New method for solving Boltzmann's equation for electrons in metals

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(Received 23 January 1978)

A new set of basis functions is introduced, consisting of products of Fermi-surface harmonics $F_J(k)$ and polynomials $\sigma_n(\epsilon)$ in the energy $(\epsilon - \mu)/k_B T$. The former are orthonormal on the Fermi surface, and the latter are orthonormal with weight function $-\partial f/\partial \epsilon$. In terms of this set the exact semiclassical Boltzmann equation takes a particularly simple form, giving a matrix equation which can probably be truncated at low order to high accuracy. The connection with variational methods is simple. Truncating at a 1×1 matrix gives the usual variational solution where ϕ_k is assumed proportional to v_{kx} for electrical conductivity and $(\epsilon - \mu)v_{kx}$ for thermal conductivity. Explicit equations are given for the matrix elements $Q_{Jn,Jn'}$ of the scattering operator for the case of phonon scattering, and a perturbation formula for ρ is given which is accurate for weak anisotropy. The matrix elements are simple integrals over spectral functions $\alpha^2(\pm,J,J')F(\Omega)$ which generalize the electron-phonon spectral function $\alpha^2 F(\Omega)$ used in superconductivity theory. Analogies are described between Boltzmann theory and Eliashberg theory for T_c of superconductors. The intimate relations between high-temperature resistance and the s- or p-wave transition temperature are made explicit.

I. INTRODUCTION AND SUMMARY

Rapid progress in band theory has opened the possibility for a microscopic theory of transport in transition metals. One of the first efforts to apply modern knowledge of Fermi surfaces and wave functions to the analysis of transport was by Yamashita and Asano.[1] In the process of making a calculation of the resistivity ρ for Nb and Mo, they obtained much other interesting information about anisotropic scattering rates and electron-phonon mass enhancements,[2] $1 + \lambda$. Four independent groups[3-6] have recently performed calculations for Nb of λ and the accompanying spectral function $\alpha^2 F(\Omega)$, which determines T_c of a superconductor.[2] These calculations amply demonstrate that microscopic calculations of transport coefficients are now possible; in fact, most of the necessary information is available already; it is mainly a matter of organization to pull out the correct coefficient.

This paper elaborates a formal language by which the Boltzmann equation can be rigorously solved. The language has been adapted from superconductivity, and enables calculations of T_c and transport to be carried out in parallel. The language is free of biases about the nature of energy bands, phonons, or coupling; it works equally well for spherical Fermi surfaces as in K, for distorted but recognizably spherical ones as in Cu, or for unrecognizably complicated ones as in the d-band elements. A key feature is a series of spectral functions $\alpha^2(\pm,J,J')F(\Omega)$ which generalize $\alpha^2 F(\Omega)$ used in superconductivity. These functions are amenable to calculation, and they are also simple enough that intelligent guesses can be made about their

shape and size. As a preliminary step, a new set of basis functions is introduced, in terms of which the Boltzmann equation takes a particularly simple form.

The Boltzmann equation for electrons in a metal with a uniform $\vec{E}$ field and a uniform thermal gradient $\vec{\nabla}T$ is[7]

$$\left(e\vec{E} \cdot \vec{v}_k + \frac{\epsilon_k}{T} \vec{\nabla}T \cdot \vec{v}_k\right)\frac{\partial f}{\partial \epsilon_k} = \sum_{k'} Q_{kk'} \phi_{k'} , \qquad (1)$$

where $\vec{v}_k$ is the velocity $\vec{\nabla}_k \epsilon_k/\hbar$, and ϵ_k is the energy (measured relative to the chemical potential μ) of the electron with quantum numbers k (short for $\vec{k}n$, wave number and band index). The scattering operator Q will be written out explicitly later for phonon and impurity scattering; for now, the important feature of Q is that energy conservation and the Pauli-principle force k and k' have nearly equal energy, near the Fermi energy. The electrical $(\vec{J}_e)$ and thermal $(\vec{J}_Q)$ currents are determined by the distribution function F_k which equals the Fermi function $f(\epsilon_k)$ in equilibrium. In terms of the deviation, $F_k - f(\epsilon_k)$, which is written $\phi_k(-\partial f/\partial \epsilon_k)$, the currents are

$$\vec{J}_e = -2e \sum_k \vec{v}_k \phi_k\left(-\frac{\partial f}{\partial \epsilon_k}\right) \equiv \beta_{00}\vec{E} + \beta_{01}\vec{\nabla}T , \qquad (2)$$

$$\vec{J}_Q = 2 \sum_k \epsilon_k \vec{v}_k \phi_k\left(-\frac{\partial f}{\partial \epsilon_k}\right) \equiv \beta_{10}\vec{E} + \beta_{11}\vec{\nabla}T , \qquad (3)$$

where the factors of 2 are for spin degeneracy. The coefficients β_{ij} are related in the standard way[7] to the transport coefficients: electrical conductivity $\sigma = \beta_{00}$; thermopower $S = -\beta_{00}^{-1}\beta_{01}$; and thermal conductivity $\kappa = -\beta_{11} + \beta_{10}\beta_{00}^{-1}\beta_{01}$.

The new basis functions are products of two types

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of functions. (i) "Fermi-surface harmonics" (FSH) $F_J(k)$ are generalizations of spherical harmonics and are used to describe "angular" variations in ϕ_k, etc., as k varies on the Fermi surface. They are orthonormal when integrated over the Fermi surface. They have been described before,[8] and applied to the problem of gap anisotropy in superconductors.[9] (ii) Energy polynomials $\sigma_n(\epsilon)$ are nth-order polynomials in $\epsilon/k_B T$, orthonormal with weight function $-\partial f/\partial \epsilon$. These functions are described here for the first time. In the product basis set labeled by Jn, Eqs. (1)–(3) take the form (assuming both $\vec{E}$ and $\vec{\nabla}T$ point in the $\hat{x}$ direction)

$$-\left(eE\delta_{n0} + \frac{\pi}{\sqrt{3}} k_B \nabla T\delta_{n1}\right)\delta_{JX} = \sum_{J'n'} Q_{Jn,J'n'}\phi_{J'n'} \quad (1')$$

$$j_e = -2e\phi_{X0}, \quad (2')$$

$$j_Q = (2\pi k_B T/\sqrt{3})\phi_{X1}, \quad (3')$$

where F_X is a particular FSH proportional to the x component of the velocity, and σ_0 and σ_1 are polynomials proportional to 1 and ϵ, respectively. From these formulas (which will be derived in Sec. II), explicit formulas for the transport coefficients can be written:

$$\sigma = 2e^2 (Q^{-1})_{X0,X0}, \quad (4)$$

$$S = -(\pi k_B/\sqrt{3}\, e)(Q^{-1})_{X0,X1}/(Q^{-1})_{X0,X0}, \quad (5)$$

$$\kappa = \tfrac{2}{3}\pi^2 k_B^2 T[(Q^{-1})_{X1,X1} - |(Q^{-1})_{X0,X1}|^2/(Q^{-1})_{X0,X0}]. \quad (6)$$

Even for very complicated band structures, the expansion in the set (Jn) should converge rapidly. Thus the integral equation (1) has been transformed into a matrix equation which can probably be truncated at fairly low order; only the upper left-hand 2×2 part of the inverse Q^{-1} of this matrix is needed to describe transport. For electrical conductivity it is usually reasonable to approximate the distribution function by a rigid translation of the Fermi distribution function $f(\epsilon(k+\delta k))$. This is equivalent to asserting that $\phi_k = \phi_{X0}F_X(k)$, i.e., only the $X0$ element of ϕ_{Jn} is large. The accuracy of this approximation is related to the smallness of off-diagonal elements $Q_{X0,Jn}$ which couple to other elements of ϕ. When the off-diagonal elements are small, the inverse matrix elements like (4) can be calculated perturbatively. The perturbation series works out to be particularly simple for the resistivity ρ:

$$\rho = 1/2e^2(Q^{-1})_{X0,X0}$$

$$= \frac{1}{2e^2}\left(Q_{X0,X0} - \sum_\alpha{}' \frac{Q_{X0,\alpha}Q_{\alpha,X0}}{Q_{\alpha,\alpha}}\right.$$

$$\left. + \sum_{\alpha,\beta}{}' \frac{Q_{X0,\alpha}Q_{\alpha,\beta}Q_{\beta,X0}}{Q_{\alpha,\alpha}Q_{\beta,\beta}} - \cdots\right), \quad (7)$$

where α is a composite index Jn, and the primes on the sums mean that $\alpha,\beta,\gamma,\ldots$ can never equal $X0$, and successive indices can never equal each other. The first term in the series (7) is the lowest-order variational solution[7] for ρ, and is thus an upper bound on ρ. This will be shown in Sec. II. In Sec. III, explicit formulas for the first term of (7) are given and in Sec. IV the higher-order $Q_{\alpha\beta}$'s are worked out. The higher terms in the expansion (7) are valid when off-diagonal elements are small compared to the diagonal ones. The first correction term gives the exact answer if Q can be approximated by a 2×2 submatrix. Truncating the series (7) at this point thus gives a generalized version of the "two-band model"[7,10] and a rigorous justification for it which does *not* rely on having two (and only two) sheets of Fermi surface. This may possibly add some clarity to the theory of deviations from Matthiessen's rule.[10-12] Finally, in Sec. V, some connections with the theory of superconducting T_c are described.

II. EXPANSION IN NEW BASIS FUNCTION

The FSH functions have already been described.[8,9] A few of their properties are reviewed here. They are defined as polynomials in the Cartesian components of the velocity (v_{kx}, v_{xy}, v_{kz}), orthonormalized according to the rule

$$\sum_k F_J(k)F_{J'}(k)\delta(\epsilon_k - \epsilon)\bigg/\sum_k \delta(\epsilon_k - \epsilon) = \delta_{JJ'}. \quad (8)$$

For spherical surfaces F_J becomes $Y_{lm}(\hat{k})$. The F_J's must be constructed separately for each metal. In practice[9] this has been quite easy to implement on a computer once the band structure ϵ_k is solved. Functions of this type, using the wave vector instead of the velocity, were first introduced by Fano[13] for analyzing x-ray response of solids, and their properties were discussed at length by Strinati and Fano.[14] For transport problems, velocity polynomials are much more useful because $\vec{v}_k$ appears on the left in Eq. (1). Some additional simplifications are that only energies ϵ near the Fermi energy are needed, and the basis functions automatically have the properties of periodicity in $\vec{k}$ space and continuity and differentiability across Brillouin-zone boundaries, as do physical quantities like ϕ_k. The functions F_J are also chosen to transform as basis functions for irreducible representations of the crystal point group. This simplifies the orthonormalization procedure because basis functions for different rows or different representations are automatically orthogonal. Further, the scattering operator $Q_{kk'}$, being invariant under the simultaneous rotation of k and k' by any element

of the group, is automatically block diagonal. There are no off-diagonal elements $\langle J' | Q | J \rangle$ coupling different rows or different representations.

First consider the formula (2) for the current j_e, which can be trivially rewritten

$$ j_{ex} = -2e \int d\epsilon \frac{-\partial f}{\partial \epsilon} \sum_k v_{kx} \phi_k \delta(\epsilon_k - \epsilon). \tag{9} $$

It is obviously convenient to choose one of the functions F_J (called F_X) to be proportional to v_{kx}. Then the other F_J's are orthogonal to v_{kx}, and only the $J = X$ component of ϕ_k contributes to the current (9). In fact, this is compulsory if there is only one sheet of Fermi surface. However, if there are N sheets, then there are N independent first-order polynomials based on v_{kx}; any set of N linearly independent combinations of $C_i v_{kx}^i$ (where i runs over the sheets) is allowed. For simplicity in solving Boltzmann's equation the additional requirement is imposed that F_X be one of the functions. The normalized form of F_X is

$$ F_X = v_{kx}/v(\epsilon_k), \tag{10} $$

$$ v(\epsilon_k) = \langle v_x^2(\epsilon) \rangle^{1/2}, \tag{11} $$

$$ N_\dagger(\epsilon)\langle v_x^2(\epsilon) \rangle = \sum_k v_{kx}^2 \delta(\epsilon_k - \epsilon) = \frac{1}{2}\left(\frac{n}{m}\right)_{\text{eff},x}, \tag{12} $$

$$ N_\dagger(\epsilon) = \sum_k \delta(\epsilon_k - \epsilon), \tag{13} $$

where $N_\dagger(\epsilon)$ is the single-spin density of states. The rms x component of velocity at energy ϵ, $\langle v_x^2(\epsilon) \rangle^{1/2}$, occurs so commonly that it is given the name $v(\epsilon)$, which should not be confused with the velocity $\vec{v}_k$. The product $N_\dagger(\epsilon)\langle v_x^2(\epsilon) \rangle$ also occurs commonly, and is the product of number of carriers in unfilled bands times inverse effective-mass tensor averaged over occupied states, or $\frac{1}{2}(n/m)_{\text{eff}}$.

The FSH's allow an efficient solution of the angular part of the problem, exactly as the spherical harmonics do in spherical symmetry. The "radial" part of the problem, i.e., the variation with energy ϵ, still needs attention. It is convenient to introduce a new set of energy polynomials $\sigma_n(\epsilon)$ defined to be orthonormal with weight function $-\partial f/\partial \epsilon$.

$$ \int_{-\infty}^{\infty} d\epsilon \left(\frac{-\partial f}{\partial \epsilon}\right) \sigma_n(\epsilon)\sigma_{n'}(\epsilon) = \delta_{nn'}. \tag{14} $$

The functions are specified by the choices $\sigma_0 = 1$ and $\sigma_n(\epsilon)$ constructed to be orthonormal to all lower polynomials, with the coefficient of the highest power of ϵ (i.e., the nth power) chosen positive. The first two functions are

$$ \sigma_0 = 1, \quad \sigma_1 = \sqrt{3}\,\epsilon/\pi k_B T. \tag{15} $$

A recursion relation for constructing all higher polynomials from these two is given in the Appen-

dix, as well as certain other properties of $\sigma_n(\epsilon)$. The combined set of functions $F_J(k)\sigma_n(\epsilon_k)$ can be used to expand any function of k. A great simplification is achieved if we define *two* complete sets of joint basis functions

$$ \chi_{Jn}(k) = F_J(k)\sigma_n(\epsilon_k)/N_\dagger(\epsilon_k)v(\epsilon_k), \tag{16} $$

$$ \xi_{Jn}(k) = F_J(k)\sigma_n(\epsilon_k)v(\epsilon_k)\left(\frac{-\partial f}{\partial \epsilon_k}\right). \tag{17} $$

These functions have a nice biorthogonality property when integrated over the whole Brillouin zone (and over all bands),

$$ \sum_k \chi_{Jn}(k)\xi_{J'n'}(k) = \delta_{JJ'}\delta_{nn'}. \tag{18} $$

This is easily proved from the orthogonality relations (8) and (14); it helps to insert $\int d\epsilon\,\delta(\epsilon_k - \epsilon)$ inside the k sum.

Any function of k can be expanded in either set χ_{Jn} or set ξ_{Jn}; the former is convenient for functions which are smooth in energy while the latter is convenient for functions (like the scattering operator) which peak at the Fermi energy. The left-hand side of the Boltzmann equation (1) can be immediately expressed in terms of the functions ξ_{Jn} with $J = X$ (Eq. 10) and $n = 0$ or 1 (Eq. 15):

$$ -eE\xi_{X0}(k) - (\pi k_B/\sqrt{3})\nabla T \xi_{X1}(k). \tag{19} $$

This suggests that we should multiply (1) by $\chi_{Jn}(k)$ and sum over k, using (18):

$$ -\left(eE\delta_{n0} + \frac{\pi k_B}{\sqrt{3}}\nabla T\delta_{n1}\right)\delta_{JX} = \sum_{kk'} \chi_{Jn}(k)Q_{kk'}\phi_{k'}. \tag{20} $$

The completeness relation for the biorthogonal set (16)–(18) is

$$ \sum_{J'n'} \chi_{J'n'}(k')\xi_{J'n'}(k'') = \delta_{k'k''}. \tag{21} $$

Inserting this in the right-hand side of (20), between $Q_{kk'}$ and $\phi_{k'}$, the final result (1') is immediately obtained. The definitions of $Q_{Jn,J'n'}$ and ϕ_{Jn} are clearly

$$ Q_{Jn,J'n'} = \sum_{kk'} \chi_{Jn}(k)Q_{kk'}\chi_{J'n'}(k'), \tag{22} $$

$$ \phi_{Jn} = \sum_k \xi_{Jn}(k)\phi_k. \tag{23} $$

The inverse relations are obtained with the help of (21):

$$ Q_{kk'} = \sum_{Jn,J'n'} \xi_{Jn}(k)Q_{Jn,J'n'}\xi_{J'n'}(k'), \tag{24} $$

$$ \phi_k = \sum_{Jn} \phi_{Jn}\chi_{Jn}(k). \tag{25} $$

This version of the Boltzmann equation is *exact,*

i.e., no approximation has entered to alter (1') from the original form (1). In Sec. III, explicit formulas for $Q_{Jn,J'n'}$ will be worked out, and certain approximate formulas exhibited. Let us now make contact with the variational method.[7] The electrical resistivity is bounded above by the functional $\rho_t(\psi(k))$,

$$\rho \leq \rho_t = \sum_{kk'} \psi_k Q_{kk'} \psi_{k'} \Big/ 2e^2 \Big(\sum_k v_{kx}\psi_k \frac{-\partial f}{\partial \epsilon_k}\Big)^2, \quad (26)$$

where ψ_k is an arbitrary trial function. The actual resistivity is the minimum value of ρ_t, and is achieved when ψ_k is proportional to the actual distribution function ϕ_k. Now expand ψ_k in the functions χ_{Jn}, keeping N terms:

$$\psi_k = \sum_{Jn}^{(N)} \psi_{Jn}\chi_{Jn}(k),$$

$$\rho \leq \rho_t = \sum_{Jn,J'n'}^{(N)} \psi_{Jn} Q_{Jn,J'n'} \psi_{J'n'} \Big/ 2e^2 \psi_{X_0}^2. \quad (27)$$

The minimum of ρ_t is found by varying the coefficients ψ_{Jn}; the answer is

$$\rho \leq \rho_t(\min, N) = 1/2e^2[Q^{-1}(N)]_{X_0,X_0}. \quad (28)$$

The least upper bound is achieved by inverting the $N \times N$ matrix. As N increases, a sequence of decreasing upper bounds on ρ is found which converges to the true answer (4) as $N \to \infty$. Thus solving the matrix equation (1') with a truncated basis set is equivalent to a variational calculation in that subspace and yields an upper bound to ρ.

The standard lowest-order variational solution assumes that $F_k = f(\epsilon(\vec{k} + \delta\vec{k}))$, i.e., that the Fermi surface is uniformly displaced in the direction of $\vec{E}$. This is equivalent to putting $\psi_k = v_{kx}$ in (26). The lowest-order result in the new basis set is the first term of the expansion (7), equivalent to the choice $\psi_k = \chi_{X_0}(k)$ in (26), or $N = 1$ in (28). Using Eqs. (10)–(12), (15), and (16), χ_{X_0} can be written

$$\chi_{X_0}(k) = 2v_{kx}/(n/m)_{\text{eff},\epsilon}. \quad (29)$$

This differs only slightly from the usual variational trial function. In most cases the ϵ dependence of $(n/m)_{\text{eff}}$ is weak compared to k_BT, so that $(n/m)_{\text{eff}}$ is a constant and cancels out, making the two lowest-order procedures identical.

III. LOWEST-ORDER RESULTS

In this section the first approximation [first term of Eq. (1)] to ρ is worked out explicitly. The final result is a familiar generalization of Bloch-Grüneisen theory to metals with complicated energy bands and phonons. There are two reasons for giving details here. First, a systematic derivation of these familiar results has never appeared in print to my knowledge. Second, the techniques and

notations used here are the same as will be used in Sec. IV, and perhaps it is best to present them in a familiar context.

For impurity or phonon scattering, the operator $Q_{kk'}$ has the form of scattering-out minus scattering-in, both determined by the equilibrium transition probability[7] $P_{kk'}$:

$$Q_{kk'} = (k_BT)^{-1}\Big(\delta_{kk'}\sum_{k''} P_{kk''} - P_{kk'}\Big). \quad (30)$$

Because $P_{kk'}$ is symmetric in k, k', Eq. (22) becomes

$$Q_{Jn,J'n'} = (2k_BT)^{-1}\sum_{kk'} P_{kk'}[\chi_{Jn}(k) - \chi_{Jn}(k')]$$
$$\times [\chi_{J'n'}(k) - \chi_{J'n'}(k')]. \quad (31)$$

Explicit forms[7] for $P_{kk'}$, due to impurity and phonon scattering are

$$P_{kk'}^{\text{imp}} = (2\pi/\hbar)|V_{kk'}|^2 f_k(1 - f_{k'})n_i\delta(\epsilon_k - \epsilon_{k'}), \quad (32)$$

$$P_{kk'}^{\text{ph}} = (2\pi/\hbar)|M_{kk'}|^2 f_k(1 - f_{k'})$$
$$\times [(N_Q + 1)\delta(\epsilon_k - \epsilon_{k'} - \Omega_Q) + N_Q\delta(\epsilon_k - \epsilon_{k'} + \Omega_Q)],$$
$$\quad (33)$$

where $V_{kk'}$ and $M_{kk'}$ are the impurity and electron-phonon scattering matrix elements; n_i and N_Q are the number of impurities and number of phonons (Bose factor); Ω_Q is the phonon energy; Q is short for wave vector $\vec{Q}$ ($\vec{k} - \vec{k}'$ reduced to the first Brillouin zone) and branch index ν (which is implicitly summed over).

We now evaluate the first term of the expansion (7), using Eq. (29) for $\chi_{X_0}(k)$, and neglecting for now the energy dependence of $(n/m)_{\text{eff}}$. The first step is

$$\rho^{(0)} = [(n/m)_{\text{eff}}e^2]^{-1}(1/\tau_{\text{imp}}^{(0)} + 1/\tau_{\text{ph}}^{(0)}), \quad (34)$$

$$\frac{1}{\tau_a^{(0)}} = \frac{1}{2}\Big(\frac{n}{m}\Big)_{\text{eff}} Q_{X_0,X_0}^a$$

$$= \Big[\Big(\frac{n}{m}\Big)_{\text{eff}} k_BT\Big]^{-1}\sum_{kk'} (v_{kx} - v_{k'x})^2 P_{kk'}^a, \quad (35)$$

where the superscript (0) is to remind that this is lowest order in energy and "angle" dependence, and a can mean "imp" or "ph." Next, consider impurity scattering, and plug (32) into (35), using the identity $f(\epsilon)[1 - f(\epsilon)] = k_BT(-\partial f/\partial\epsilon)$ and the approximation $-\partial f/\partial\epsilon \simeq \delta(\epsilon)$ and Eq. (12) for $(n/m)_{\text{eff}}$:

$$\frac{1}{\tau_{\text{imp}}^{(0)}} = \frac{2\pi n_i}{\hbar} N_t(0) \frac{\sum_{kk'} (v_{kx} - v_{k'x})^2 |V_{kk'}|^2\delta(\epsilon_k)\delta(\epsilon_{k'})}{2\sum_{pp'} v_{px}^2\delta(\epsilon_p)\delta(\epsilon_{p'})}. \quad (36)$$

This result is the analog for complicated bands of the familiar formula[7] which (36) reduces to for single-plane-wave electrons,

$$\frac{1}{\tau_{imp}^{(1PW)}} = \frac{2\pi n_i}{\hbar} N_\uparrow(0) \int_{-1}^{1} \frac{d\cos\theta}{2} (1 - \cos\theta)[V(2k_F(1 - \cos\theta))]^2 . \tag{36a}$$

Note that $(v_{kx} - v_{kx'})^2/2 \langle v_x^2 \rangle$ is the generalization for complicated bands of the angular weighting factor $1 - \cos\theta$. The notation τ in (34)–(36) should not be taken to imply that a relaxation time "exists," i.e., that $Q\phi$ can be written ϕ/τ. Only in the special case to which (36a) refers is a true relaxation time meaningful. Equations (34)–(36) are *not* "relaxation-time approximations."

Next, consider the analogous formula for phonon scattering:

$$\frac{1}{\tau_{ph}^{(Q)}} = \frac{2\pi}{\hbar} \frac{N_\uparrow(0)}{k_B T} \int d\epsilon \int d\epsilon' \int d\Omega \frac{\sum_{kk'} (v_{kx} - v_{k'x})^2 |M_{kk'}|^2 \delta(\epsilon_k - \epsilon)\delta(\epsilon_{k'} - \epsilon')}{2\sum_{pp'} v_{px}^2 \delta(\epsilon_p)\delta(\epsilon_{p'})}$$

$$\times \delta(\Omega - \Omega_Q) f(\epsilon)[1 - f(\epsilon')]\{[N(\Omega)+1]\delta(\epsilon - \epsilon' - \Omega) + N(\Omega)\delta(\epsilon - \epsilon' + \Omega)\} . \tag{37}$$

Three δ functions have been inserted, and integrated out, which separates energy from angular variations. Now define an "electron-phonon spectral function"[15]

$$\alpha_{tr}^2 F(\Omega, \epsilon, \epsilon') \equiv N_\uparrow(0) \frac{\sum_{kk'} (v_{kx} - v_{k'x})^2 |M_{kk'}|^2 \delta(\epsilon_k - \epsilon)\delta(\epsilon_{k'} - \epsilon')\delta(\Omega_Q - \Omega)}{2\sum_{pp'} v_{px}^2 \delta(\epsilon_p)\delta(\epsilon_{p'})} . \tag{38}$$

Except for the extra factors of velocity which reduce to $1 - \cos\theta$ in the spherical case, this is identical to the analogous function $\alpha^2 F(\Omega)$ used in Eliashberg theory of superconductivity and measured by tunneling. It is very convenient to introduce this spectral function into transport theory because, in the absence of detailed knowledge, we can still make good guesses about $\alpha_{tr}^2 F$. It is customary to argue that $\alpha_{tr}^2 F$ depends only weakly on ϵ and ϵ', compared with the rapid variation of the subsequent factors which vary on the scales $k_B T$ and $\hbar\Omega_Q$. This justifies neglecting the ϵ, ϵ' dependence of (38), i.e., setting ϵ and ϵ' to zero and calling the result $\alpha_{tr}^2 F(\Omega)$. This approximation will begin to break down at high T if there is rapid variation of electronic parameters like $N(\epsilon)$ ("Fermi smearing" effects). Thus (37) becomes

$$\frac{1}{\tau_{ph}^{(Q)}} = \frac{4\pi k_B T}{\hbar} \int_0^\infty d\Omega \, \alpha_{tr}^2 F(\Omega) I(\Omega/2k_B T)/\Omega , \tag{39}$$

$$I(\Omega/2k_B T) = \frac{\Omega}{2k_B^2 T^2} \int_{-\infty}^\infty d\epsilon \int_{-\infty}^\infty d\epsilon' f(\epsilon)[1 - f(\epsilon')]\{[N(\Omega)+1]\delta(\epsilon - \epsilon' - \Omega) + N(\Omega)\delta(\epsilon - \epsilon' + \Omega)\} . \tag{40}$$

By a tedious but elementary integration, $I(x)$ can be shown to be $(x/\sinh x)^2$. At high temperatures, $I(x)$ approaches rapidly to 1, and (39) becomes[16]

$$1/\tau_{ph}^{(Q,highT)} = (2\pi/\hbar)k_B T \lambda_{tr} , \tag{41}$$

$$\lambda_{tr} = 2 \int_0^\infty d\Omega \frac{\alpha_{tr}^2 F(\Omega)}{\Omega} = N_\uparrow(0) \frac{\sum_{kk'} (v_{kx} - v_{k'x})^2 (|M_{kk'}|^2/\hbar\Omega_Q)\delta(\epsilon_k)\delta(\epsilon_{k'})}{\sum_{pp'} v_{px}^2 \delta(\epsilon_p)\delta(\epsilon_{p'})} . \tag{42}$$

The coupling constant λ_{tr} differs only by velocity factors from the coupling constant λ which determines T_c of superconductors and enhances the low-temperature specific heat γ. At low temperatures, only the small Ω part of $\alpha_{tr}^2 F(\Omega)$ contributes to the integral (39). The superconducting function $\alpha^2 F$ behaves as Ω^2 for small Ω, but the extra factor $(v_{kx} - v_{k'x})^2$ changes $\alpha_{tr}^2 F$ to an Ω^4 behavior. This gives a T^5 contribution to ρ. Equations (34) and (39) are the appropriate generalization of the Bloch-Grüneisen formula to metals with real (non-Debye) phonon spectra and real (nonspherical) energy bands. In Debye approximation, the standard Bloch-Grüneisen result is obtained by setting $\alpha_{tr}^2 F$ to $2\lambda_{tr}(\Omega/\Omega_D)^4\Theta(\Omega_D - \Omega)$. At room temperature, Eqs. (34) and (41) appear to give an excellent semi-quantitative account of the resistivity of transition metals, with $\lambda_{tr} \simeq \lambda$, provided $(n/m)_{eff}$ is calculated from reliable energy bands.[16] However, they are only the first approximation, and especially at low temperatures, the corrections due to anisotropy and ϵ dependence of ϕ_k can be significant. Finally, it is worth mentioning that experience with many superconducting metals show that $\alpha^2 F(\Omega)$ is surprisingly similar in shape to $F(\Omega)$, the phonon density of states. It is reasonable to expect the same

for $\alpha_{tr}^2 F(\Omega)$, except for the low-frequency region $(\Omega \lesssim \frac{1}{10}\Omega_D)$ where the power law is altered from Ω^2 to Ω^4.

IV. HIGHER-ORDER TERMS

In this section the general term $Q_{Jn,J'n'}$ of the scattering operator is worked out. The first step is to factorize the "angular" and energy variations occurring in Eq. (31). The shorthand notation $\chi_{Jn}(k) = (Jk)(n\epsilon)$ is helpful, where (Jk) means $F_J(k)$ and $(n\epsilon)$ means $\sigma_n(\epsilon)/N_\uparrow(\epsilon)v(\epsilon)$. Factorization is accomplished by the identity

$$[(Jk)(n\epsilon) - (Jk')(n\epsilon')][(J'k)(n'\epsilon) - (J'k')(n'\epsilon')]$$

$$= \frac{1}{4}\sum_{s,s'=\pm 1} [(Jk) - s(Jk')][(J'k) - s'(J'k')]$$

$$\times [(n\epsilon) + s(n\epsilon')][(n'\epsilon) + s'(n'\epsilon')]. \quad (43)$$

Now define the generalized spectral functions

$$\alpha^2(s,s',J,J',\epsilon,\epsilon')F(\Omega)$$

$$= [2N_\uparrow(0)]^{-1}\sum_{kk'} |M_{kk'}|^2[F_J(k) - sF_J(k')]$$

$$\times [F_{J'}(k) - s'F_{J'}(k')]$$

$$\times \delta(\epsilon_k - \epsilon)\delta(\epsilon_{k'} - \epsilon')\delta(\Omega_Q - \Omega) \quad (44)$$

and joint energy polynomials

$$J(s,s',n,n',\epsilon,\epsilon')$$

$$= \frac{1}{4}[(n\epsilon) + s(n\epsilon')][(n'\epsilon) + s'(n'\epsilon')], \quad (45)$$

where s,s' can take the values ± 1. The exact result for the scattering operator (31) due to phonon scattering (33) is

$$Q_{Jn,J'n'}^{ph} = \frac{2\pi N_\uparrow(0)}{\hbar k_B T}\int d\epsilon \int d\epsilon \int d\Omega \sum_{s,s'=\pm 1} \alpha^2(s,s',J,J',\epsilon,\epsilon')F(\Omega)f(\epsilon)[1 - f(\epsilon')]J(s,s',n,n',\epsilon,\epsilon')$$

$$\times \{[N(\Omega) + 1]\delta(\epsilon - \epsilon' - \Omega) + N(\Omega)\delta(\epsilon - \epsilon' + \Omega)\}. \quad (46)$$

This is quite a formidable expression. One suspects theorists will not be quick to evaluate it. The complexity is unavoidable if we wish to solve exactly, taking both angular (JJ') and energy (nn') variation of ϕ_k into account. In simple metals like potassium it is found[17] that energy and angular variation give comparable corrections to ρ, neither one large. In d-band metals which can have very anisotropic velocities, it is reasonable to expect that the angular corrections will be larger, while energy corrections may be similar to those found in K. Let us consider the sources of ϵ dependence with an eye to making approximations. There are two sources. (i) Electronic parameters like $N_\uparrow(\epsilon)$, $v(\epsilon)$, and $\alpha^2(s,s,J,J',\epsilon,\epsilon')$ vary on a scale determined by band structure. A typical scale might be 2 eV for simple metals and 0.2 eV for d-band metals. (ii) Energy conservation and the Pauli principle introduce $\delta(\epsilon - \epsilon' \pm \Omega)$ and $f(1 - f')$ which vary on a faster scale, Ω and $k_B T$. At low temperatures it is appropriate to neglect (i), whereas (ii) can cause significant corrections to the lowest-order result, especially for thermal conductivity. At high temperatures, $kT > \Omega_D$, it becomes reasonable to set Ω to 0 inside the δ functions, treating phonon scattering as effectively elastic. In this situation, the Boltzmann integral equation does not couple different energies ϵ and ϵ'; the apparatus of $\sigma_n(\epsilon)$ polynomials is no advantage, and the equation is easily solved by other means.[8] The energy variation of $N(\epsilon)$, $v(\epsilon)$, and $\alpha^2(s,s',J,J',\epsilon,\epsilon')$ can cause a significant "Fermi-smearing" correction to ρ, but in the elastic approximation this is more easily

handled by techniques other than those used here. In some cases it may be important to know the simultaneous effect of inelasticity and Fermi smearing, making the full formula (46) inescapable. The rigorous procedures developed here are likely to be most useful (i.e., most readily implemented) when Fermi-smearing effects can be neglected. This means the ϵ,ϵ' dependence of $\alpha^2 F$ can be neglected [by evaluating at $\epsilon = \epsilon' = 0$, calling the result $\alpha^2(s,s',J,J')F(\Omega)$]. In this approximation another helpful simplification occurs. When the signs s,s' are the same (opposite), both $\alpha^2(s,s',J,J',\epsilon,\epsilon')F$ and $J(s,s',n,n',\epsilon,\epsilon')$ are even (odd) under interchange of ϵ and ϵ'. The odd combinations $(s \neq s')$ vanish when particle-hole symmetry is assumed (Fermi smearing neglected). Evaluated at $\epsilon,\epsilon' = 0$, the odd parts, $\alpha^2(s, -s,J,J',0,0)F$, clearly vanish. We can keep only the even $(s = s')$ parts and contract the notation still further, to $\alpha^2(s,JJ')F(\Omega)$ and $J(s,n,n',\epsilon,\epsilon')$. Further, the energy polynomial $(n\epsilon) = \sigma_n(\epsilon)/N(\epsilon)v(\epsilon)$ can be replaced by $\sigma_n(\epsilon)/N(0)v(0)$. The joint energy polynomial (45) becomes

$$J(s,n,n',\epsilon,\epsilon') = [N_\uparrow(0)(n/m)_{eff}]^{-1}$$

$$\times H(s,n,n',\epsilon,\epsilon'),$$

$$\quad (47)$$

$$H(\pm,n,n',\epsilon,\epsilon') = \frac{1}{4}[\sigma_n(\epsilon) \pm \sigma_n(\epsilon')]$$

$$\times [\sigma_{n'}(\epsilon) \pm \sigma_{n'}(\epsilon')],$$

where Eq. (12) has been used. Then (46) becomes

$$Q^{ph}_{Jn,J'n'} \simeq 2[(n/m)_{eff}\tau^{ph}_{Jn,J'n'}]^{-1},$$

(48)

$$\frac{1}{\tau^{ph}_{Jn,J'n'}} = \frac{4\pi k_B T}{\hbar} \sum_{s=\pm 1} \int_0^\infty d\Omega \, \frac{\alpha^2(s,J,J')F(\Omega)I(s,n,n',\Omega/2k_B T)}{\Omega}$$

$$I\left(\pm,n,n',\frac{\Omega}{2k_B T}\right) = \frac{\Omega}{2k_B^2 T^2} \int d\epsilon \int d\epsilon' \, H(\pm,n,n',\epsilon,\epsilon')f(\epsilon)[1 - f(\epsilon')]$$

$$\times \{[N(\Omega) + 1]\delta(\epsilon - \epsilon' - \Omega) + N(\Omega)\delta(\epsilon - \epsilon' + \Omega)\}$$

$$= I(\pm,n,n',x) \equiv (x/\sinh x)^2 I^{\pm}_{nn'}(x).$$

(49)

It can be shown that $I^s_{nn'}(x)$ defined in the last line of (49) is a polynomial of order $n + n'$ in x. Finally (48) can be written

$$\frac{I}{\tau^{ph}_{Jn,J'n'}} = \frac{4\pi k_B T}{\hbar} \sum_{s=\pm 1} \int_0^\infty \frac{d\Omega}{\Omega} \alpha^2(s,J,J')F(\Omega)$$

$$\times \left(\frac{x}{\sinh x}\right)^2 I^s_{nn'}(x).$$

(50)

This is the final formula for the electron-phonon scattering operator. The lowest-order result $1/\tau^{(0)}_{ph}$ [Eq. (39)] is just $1/\tau^{ph}_{\chi 0,\chi 0}$. This follows because I^+_{00} is 1, I^-_{00} is 0, and $\alpha^2(+,X,X)F(\Omega)$ is $\alpha^2_{tr}F(\Omega)$ [Eq. (38)]. The result (50) is considerably less forbidding than (46). It is already possible to calculate $\alpha^2(s,J,J')F(\Omega)$ for d-band elements by a slight generalization of the programs developed[3-6] to do $\alpha^2 F(\Omega)$. The rest is algebra. It must be possible to derive an analytic or at least recursive formula for $I^{\pm}_{nn'}(x)$, but I have not succeeded. It can be shown to be an *even* polynomial in x, of order $n + n'$ if $n + n'$ is even, and vanishing if $n + n'$ is odd. Some specific results are

$$I^+_{nn'}(0) = \delta_{nn'}, \quad I^-_{nn'}(0) = 0,$$

$$I^+_{00}(x) = 1, \quad I^-_{n0}(x) = 0,$$

$$I^+_{11}(x) = 1 + (x/\pi)^2, \quad I^-_{11}(x) = 3(x/\pi)^2,$$

$$I^+_{20}(x) = \sqrt{5}\,(x/\pi)^2,$$ (51)

$$I^+_{22}(x) = 1 + 5(x/2\pi)^2 + 21(x/2\pi)^4,$$

$$I^-_{22}(x) = 15(x/2\pi)^2 + 15(x/2\pi)^4.$$

The fact that $I^{\pm}_{nn'}$ vanishes if $n + n'$ is odd means that the scattering operator $Q_{Jn,J'n'}$ block diagonalizes into two parts with n, n' even and odd, respectively, with no coupling between them. Thus the thermopower vanishes [Eq. (5)], as does the second term of the thermal conductivity [Eq. (6)]. These results fail when Fermi smearing is included. The thermopower arises completely because of Fermi smearing (i.e., states below ϵ_F have a different ability to carry current from states above ϵ_F; particle-hole symmetry fails).

These formulas allow an explicit result to be written for the thermal conductivity κ in lowest-order variational approximation. Taking for the variational function $\phi_k = \alpha_0 \chi_{X0} + \alpha_1 \chi_{X1}$, we are left with a 2×2 matrix which is already diagonal. The variational formula for the thermal resistivity $W = \kappa^{-1}$ is then

$$W^{(0)} = (3/2\pi^2 k_B^2 T)Q_{X1,X1}.$$

(52)

Using Eq. (50), the result for the phonon part is

$$W^{(Q)}_{ph} = \frac{6}{\pi \hbar k_B (n/m)_{eff}}$$

$$\times \left\{ 2 \int \frac{d\Omega}{\Omega} \alpha^2(+XX)F(\Omega)\left(\frac{x}{\sinh x}\right)^2 \left(1 + \frac{x^2}{\pi^2}\right) \right.$$

$$\left. + 2 \int \frac{d\Omega}{\Omega} \alpha^2(-XX)F(\Omega)\left(\frac{x}{\sinh x}\right)^2 \left(3\frac{x^2}{\pi^2}\right) \right\},$$

(53)

where $x = \Omega/2k_B T$. The spectral function $\alpha^2(+XX)F$ is identical to $\alpha^2_{tr}F$ [Eq. (38)], while $\alpha^2(-XX)F$ has $(v_{kx} - v_{k'x})^2$ replaced by $(v_{kx} + v_{k'x})^2$. The low-Ω behavior of $\alpha^2(-XX)F$ is Ω^2; the extra two powers of Ω in $\alpha^2_{tr}F$ arise from the cancellation of $(v_{kx} - v_{k'x})^2$ at small Q. At high temperatures, x is small and the first term of (53) is dominant, with x^2/π^2 negligible compared to 1. This gives $W^{(Q)}_{ph}$ proportional to $\rho^{(0)}_{ph}$ [Eq. (39)], so that the Wiedemann-Franz law holds. At low temperatures, the first term of (53) goes as T^4 and obeys the Wiedemann-Franz law (with an altered Lorentz number), but the thermal resistivity is dominated by the second term which goes as T^2 and violates the Wiedemann-Franz law. Equation (53) generalizes the well-known results for spherical metals to more-complicated band structures. However, just as in the spherical case, a more-careful treatment of the energy inelasticity (i.e., a larger number of odd-n basis functions) is needed to get a numerically accurate solution at low temperatures. In a perturbative expansion for W^{ph} analogous to (7) for ρ, the second correction has the same low-temperature power law (T^2) as the first, unlike the case of resistivity where higher-order phonon terms with $n \neq 0$ go as T^7 while the first term goes as T^5. A variational calculation by Klemens[18] gives a reduction in the low-

T phonon-induced thermal resistivity by 33% below the result (53), arising from higher-order energy dependence of ϕ coming from inelasticity.

V. CONNECTION WITH SUPERCONDUCTIVITY

The theories of ρ and T_c are similar in two different ways: (i) they both depend on the same electron-phonon scattering matrix elements, and (ii) the formal structure of the theories is similar in many ways. Eliashberg theory[19] gives a nonlinear integral equation for the energy gap $\Delta(k, \omega)$ which is complex and wave-vector and frequency dependent. As T approaches T_c, Δ approaches 0, and the integral equation becomes linear (and homogeneous, in contrast to Boltzmann's equation). By analytic continuation to the imaginary frequency axis, the kernel K becomes well behaved and real, as does Δ. The transition temperature is the temperature at which the largest eigenvalue of K is zero. In practice, the k dependence of Δ is usually neglected, and the resulting theory is formulated as a one-dimensional integral equation with K a functional of the spectral function $\alpha^2 F(\Omega)$. This approximation gives a variational estimate of the actual largest eigenvalue of K, and thus gives a lower bound to T_c. There is an almost precise analogy

with the lowest-order variational procedure in transport which gives a lower bound in σ. In each theory a variational functional exists which is a lower bound on (T_c, σ) for any trial value of the (gap Δ, distribution function ϕ). The actual (Δ, ϕ) is the one which maximizes (T_c, σ). The lowest-order trial function is a constant (gap Δ, displacement δk). If the error in the trial function is order α, the error in (T_c, σ) is order α^2. This "error" is the anisotropy enhancement of (T_c, σ). In nearly all metals, α is apparently fairly small. A probe of the anisotropy of (Δ, ϕ) is the effect of impurities on (T_c, σ). In both cases, heavy doping with impurities will eliminate much of the anisotropy enhancement of (T_c, σ). In transport there is of course another effect of impurities—the residual resistivity— which has no analog in s-wave superconductivity (but does for other pairing schemes as in ^{3}He). The destruction by impurities of the anisotropy enhancement of σ shows up as a deviation from Mattheissen's rule.[10-12]

A scheme for solving the Eliashberg equations exactly, taking anisotropy into account using FSH's, was proposed in Ref. 8 and partly implemented in Ref. 9. The spectral function $\alpha^2 F$ becomes generalized to

$$\alpha^2_{JJ'}F(\Omega) = N_\dagger(0) \frac{\sum_{kk'} |M_{kk'}|^2 F_J(k)F_{J'}(k')\delta(\epsilon_k)\delta(\epsilon_{k'})\delta(\Omega_Q - \Omega)}{\sum_{pp'} \delta(\epsilon_p)\delta(\epsilon_{p'})} . \tag{54}$$

It is also convenient to define another related function which enters because of the occurrence of the "normal" self-energy Z in the Eliashberg equations

$$A^2_{JJ'}F(\Omega) = N_\dagger(0) \frac{\sum_{kk'} |M_{kk'}|^2 F_J(k)F_{J'}(k)\delta(\epsilon_k)\delta(\epsilon_{k'})\delta(\Omega_Q - \Omega)}{\sum_{pp'} \delta(\epsilon_p)\delta(\epsilon_{p'})} . \tag{55}$$

This differs from $\alpha^2_{JJ'}F$ only in having $F_{J'}(k)$ in place of $F_{J'}(k')$. Because of the completeness of FSH's, the two functions are not independent; $\alpha^2_{JJ'}F$ alone contains all necessary information, and $A^2_{JJ'}F$ can be expanded, using the Clebsch-Gordan coefficients $C_{JJ'J''}$:

$$A^2_{JJ'}F(\Omega) = \sum_{J''} C_{JJ'J''}\alpha^2_{J''0}F(\Omega) , \tag{56}$$

$$C_{JJ'J''} = \frac{\sum_k F_J(k)F_{J'}(k)F_{J''}(k)\delta(\epsilon_k)}{\sum_p \delta(\epsilon_p)} , \tag{57}$$

where the function F_0 is defined to be 1. The spectral functions defined for transport can be immediately written in terms of $\alpha^2_{JJ'}F$ and $A^2_{JJ'}F$,

$$\alpha^2(\pm JJ')F(\Omega) = A^2_{JJ'}F(\Omega) \mp \alpha^2_{JJ'}F(\Omega) . \tag{58}$$

At room temperature and above, because of the small parameter $\Omega/2k_BT$, the $n = n' = 0$ terms of

$Q_{Jn,J'n'}$ will dominate. Neglecting Fermi smearing, these can be written

$$Q^{(ph, high\ T)}_{J0,J'0} = \frac{2}{(n/m)_{eff}} \frac{4\pi k_B T}{\hbar} \int \frac{\delta\Omega}{\Omega} \alpha^2(+JJ')F(\Omega) . \tag{59}$$

Using Eq. (58), this can be written

$$Q^{(ph, high\ T)}_{J0,J'0} = \frac{2}{(n/m)_{eff}} \frac{2\pi k_B T}{\hbar} (\Lambda_{JJ'} - \lambda_{JJ'}) , \tag{60}$$

where the coefficients $\Lambda_{JJ'}$ and $\lambda_{JJ'}$ have been defined[9] because of their importance in superconductivity:

$$\lambda_{JJ'} = 2 \int d\Omega \frac{\alpha^2_{JJ'}F(\Omega)}{\Omega} , \tag{61}$$

$$\Lambda_{JJ'} = 2 \int d\Omega \frac{A^2_{JJ'}F(\Omega)}{\Omega} \tag{62}$$

$$= \sum_{J''} C_{J J' J''} \lambda_{J'' 0} . \tag{63}$$

The two matrices $\underline{\Lambda}$ and $\underline{\lambda}$, together with a matrix $\underline{\mu}^*$ which gives the weak Coulomb repulsion, determine T_c of a superconductor to good approximation (unless T_c is very large):

$$T_c = (\omega_{\log}/1.2) \exp(-1/\lambda_{\text{eff}}), \tag{64}$$

$$\lambda_{\text{eff}} = \text{max eigenvalue of } (\underline{1} + \underline{\Lambda})^{-1} (\underline{\lambda} - \underline{\mu}^*) . \tag{65}$$

This is the generalization of McMillan's[2] formula to superconductors with anisotropic energy gaps. Just like the scattering operator Q, these matrices are block diagonal in the different rows and representations of the crystal point group. For all known superconducting metals it is strongly suspected that the largest eigenvalue (65) occurs in the Γ_1 submatrix (s-wave superconductivity), although there is no fundamental reason why certain metals[20] might not choose a different submatrix, probably Γ_{15} (crudely, p wave). Transport is of course determined by the Γ_{15} submatrix of Q. We see from (60), (64), and (65) that high-temperature transport depends on *exactly* the same coefficients as the "p-wave T_c." The lowest-order variational solution at high T [Eqs. (34) and (41)] uses $\lambda_{\text{tr}} = \Lambda_{XX} - \lambda_{XX}$. The analogous lowest-order variational estimate for the p wave (more correctly, Γ_{15}) T_c is

$$T_c^{(0)}(\Gamma_{15}) = \frac{\omega_{\log}}{1.2} \exp\left(\frac{1 + \Lambda_{XX}}{\lambda_{XX} - \mu_{XX}^*}\right). \tag{66}$$

If the two numbers Λ_{XX} and λ_{XX} were separately known, this would allow a lowest-order variational lower bound on the p-wave T_c, which would be of great interest, for example, for Pd. The coefficient λ_{tr} is also closely related to $\lambda = \lambda_{00} = \Lambda_{00}$ which determines the Γ_1 (s-wave) transition temperature. This comes about because of Eq. (63) and the properties of the Clebsch-Gordan coefficients (57). As was shown in Ref. 8, C_{XXJ} vanishes for all Γ_1 elements J except for two, $C_{XX0} = 1$ and $C_{XXR2} = (\langle v^4 \rangle - \langle v^2 \rangle^2)^{1/2}/\langle v^2 \rangle$. Thus we can write

$$\lambda_{\text{tr}} = \lambda_{00} + C_{XXR2} \lambda_{0R2} - \lambda_{XX} . \tag{67}$$

Empirically[16] it appears that λ_{tr} and $\lambda_{00} = \lambda$ are very similar for those d-band elements examined so far. Probably both the second and third terms of (67) are quite a bit smaller than the first, and they occur with opposite signs.

Several other interesting quantities can be calculated simultaneously with resistivity, namely, the anisotropic quasiparticle mass enhancement λ_k and scattering rate $1/\tau_k$. These both can be calculated (at any value of T and external frequency ω) as integrals[21] over $\alpha^2 F(k, \Omega)$, defined as

$$\alpha^2 F(\vec{k}\Omega) = \sum_J F_J(k) \alpha_{0J}^2 F(\Omega) . \tag{68}$$

Thus, for example, when $\omega = 0$, λ_k can be written

$$\lambda_k = \sum_J F_J(k) \lambda_{0J} . \tag{69}$$

For many materials it is probable that the anisotropy in λ_k is reasonably accounted for by only a few terms in (69), possibly just λ_{00} and λ_{0R2}, both of which are contained in a resistivity calculation. Finally, the anisotropy of the superconducting gap Δ_k, for weak anisotropy, can be written[9]

$$\Delta_k = \sum_J F_J(k) \Delta_J ,$$
$$\Delta_J/\Delta_0 \simeq (1 + \mu^*)(1 + \lambda)^{-1}(\lambda - \mu^*)^{-1} \lambda_{0J} . \tag{70}$$

This anisotropy causes a T_c enhancement δT_c, which can be written for weak anisotropy[9]

$$\delta T_c/T_c = (1 + \mu^*)(1 + \lambda)^{-1}(\lambda - \mu^*)^{-3}(\langle \lambda_k^2 \rangle - \lambda^2),$$
$$\langle \lambda_k^2 \rangle - \lambda^2 = \sum_{J \neq 0} \lambda_{0J}^2 . \tag{71}$$

These formulas demonstrate that one virtue of the Fermi-surface harmonic method is to achieve a simple unification of physical quantities whose interrelation appeared previously quite complicated.

ACKNOWLEDGMENTS

APPENDIX

A set of orthogonal polynomials has been defined by Eq. (17). Some properties of these polynomials are worked out here. First, transform to a dimensionless variable $x = \epsilon/2\pi k_B T$

$$\sigma_n(\epsilon) = (2n + 1)^{1/2} \zeta_n(\epsilon/2\pi k_B T), \tag{A1}$$

$$\pi \int_{-\infty}^{\infty} dx \, \frac{\zeta_n(x) \zeta_{n'}(x)}{\cosh^2 \pi x} = \delta_{nn'} \frac{2}{2n + 1} . \tag{A2}$$

A factor of $(2n + 1)^{1/2}$ has been introduced into (A1) because it simplifies the form of the resulting polynomials $\zeta_n(x)$. Lawrence has pointed out to me that the Legendre polynomials of $\tanh \pi x$ are a possible choice for an orthonormal set satisfying (A2). For the present purposes it is more convenient to have ζ_n be a polynomial in x rather than $\tanh \pi x$; otherwise the simple results (3'), (5), and (6) would be replaced by infinite series. Sykes and Brooker[22] have used the associated Legendre polynomials to define functions

$$\zeta_n(x) = (2n+3)^{1/2}(n+1)^{-1/2}(n+2)^{-1/2}$$
$$\times (2n+1)^{-1/2}P^1_{n+1}(\tanh \pi x)$$

which also satisfy (A2). However, these are even less convenient for the present purposes. The polynomials defined here are in some sense a natural analog for degenerate quantum electrons of the Sonine polynomials of classical kinetic theory.[23] I have been unable to find these polynomials in the literature or to relate them to any set of known polynomials.

The low-order polynomials $\zeta_n(x)$ are readily constructed by orthogonalization

$$\zeta_0(x) = 1, \quad \zeta_1(x) = 2x, \quad \zeta_2(x) = 3x^2 - \tfrac{1}{4}. \quad \text{(A3)}$$

The polynomials up to $\zeta_6(x)$ were constructed this way, and a conjecture for the leading coefficient was found

$$\zeta_n(x) = [2^n(2n-1)!!/(n!)^2]x^n + \cdots. \quad \text{(A4)}$$

Beyond $n=6$, brute-force construction by hand was too tedious. The conjecture (A4) was verified numerically to 11-figure accuracy for polynomials up to order $n=17$ on a Univac 1110 computer. Although a rigorous proof is lacking, (A4) is surely correct. The recursion relation follows imme-

diately from knowledge of the leading coefficient[24]

$$n^2\zeta_n(x) = 2(2n-1)x\zeta_{n-1}(x) - (n-1)^2\zeta_{n-2}(x). \quad \text{(A5)}$$

This gives an efficient method for generating numerical values of $\zeta_n(x)$ if n is not too high. General theory of orthogonal polynomials[24] shows that the set ζ_n is complete in the sense that for a given $\bar{\epsilon}$, arbitrarily small, and a given real function $a(x)$, some finite N exists such that, for suitably chosen expansion coefficients a_n,

$$\left\| a(x) - \sum_{n=0}^{N} a_n\zeta_n(x) \right\| < \bar{\epsilon},$$

$$\|b(x)\|^2 \equiv \pi \int_{-\infty}^{\infty} dx \, \frac{[b(x)]^2}{\cosh^2\pi x}. \quad \text{(A6)}$$

The optimum choice of expansion coefficients is

$$a_n = (2n+1)\frac{\pi}{2}\int_{-\infty}^{\infty} dx \, \frac{a(x)\zeta_n(x)}{\cosh^2\pi x}. \quad \text{(A7)}$$

It remains to be determined from experience whether the transport coefficients converge rapidly in these polynomials. An argument by Klemens[18] shows that for low-temperature thermal conduction, ϕ will not converge rapidly, but this does not prove that calculation of κ converges slowly.

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