarrow k+q+G}$  approaches zero as  $q$  goes to zero (this follows from the deformation-potential theorem), and  $\alpha^2$  goes like  $\omega$  for small frequencies.

It is clear from the example of model 1' that the unphysical divergence in  $\alpha^2$  will have the effect of severely depressing the predicted temperature shift of  $\lambda$ . Thus, in order to calculate  $\lambda(T)$  reliably, the small-frequency divergences must be eliminated. The examples of models 2', 3', and 4' indicate that the exact manner in which this is done is not very important, especially in determining  $\lambda(T)$  for temperatures below 15°K. Thus, we chose an arbitrary phenomenological form, namely one where  $\alpha_{LN}^2$  and  $\alpha_{LN}^2$  were taken to be linear in  $\omega$  below  $\frac{1}{2}\omega_D$ , and joined continuously with their single-OPW values at that point. This has the effect of decreasing the predicted value of  $\lambda(0)$  by a few

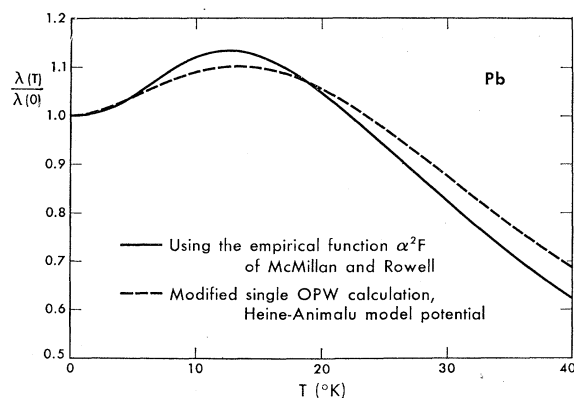


FIG. 5. Comparison of a modified single-OPW calculation and a calculation using the empirical function  $\alpha^2 F$  for lead.

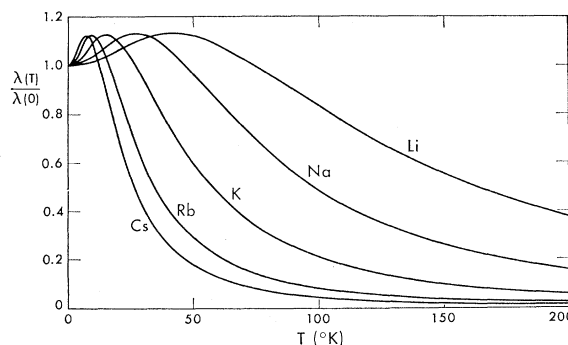


FIG. 6. Predicted temperature dependence of  $\lambda$  for alkali metals using the Heine-Animalu model potential.

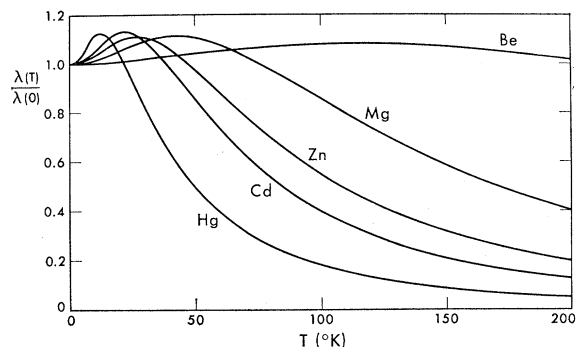


FIG. 7. Predicted temperature dependence of  $\lambda$  for group-II metals using empirical nonlocal pseudopotentials (and a Heine-Animalu potential for mercury).

percent, and increasing  $\lambda(T) - \lambda(0)$  by over 100% at small temperatures. The resulting values of  $[\lambda(T) - \lambda(0)]/\lambda(0)$  are shown in Fig. 4 for zinc and compared with both the experimental values of Sabo and the values obtained from a constant coupling  $\alpha^2$  and the experimental density of states. The one-OPW theory and the constant- $\alpha^2$  theory are in remarkably good agreement. Also shown in Fig. 4 is the result of a one OPW calculation using the Heine-Animalu model potential.<sup>19</sup> This potential underestimates  $\lambda(0)$  by 35%, and predicts a slower increase of  $\lambda$  with  $T$  than the other calculations.

As an additional test of our modified single OPW scheme for calculating  $\lambda(T)$ , we show in Fig. 5 a comparison between a one-OPW calculation for lead using the Heine-Animalu potential,<sup>19</sup> and a calculation using the experimental values of  $\alpha^2 F$  of McMillan and Rowell.<sup>15</sup> The agreement is satisfactory, especially considering that the density of states used in the one-OPW calculation is based on a quadratic-phonon spectrum, and is somewhat different from the actual density of states for lead. It would appear that, because of the sensitive nature of the temperature dependence, there is an inherent uncertainty in our calculations of 20–30%

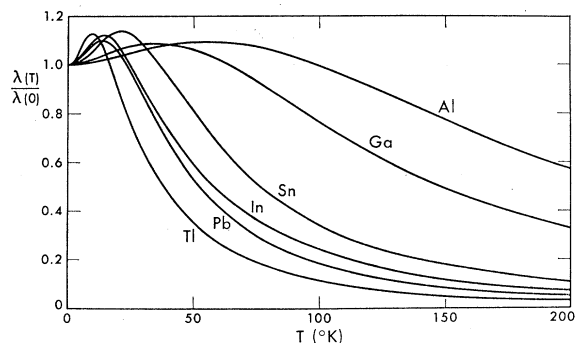


FIG. 8. Predicted temperature dependence of  $\lambda$  for metals of groups III and IV using the Heine-Animalu model potential.

in the form of  $\lambda(T)$  and the position of the maximum. Thus, although a reliable pseudopotential is the dominant factor in calculating  $\lambda(0)$ , the state of the calculation of  $\lambda(T)/\lambda(0)$  is such that uncertainties in the pseudopotential are not much more important than other uncertainties.

We have used the modified single-OPW scheme to calculate  $\lambda(T)/\lambda(0)$  for 16 nontransition metals. The results are shown in Figs. 6–8. The parameters needed in the calculation are given in Ref. 8. Heine-Animalu model potential<sup>19</sup> were used for all metals except beryllium, magnesium, zinc, and cadmium, where empirical nonlocal potentials were used from Refs. 20, 13, 18, and 18, respectively.

#### IV. CONCLUSIONS

Temperature-dependent shift of electronic masses has been observed in cyclotron resonance by Sabo in zinc at temperatures up to 11°K. A simple theoretical estimate of the shift requiring only a knowledge of the phonon density of states gives good agreement with experiment, but cannot explain a variation of the temperature shift from orbit to orbit. A reliable first-principle calculation of the shift requires at least modest improvements on the one-OPW model. The more challenging problem of calculating shifts for individual orbits requires detailed information about the band structure and the phonon spectra, and has not been attempted in this paper. It is possible, however, to draw certain qualitative conclusions based on the model calculations in Sec. III. It was shown there that the coupling to long-wavelength phonons is crucial in determining the low-temperature increase of  $\lambda(T)$ , e.g., a particularly strong coupling to long-wavelength phonons result in a smaller increase in  $\lambda(T)$ .

An electron at a point  $\mathbf{k}$  on the Fermi surface couples by long-wavelength phonons to nearby states  $\mathbf{k} + \mathbf{q}$ . The relevant wave vectors  $\mathbf{q}$  lie in the plane tangent to the Fermi surface at  $\mathbf{k}$ . The function  $\alpha_k^2 F_k$  for small frequency will scale as the inverse square of the velocity of the longitudinal phonons in the plane tangent at  $\mathbf{k}$ . Thus, phonon-anisotropy effects can cause a marked variation in  $\alpha_k^2 F_k$  from point to point. For example, at the limiting point on the top of the lens in zinc, the relevant phonons lie in the base plane of the hexagonal cell, where the velocities are 60% higher than they are in the direction of the  $c$  axis. Thus,  $\alpha_k^2 F_k$  for the limiting point should be lower at small frequencies than for points along the rim of the lens which couple to phonons in the direction of the  $c$  axis. This provides a possible explanation for the fact that the temperature increase of the mass enhancement of the limiting point appears to be larger than that of the lens orbits which explore the region of the rim. It does not, however, explain the fact that the mass of the lens orbit around the rim

<sup>19</sup> A. E. O. Animalu and V. Heine, *Phil. Mag.* **12**, 1249 (1965).

<sup>20</sup> J. H. Tripp, W. L. Gordon, P. M. Everett, and R. W. Stark, *Phys. Letters* **26A**, 98 (1967).

( $\mathbf{H}$  parallel to the  $c$  axis) appears more strongly temperature-dependent than the mass of the lens orbit over the poles ( $\mathbf{H}$  perpendicular to the  $c$  axis). A possible explanation for this is that the bare band masses for these orbits should be chosen somewhat differently. For example, if the estimated band mass of the orbit with  $\mathbf{H}$  perpendicular to  $c$  were increased slightly, this would readjust the points in Fig. 4 upward, and could actually change the ordering of the two lens orbits. To resolve this question, we need either a band-structure mass calculation or a calculation of the enhancement  $\lambda(O_k)$  for these orbits. It would be an interesting test of the pseudopotential model of electron-phonon coupling to attempt the detailed calculation of the mass enhancement for different orbits. Once the zero-temperature mass is calculated, there is no added difficulty in calculating the temperature dependence. The experimental knowledge of the low-temperature increase in  $\lambda(T)$  then provides a useful extra check on the theory of the mass enhancement.

The experimental observation of the maximum in the mass enhancement as a function of temperature would be an interesting verification of the theory.

Unfortunately, this is a difficult experiment at the present time, at least by the cyclotron-resonance method, because of temperature-dependent lifetime effects which prevent the observation of resonance at temperatures closer to the Debye temperature.

*Note added in proof.* Since submitting this paper, we have learned of several studies of the temperature dependence of the mass renormalization. Apparently the first was by Eliashberg<sup>21</sup> who pointed out the existence of a  $T^2 \log T$  term in the electronic specific heat. Grimvall<sup>22</sup> has presented calculations similar to ours for  $\lambda(T)$  in lead and mercury using experimental values of  $\alpha^2(\omega)F(\omega)$ . Appel<sup>23</sup> has studied the influence of this effect on the superconducting transition temperature.

#### ACKNOWLEDGMENTS

We would like to thank Dr. J. J. Sabo and Professor A. F. Kip for many helpful discussions.

<sup>21</sup> G. M. Eliashberg, *Zh. Eksperim. i Teor. Fiz.* **43**, 1005 (1962) [English transl.: *Soviet Phys.—JETP* **16**, 780 (1963)].

<sup>22</sup> G. Grimvall, *Physik Kondensierten Materie* **9**, 283 (1969).

<sup>23</sup> J. Appel, *Phys. Rev. Letters* **21**, 1164 (1968).

### Effects of Off-Diagonal Randomness in the Tight-Binding Model of Random Binary Alloys: Weak-Coupling Limit\*

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The single-band tight-binding model of random binary alloys is studied in the limit of second-order self-consistent perturbation theory, allowing the off-diagonal, as well as the diagonal, matrix elements of the model Hamiltonian to be dependent upon alloy composition. Fluctuations of both types of matrix elements about their configurational averages are assumed to be small but comparable, so that the randomness introduced into both parts of the Hamiltonian must be treated on an equal footing. Only nearest-neighbor hopping between constituent atoms (type  $A$  or  $B$ ) is considered, with the hopping integrals parametrized by the three numbers  $\alpha$ ,  $\beta$ , and  $\gamma$  for  $A$ - $A$ ,  $B$ - $B$ , and  $A$ - $B$  hopping, respectively. The single-particle alloy spectrum and the alloy density of states are obtained from an equation for the effective single-particle self-energy using standard techniques and with the dependence on model parameters explicitly displayed. With the assumption that  $\gamma = \frac{1}{2}(\alpha + \beta)$ , the theory is found to be rather simply characterized by the wave-vector-dependent displacement  $E_A(\mathbf{k}) - E_B(\mathbf{k})$  of the pure constituent spectra  $E_A(\mathbf{k})$  and  $E_B(\mathbf{k})$ .

#### I. INTRODUCTION

**A**N important contribution to the one-electron theory of disordered alloys has been Soven's<sup>1</sup> introduction of the coherent potential approximation (CPA), with subsequent development and application

to a model alloy Hamiltonian by Soven,<sup>2</sup> and by Velický, Kirkpatrick, and Ehrenreich.<sup>3</sup>

These authors have shown that, with certain limitations, the CPA provides a powerful and elegant means of extending the theory of simple binary alloys beyond the confines of low-order perturbation (or "weak-coupling") theory to the regime of relatively large con-

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<sup>1</sup> Paul Soven, *Phys. Rev.* **156**, 809 (1967).

<sup>2</sup> Paul Soven, *Phys. Rev.* **178**, 1136 (1969).

<sup>3</sup> B. Velický, S. Kirkpatrick, and H. Ehrenreich, *Phys. Rev.* **175**, 747 (1968).