PHYSICAL REVIEW B VOLUME 21, NUMBER 10 15 MAY 1980

Solutions to the Boltzmann equation for electrons in a metal: Energy dependence

F. J. Pinski
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830
and Department of Physics, State University of New York, Stony Brook, New York 11794

(Received 14 November 1979)

The solution to the Boltzmann equation for electrons in a metal is a distribution function which depends on energy and wave vector. This paper solves for the energy dependence by expanding the distribution function in sets of orthogonal functions, (a) energy polynomials, (b) Legendre polynomials in $\tanh(\epsilon_k/2k_BT)$, or (c) a combination of these two choices. To study *only* the effects of the energy dependence, the electrical and thermal conductivities were calculated for a class of isotropic models. For one of these models, the electrical resistivity is 37% lower than the Bloch-Grüneisen result at a temperature of 0.15 (in units of the Debye temperature, Θ_D). For thermal resistivity, this method is consistent with the result of Klemens; i.e., at very low temperature the correction to the lowest-order result is 51%. Corrections are important at temperatures as high as 0.3 Θ_D. These results show that the standard, i.e., simple variational, results for the temperature dependence of transport coefficients make significant errors. However, by the methods of this paper, accurate results can be obtained quite easily by computer, not only for simple isotropic models, but also for realistic metals. Results for transition metals are briefly mentioned; more complete calculations will be presented elsewhere.

I. INTRODUCTION

The electrical and thermal conductivities of a metal can be obtained by solving the semiclassical Boltzmann equation[1] which determines the electronic distribution function. In general, the distribution function depends on both energy and wave vector. The wave-vector dependence has been calculated by several groups.[2-4] In this paper, I investigate methods of calculating the energy dependence and the effects on conductivities. It has been known[5] that the energy dependence can have a substantial effect on the thermal conductivity at low temperatures, but it was believed that the effect[6] on electrical resistivity was small. However, while calculating the transport coefficients for Pd (Refs. 7, 8) and Nb (Ref. 8) using realistic models, the enhancement of the electrical resistivity was unexpectedly found to be as large as 28%. To understand this effect, I extended a formalism suggested by Allen to a point where calculations of the energy dependence in the distribution function could be performed. To isolate the effect of the energy dependence, I calculated conductivities for completely isotropic models, i.e., using spherical Fermi surfaces and Debye phonons. These calculations show that the energy dependence can be responsible for enhancements as large as 37% in the electrical conductivity.

Some preliminaries are presented in the next section, where the Boltzmann equation and Allen's[9] method of solution are briefly restated. The subject of energy dependence is addressed in Sec. III. This dependence can be found by using expansions of orthogonal functions, which can be (a) polynomials[9] in the energy, (b) Legendre polynomials[9,10] of $\tanh(\epsilon_k/2k_BT)$, or (c) a mixture of these (hereafter called the "mixed basis"). The isotropic models are defined in Sec. IV, and the conductivities are calculated for these models. The rates of convergence of the various methods are compared, and the "mixed basis" is shown to be most useful for calculating thermal conductivities at all temperatures.

II. THE BOLTZMANN EQUATION

As used by Allen,[9] the distribution function and Boltzmann scattering operator can be expanded using the basis sets χ_{Jn} and ξ_{Jn}, given by

$$\chi_{Jn}(k)=F_J(k)\sigma_n(\epsilon_k)/N_\uparrow(\epsilon_k)v(\epsilon_k)\,, \tag{2.1a}$$

$$\xi_{Jn}(k)=F_J(k)\sigma_n(\epsilon_k)(-\partial f/\partial\epsilon_k)\,, \tag{2.1b}$$

$$\sum_k F_J(k)F_{J'}(k)\delta(\epsilon-\epsilon_k)=\delta_{JJ'}N_\uparrow(\epsilon)\,, \tag{2.2a}$$

$$\int d\epsilon\,\sigma_n(\epsilon)\sigma_{n'}(\epsilon)(-\partial f/\partial\epsilon)=\delta_{nn'}\,, \tag{2.2b}$$

where f is the Fermi function and $N_\uparrow(\epsilon)$ is the single-spin density of states and $v(\epsilon)$ is one-third of the rms velocity on the energy surface. The functions χ_{Jn} and ξ_{Jn} are biorthogonal, since the energy functions σ_n and Fermi surface harmonics[11] F_J are orthogonal [Eqs. (2.2a) and (2.2b)]. The scattering operator and distribution function written in this basis are

$$Q_{JnJ'n'}=\sum_{kk'}\chi_{Jn}(k)Q_{kk'}\chi_{J'n'}(k')\,, \tag{2.3}$$

$$\phi_{Jn}=\sum_k \xi_{Jn}(k)\phi_k\,, \tag{2.4}$$

where $-(\partial f/\partial\epsilon_k)\phi_k$ is the deviation of the distribution function from the Fermi factor. Note that the energies are measured from the chemical potential and that k is shorthand for $\{\vec{k}, n\}$, where $\vec{k}$ is the wave vector and n is the band index.

The linearized Boltzmann equation for electrons in the presence of a uniform electric field $\vec{E}$ and a uniform temperature gradient $\vec{\nabla}T$ can be expressed as

$$-\left(eEA_n+\frac{\pi k_B}{\sqrt{3}}\vec{\nabla}TB_n\right)C_J=\sum_{J'n'} Q_{JnJ'n'}\phi_{J'n'}\,, \tag{2.5}$$

where the quantities A_n, B_n, and C_J are given by

$$A_n=\int_{-\infty}^{\infty} d\epsilon\,\sigma_n(\epsilon)\left(-\frac{\partial f}{\partial\epsilon}\right), \tag{2.6}$$

$$B_n=\frac{\sqrt{3}}{\pi k_B T}\int_{-\infty}^{\infty} d\epsilon\,\epsilon\,\sigma_n(\epsilon)\left(-\frac{\partial f}{\partial\epsilon}\right), \tag{2.7}$$

$$C_J=\sum_k v_{kx}F_J(k)\delta(\epsilon_k)/N_\uparrow(0)v(0)\,. \tag{2.8}$$

The scattering operator due to phonons is then given approximately by

$$Q^{e\text{-}p}_{JnJ'n'}\approx\frac{4\pi k_B T}{\hbar N_\uparrow(0)v(0)}\sum_{s=\pm1}\int_0^\infty\frac{d\Omega}{\Omega}\alpha^2(s,J,J')F(\Omega)\left[\left(\frac{x}{\sinh x}\right)^2 I^s_{nn'}(x)\right], \tag{2.9}$$

where x is the dimensionless variable, $x=\hbar\Omega/2k_BT$. The function $\alpha^2(s,J,J')F(\Omega)$ is similar to the Eliashberg function[12] $\alpha^2F(\Omega)$ and is given by

$$\alpha^2(s,J,J')F(\Omega)\cong[2N_\uparrow(0)]^{-1}\sum_{kk',\nu}|M^\nu_{kk'}|^2\delta(\epsilon_k)\delta(\epsilon_k')\delta(\Omega-\Omega^\nu_{kk'})[F_J(k)-sF_J(k')]\,[F_{J'}(k)-sF_{J'}(k')]\,. \tag{2.10}$$

The quantity $M^\nu_{kk'}$ is the electron-phonon matrix element.[13] The use of $\alpha^2(s,J,J')F(\Omega)$ in $Q_{JnJ'n'}$ is an approximation. Both initial and final electron energies have been set equal to the Fermi energy, with corrections being smaller by a factor of $(k_BT/\epsilon_F)^2$. Finally, in Eq. (2.9), the function $I^s_{nn'}(x)$ is given for $s=\pm1$ by

$$\left(\frac{x}{\sinh x}\right)^2 I^s_{nn'}(x)=\frac{\hbar\Omega}{8k_B^2T^2}\int d\epsilon\int d\epsilon' f(\epsilon)[1-f(\epsilon')]\,\{[N(\Omega)+1]\delta(\epsilon-\epsilon'-\hbar\Omega)+N(\Omega)\delta(\epsilon-\epsilon'+\hbar\Omega)\}$$
$$\times[\sigma_n(\epsilon)+s\sigma_n(\epsilon')]\,[\sigma_{n'}(\epsilon)+s\sigma_{n'}(\epsilon')]\,, \tag{2.11}$$

where $f(\epsilon)[N(\Omega)]$ is a Fermi [Bose] factor. The functions $I^s_{nn'}(x)$ vanish unless $n+n'$ is even.

An equivalent expression for $I^s_{nn'}$ is (see Appendix A)

$$8I^s_{nn'}(x)=g_{nn'}(x/\pi)+g_{nn'}(-x/\pi)+sh_{nn'}(x/\pi)+sh_{nn'}(-x/\pi)\,, \tag{2.12}$$

where the functions g and h are defined by

$$g_{nn'}(z)=\underline{J}\sigma_n(2\pi k_BTy)\sigma_{n'}(2\pi k_BTy)\,, \tag{2.13}$$

$$h_{nn'}(z)=\underline{J}\sigma_n(2\pi k_BTy)\,\sigma_{n'}(2\pi k_BTy+2\pi k_BTz)\,, \tag{2.14}$$

with the operator $\underline{J}$ being expressed in two ways as

$$\underline{J}=\pi\int_{-\infty}^{\infty}dx\cosh^{-2}(\pi x)\frac{1}{z}\int_{x-z}^{x}dy\,, \tag{2.15}$$

$$\underline{J}=\frac{1}{\pi z}\int_{-1}^{1}d\alpha\frac{\alpha}{\gamma+\alpha}\,, \tag{2.16}$$

where $\alpha=\tanh\pi y$ and $\gamma=\coth z$. In the following section, expressions for $I^s_{nn'}$ will be found for the two choices of energy functions given by Allen,[9] (a) polynomials in ϵ_k, or (b) Legendre polynomials in $\tanh(\epsilon_k/2k_BT)$. A mixture of these functions is useful in calculating the thermal conductivity as shown in Sec. IV.

III. ENERGY EXPANSIONS

The work of Wilson[14] and Sondheimer[6] used expansions of the distribution function ϕ in powers of ϵ_k. Allen[9] suggested using instead an orthogonal set of polynomials in ϵ_k, i.e., choice (a) of the previous section. The polynomials of dimensionless argument $y=\epsilon_k/2\pi k_BT$ are generated by the following recursion formula for $n\geq 2$:

$$n^2\zeta_n(y)=2(2n-1)y\zeta_{n-1}(y)-(n-1)^2\zeta_{n-2}(y)\,, \tag{3.1}$$

with $\zeta_0(y)=1$ and $\zeta_1(y)=2y$. The connection with the energy polynomials is

$$\sigma_n(\epsilon)=(2n+1)^{1/2}\zeta_n(y)\,. \tag{3.2}$$

The values of A_n and $B_{n'}$ [see Eqs. (2.6) and (2.7)] vanish except for $n=0$ and 1, respectively, A_n

$=\delta_{n0}$ and $B_n=\delta_{n1}$. However, Allen did not show how to evaluate the functions $I^s_{nn'}$ [Eq. (2.11)] but only calculated a few results. This paper not only shows how to evaluate $I^s_{nn'}$ (on a computer) but tabulates a large subset of its values.

Since the moments of $\cosh^{-2}\pi y$ are related to the Bernoulli numbers β by

$$N_n=\pi\int_{-\infty}^{\infty} dy\,\cosh^{-2}(\pi y)y^{2n}=2\,|\,1-2^{1-n}|\,\beta_{2n}\,, \quad (3.3)$$

the functions $g_{nn'}$ and $h_{nn'}$ can be found from

$$\underline{J}y^{2n}=\sum_{q=0}^{n}\frac{(2n)!\,z^{2n-2q}N_q}{(2q)!\,(2n-2q+1)!}\,, \quad (3.4)$$

and

$$\underline{J}y^i(y+z)^j=\sum_{r=0}^{(i+j)/2}\frac{j!}{(2r)!}z^{i+j-2r}N_r\sum_{s=\max(2r,i)}^{(i+j)/2}\frac{(-1)^s s!}{(s-i)!\,(i+j-s)!\,(s+1-2r)!}\;. \quad (3.5)$$

To derive these expressions, the first form of $\underline{J}$ [Eq. (2.15)] is the more expedient form.

In Table I, $I^{\pm}_{nn'}$ is displayed in fractional form for $n, n' \leq 5$; calculations were done for $n, n' \leq 49$, and a listing is available on request. Note that $I^-_{n0}(z)=0$ and $I^s_{nn'}(0)=\delta_{nn'}\delta_{s+}$ and that they are even functions; the highest power in z is $n+n'$. The lowest-order result for electrical resistivity does not include $\alpha^2(-JJ')F(\Omega)$ because $I^-_{00}=0$. However, the lowest-order result for thermal resistivity and higher-order results for both resistivities include both $\alpha^2(+JJ')F(\Omega)$ and $\alpha^2(-JJ')F(\Omega)$. In Sec. IV, where the Debye model is discussed, an enhancement of the electrical

TABLE I. Coefficients of $I^s_{nn'}(\pi z)$ for the energy polynomials. Blank entries are zero. Entries with a * are a correction to the calculations in Ref. 9.

n	n'	s	1	z^2	z^4	z^6	z^8	z^{10}
0	0	+	1					
0	0	−						
2	0	+		$\sqrt{5}$				
2	0	−						
2	2	+	1	$\frac{5}{4}$	$\frac{21}{4}$*			
2	2	−		$\frac{15}{4}$	$\frac{15}{4}$*			
4	0	+		$-\frac{5}{4}$	$\frac{7}{4}$			
4	0	−						
4	2	+		$\sqrt{5}$		$2\sqrt{5}$		
4	2	−		$-\sqrt{5}/2$	$5\sqrt{5}/4$	$7\sqrt{5}/4$		
4	4	+	1	$\frac{205}{144}$	$\frac{1351}{192}$	$\frac{186}{96}$	$\frac{2485}{576}$	
4	4	−		$\frac{205}{48}$	$\frac{215}{64}$	$\frac{105}{32}$	$\frac{805}{192}$	
1	1	+	1	1				
1	1	−		3				
3	1	+		$\sqrt{21}/2$	$\sqrt{21}/2$			
3	1	−		$-\sqrt{21}/6$	$5\sqrt{21}/6$			
3	3	+	1	$\frac{49}{36}$	$\frac{203}{36}$	$\frac{95}{18}$		
3	3	−		$\frac{49}{12}$	$\frac{35}{12}$	$\frac{35}{6}$		
5	1	+		$-\sqrt{33}/4$		$\sqrt{33}/4$		
5	1	−		$\sqrt{33}/15$	$-7\sqrt{33}/12$	$7\sqrt{33}/20$		
5	3	+		$\sqrt{77}/4$	$-5\sqrt{77}/144$	$7\sqrt{77}/72$	$55\sqrt{77}/144$	
5	3	−		$-3\sqrt{77}/20$	$19\sqrt{77}/48$	$-7\sqrt{77}/120$	$19\sqrt{77}/48$	
5	5	+	1	$\frac{5269}{3600}$	$\frac{21\,329}{2880}$	$\frac{4103}{900}$	$-\frac{539}{2880}$	$\frac{1757}{800}$
5	5	−		$\frac{5269}{1200}$	$\frac{2849}{960}$	$\frac{4081}{600}$	$-\frac{539}{960}$	$\frac{1771}{800}$

TABLE II. $I^s_{nn'}(x)$ for the expansion using the Legendre polynomials of $\tanh(\epsilon_k/2k_BT)$. The notation that $\gamma = \coth x$ is used.

$$I^+_{00}(x)=1 \quad I^-_{00}(x)=0 \quad I^-_{20}(x)=0$$

$$I^+_{11}(x)=1.5(1-\gamma^2+\gamma/x)$$

$$I^-_{11}(x)=1.5(-1+3\gamma^2-3\gamma/x)$$

$$I^+_{20}(x)=\tfrac{1}{2}\sqrt{5}(-1+3\gamma^2-3\gamma/x)$$

$$I^+_{22}(x)=\tfrac{5}{8}(11-66\gamma^2+63\gamma^4+45\gamma/x-63\gamma^3/x)$$

$$I^-_{22}(x)=\tfrac{5}{8}(-9+54\gamma^2-45\gamma^4-39\gamma/x+45\gamma^3/x)$$

$$I^+_{31}(x)=\tfrac{1}{4}\sqrt{21}(-3+18\gamma^2-15\gamma^4-13\gamma/x+15\gamma^3/x)$$

$$I^-_{31}(x)=\tfrac{1}{4}\sqrt{21}(3-24\gamma^2+25\gamma^4+47\gamma/3x-25\gamma^3/x)$$

$$I^+_{33}(x)=\tfrac{7}{8}(34-399\gamma^2+840\gamma^4-475\gamma^6+214\gamma/x-2045\gamma^3/3x+475\gamma^5/x)$$

$$I^-_{33}(x)=\tfrac{7}{8}(-34+417\gamma^2-900\gamma^4+525\gamma^6-222\gamma/x+725\gamma^3/x-525\gamma^5/x)$$

conductivity can arise from the higher-order terms, which also include $\alpha^2(-JJ')F(\Omega)$.

Another choice for the basis set to be used in expanding the distribution function is the set of Legendre polynomials of $\tanh(\epsilon_k/2k_BT)$, choice (b) of Sec. II. This set has the advantage of being well known. Also, the zero-order function is a constant which gives the lowest-order result for the electrical conductivity. For the thermal conductivity, the first-order term gives a result very close to the result by Klemens,[5] who calculated the thermal conductivity by solving the Boltzmann equation exactly within a Debye model. Kus[10] used $\tanh(\eta\epsilon_k/2k_BT)$, where η was used as a variational parameter; the value of $\eta=1$ gives the first Legendre polynomial and was found to give a good result for thermal conductivity at low temperature. The results for $I^{\pm}_{nn'}$, $n, n' \leq 3$ are given in Table II. Notice that since $I^s_{nn'}(0)=\delta_{nn'}\delta_{s+}$, a large amount of cancellation between terms takes place. This table is most easily constructed with the second form of $\underline{J}$ [Eq. (2.16)]. The value B_n is given for odd n by

$$B_n=\frac{2[3(2n+1)]^{1/2}}{[\pi n(n+1)]}, \tag{3.6}$$

with the value of A_n vanishing unless $n=0$ ($A_n = \delta_{n0}$).

The advantage of energy polynomials is that the lowest-order solution gives good results at high temperature[14]; the $\tanh(\epsilon_k/2k_BT)$ gives a good representation at low temperatures.[10] Both of which will be again demonstrated in the next section. The mixture of the two functions should give good results at both extremes. The Gram-Schmidt orthogonalization process can be used to form the two functions

$$\sigma^M_1(\epsilon)=\sqrt{6}\,z, \tag{3.7}$$

$$\sigma^M_2(\epsilon)=[\tfrac{2}{3}(\pi^2-9)]^{-1/2}(\pi\tanh\pi z-6z), \tag{3.8}$$

with $z=\epsilon/2\pi k_BT$. The functions $I^{sM}_{nn'}$ can be calculated as shown using Eq. (2.16). The results are summarized in Table III.

IV. MODEL CALCULATIONS

To isolate the effect of the energy dependence of the distribution function on the conductivity, I chose to study a class of isotropic models. In these models, the isotropy is achieved by using a spherical Fermi surface and a Debye phonon spectrum. The functions $F_J(k)$ become simply

Table III. $I^s_{nn'}(x)$ for the expansion using the mixed basis. The notation that $\gamma=\coth x$ is used.

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

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

$$I^+_{21}(x)=-3(\pi^2-9)^{-1/2}(x/\pi)^2$$

$$I^-_{21}(x)=-3(\pi^2-9)^{-1/2}[1+3(x/\pi)^2-\gamma x]$$

$$I^+_{22}(x)=1.5(\pi^2-9)^{-1}[\pi^2-6+6(x/\pi)^2-\pi^2\gamma^2+\pi^2\gamma/x]$$

$$I^-_{22}(x)=1.5(\pi^2-9)^{-1}[-\pi^2+12+18(x/\pi)^2-3\pi^2\gamma^2-3\pi^2\gamma/x-12\pi^2\gamma x]$$

spherical harmonics $Y_{lm}(\hat{k})$. Furthermore, only $l=1$ enters because of the vector nature of the applied fields. The functions $\alpha^2(sJJ')F(\Omega)$ with $J=J'=(lm)=(1,0)$ are called $\alpha^2(sxx)F(\Omega)$ to conform with the notation of Allen.[9] These functions have a cutoff frequency Ω_c which may be different from the Debye cutoff, ω_D. If the Debye wave vector is smaller than the Fermi surface diameter $q_D < 2k_F$, then the two frequencies are the same. However, the formula for $\alpha^2(sJJ')F$ [see Eq. (2.10)] has a matrix element which is nonvanishing only when crystal momentum is conserved. If $q_D > 2k_F$ and assuming that q_D is less than any reciprocal lattice vector, the maximum phonon wave vector contributing to $\alpha^2(sJJ')F$ is the Fermi-surface diameter and $\Omega_C = \omega_{q=2k_F}$. However, in this paper, the differences between Ω_C and ω_D will now be ignored.

Following McMillan's definition[15] of λ, the definitions of $\lambda_\pm$ are

$$\lambda = 2\int \frac{d\Omega}{\Omega}\alpha^2 F(\Omega)\,, \tag{4.1}$$

$$\lambda_\pm = 2\int \frac{d\Omega}{\Omega}\alpha^2(\pm xx)F(\Omega)\,. \tag{4.2}$$

The index x refers to the use of the Fermi-surface harmonic F_x which is proportional to k_x or equivalently proportional to Y_{10}. Within these definitions, $\alpha^2(\pm xx)F$ can be calculated (see Appendix B):

$$\alpha^2(+xx)F(\Omega) = 2\lambda_+(\Omega/\Omega_C)^4\Theta(\Omega_C-\Omega)\,, \tag{4.3}$$

$$\alpha^2(-xx)F(\Omega) = 2(\Omega/\Omega_C)^2[\lambda - \lambda_+(\Omega/\Omega_C)^2] \times\Theta(\Omega_C-\Omega)\,, \tag{4.4}$$

where Θ is the Heaviside or step function. Note that in this model $\lambda_+ + \lambda_- = 2\lambda$ and that λ_+ has in the past been called λ_{tr}.[16]

The three parameters are Ω_C, λ_+, and λ_-. The first sets the temperature scale; the second sets the scale for the resistance. However, the third parameter is, for convenience, taken to be the ratio λ_+/λ, instead of $\lambda_- = 2\lambda - \lambda_+$. To ensure that $\alpha^2(\pm xx)F$ is positive, the bounds of this ratio are $0 \leq \lambda_+/\lambda \leq 1$. If the identification with free electrons is taken seriously, then the ratio is

$$\lambda_+/\lambda = q_D^2/4k_f^2\,. \tag{4.5}$$

The model which corresponds to one "free" electron per atom has been studied in the past by Bloch,[17,18] Wilson,[14] Sondheimer,[6] Rhodes,[19] and Klemens[5]; this ratio λ_+/λ is then fixed at $2^{-4/3}$.

A. Electrical resistivity

By suitable expansions, Bloch[17,18] showed that the lowest-order solutions to the Boltzmann equation are correct at both high and low temperature extremes. At intermediate temperatures, Rhodes[19] and Sondheimer[6] showed that corrections to this solution were at most 10% for the value of $\lambda_+/\lambda = 2^{-4/3}$. However, for metals without a free-electron-like band structure, the value of λ_+/λ can be as large as 1. As demonstrated in Fig. 1, at a low value of λ_+/λ, very little reduction of the electrical resistivity from the Bloch-Grüneisen formula is observed. For potassium, Leavens[6] has shown that the corrections due to the correct energy dependence cannot be ignored.

For larger values of λ_+/λ, the enhancement in the electrical conductivity is more important. At the value of $\lambda_+/\lambda = 2^{-4/3}$, the enhancement is at most 10% (see Fig. 1). However, as the value of λ_+/λ increases to its maximum of one, the effect is more significant. At $\lambda_+/\lambda = 0.766$, the maximum enhancement of the electrical conductivity is 25% which occurs at a temperature of 0.15 Θ_D, also shown in Fig. 1. For the largest allowable value of $\lambda_+/\lambda = 1$, the enhancement is at its maximum of all the models, 37% at 0.15 Θ_D.

These results have been calculated using the energy polynomials and the $\tanh(\epsilon/2k_BT)$ expansion (see Sec. III). At most six polynomials are needed to given conductivities to within 1%. At temperatures near 0.1 Θ_D, the $\tanh(\epsilon/2k_BT)$ expansion converges at a slower rate, as shown in

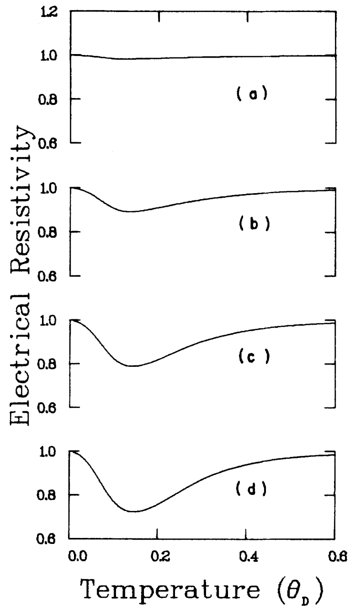

FIG. 1. Electrical resistivity for the model systems. The curves are the result of using six energy polynomials (see Sec. III) and are normalized to the Bloch-Grüniesen formula. The temperature is in units of Θ_D. Curves (a), (b), (c), and (d) correspond to values of $\lambda_+/\lambda = 0.06$, $2^{-4/3}$, 0.766, and 1, respectively.

TABLE IV. Comparisons of two expansions for the electrical resistivity for the Debye models. For each temperature, the resistivity is normalized to the lowest-order result, which is the Bloch-Grüneisen result. The temperature T is measured in units of θ_D.

λ_{tr}/λ	T	Number of energy polynomials 2	4	6	two Legendre polynomials
0.063	0.10	0.987	0.986	0.985	0.988
0.397	0.15	0.908	0.895	0.893	0.908
0.397	0.10	0.917	0.910	0.909	0.928
0.766	0.20	0.861	0.824	0.819	0.835
0.766	0.15	0.825	0.794	0.791	0.820
0.766	0.10	0.842	0.827	0.826	0.864
1.0	0.20	0.822	0.764	0.756	0.774
1.0	0.15	0.773	0.726	0.723	0.762
1.0	0.10	0.794	0.775	0.774	0.824

Table IV. At higher temperatures, the effect of the energy dependence is diminished and the polynomial expansion converges at a slower rate.

B. Thermal resistivity

The lowest-order result for the thermal resistivity was first derived by Wilson.[14] Calculations by Sondheimer[6] showed that the lowest-order result was accurate at high temperature, but at low temperature, a large number of terms in the energy expansion of the distribution function was needed to determine a converged result. Klemens[5] showed that the lowest-order solution overestimated the exact resistivity by 50%. Furthermore, Klemens[5] graphed the distribution function and showed that at large energies $\phi(\epsilon)$ approaches a constant. Kus[10] used this result and used a combination of an exponential and a term containing $\tanh(\epsilon_k/2k_BT)$ to calculate the thermal resistivity.

The mixed basis and the analytic expressions in Sec. III make it possible to solve the Boltzmann equation for the thermal resistivity within ~2% by a (2×2) matrix inversion. At low temperatures $T < 0.1\ \Theta_D$, the Wilson[14] formula gives a thermal resistivity a factor of ~1.51 larger than the exact answer.[5] Six terms in the energy expansion give 1.06. However, by extrapolating[20] the series of approximations, obtained by increasing the size of the matrix, an answer can be estimated to better than 2% (see Appendix C). With the Legendre-polynomial expansion, one term gives 1.05; two terms give 1.002 ± 0.002. The resistivity given by the mixture is accurate to within 1.5%. At high temperatures the lowest-order solution of Wilson gives an accurate result, but the first term in the Legendre expansion gives a resistivity 10% larger. The mixture then is the appropriate solution at all temperatures. These results are summarized in Table V.

The effect of the parameter λ_+/λ is to extend the importance of the energy dependence to higher temperatures. For $\lambda_+/\lambda=0.06$, the enhancement of the conductivity over the lowest-order result becomes unimportant at $\sim0.2\ \Theta_D$. For $\lambda_+/\lambda=(2^{-4/3}, 0.766, \text{and } 1)$ this effect becomes small at $(0.25\ \Theta_D, 0.4\ \Theta_D, \text{and } 0.5\ \Theta_D)$, respectively, as shown in Fig. 2.

TABLE V. Comparison of three expansions for the thermal resistivity of the Debye models. For each temperature, the resistivity is normalized to the result of Wilson, i.e., using only the first-order energy polynomial. The temperature T is measured in units of θ_D.

λ_{tr}/λ	T	Number of energy polynomials 2	6	Terms in Legendre expansion 1	2	Mixed basis	Cont. fract.
All	0.01	0.812	0.697	0.695	0.662	0.669	0.660
0.063	0.10	0.830	0.721	0.725	0.696	0.705	0.696
0.397	0.10	0.808	0.706	0.710	0.684	0.688	0.681
0.766	0.20	0.879	0.808	0.807	0.800	0.799	0.799
0.766	0.10	0.780	0.687	0.692	0.668	0.668	0.658
1.0	0.20	0.836	0.742	0.762	0.744	0.735	0.734
1.0	0.10	0.761	0.673	0.680	0.657	0.654	0.646

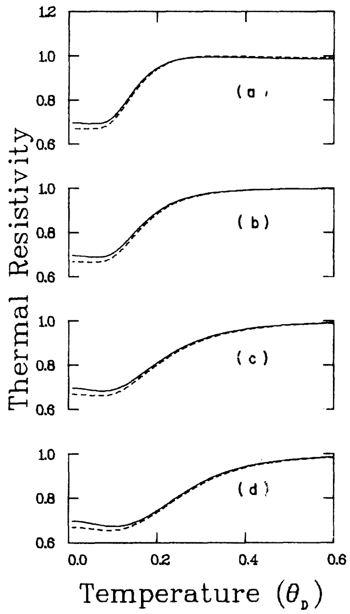

FIG. 2. Thermal resistivity for the model systems. The solid curves result from using six energy polynomials. The dashed curves are the results of using the mixed basis. The curves are normalized to Wilson's formula. The temperature is in units of Θ_D. Curves (a), (b), (c), and (d) correspond to values of $\lambda_+/\lambda = 0.06$, $2^{-4/3}$, 0.766, and 1, respectively.

V. CONCLUSIONS AND IMPLICATIONS

The energy dependence in the solution to the Boltzmann equation gives significant contributions to the electrical and thermal conductivities in the temperature range below 0.5 Θ_D. The calculation of the electrical resistivity to within 1% needs at most six polynomials in the expansion of the distribution function. Furthermore, the thermal resistivity can now be calculated within 2% by using a two-term expansion, the "mixed basis."

For transition metals, the quantities $\alpha^2(sJJ')F$ can now be calculated within the rigid-muffin-tin approximation.[7,8,21] The phonon spectra and Fermi surfaces are complicated, which destroys any relationship between λ_+/λ and q_D/k_f. The simple power-law behavior of $\alpha^2(\pm xx)F$ is also no longer valid. A realistic $\alpha^2(+xx)F = \alpha^2_{tr}F$ has been calculated by several groups.[2,3,7] The large difference between $\alpha^2(+xx)F$ and $\alpha^2(-xx)F$ at low Ω is caused by the weighting of $\alpha^2(+xx)F$ by $(1-\cos\phi)$ (see Appendix B). This difference is small at large Ω as shown by a calculation[7] of the function $\alpha^2_{xx}F(\Omega)$ which only has a weighting of $\vec{v}_k \cdot \vec{v}_{k'} \sim \cos\phi$ for Pd. This function was an order of magnitude smaller than $\alpha^2(+xx)F$ at frequencies larger than $0.15\omega_D$.

To summarize, the models do not have a direct correspondence to realistic calculations for transition metals. The simplifying assumptions are not suitable for metals with complicated Fermi surfaces. However, these calculations have shown how to include the energy dependence in the distribution function and that it is important. The energy polynomial method is suitable for calculating the electrical resistivity. The mixed basis is very useful for calculating thermal conductivities.

After this work was completed, two papers were received from Engquist and Grimvall[22,23] These papers addressed a similar topic, effects of energy dependence of the distribution function on electrical resistivity. They have used an equivalent but slightly different method of solving the Boltzmann equation, which they have applied to an isotropic system. However, a different form of $\alpha^2(+xx)F(\Omega)$ was used, proportional to Ω^2, which leads to electrical resistivities proportional to T^3 (instead of T^5) at low temperature. They discovered that for their model, only at temperatures ~0.10 Θ_D did the energy polynomial expansion for electrical resistivity converge faster than the expansion in Legendre polynomials [in $\tanh(\epsilon/2k_BT)$]. For the models considered in this paper, this conclusion also holds. Furthermore, near this temperature, the largest effects are seen (see Fig. 1). They calculated electrical resistivities for systems with impurities, but did not calculate thermal conductivities. I have analytically evaluated integrals in this paper which will be useful in further calculations in either method of solving the Boltzmann equation.

ACKNOWLEDGMENTS

I wish to thank P. B. Allen for suggesting these calculations and to thank him and W. H. Butler for their useful conversations during the completion of this paper. I also thank W. E. Lawrence for pointing out certain papers in the literature. This research was jointly sponsored by the National Science Foundation under Grant No. DMR-79-00837 and by the Division of Material Sciences, U. S. Department of Energy under Contract No. W-7405-eng-26 with the Union Carbide Corporation.

APPENDIX A

In this section, one of the integrals useful in defining the operator $\underset{=}{J}$ is derived [see Eq. (2.15)]. The starting point is Eq. (2.11); only one of the eight parts of this expression is considered here. This element $R_{nn'}$ is defined by

$$R_{nn'}(\Omega)=\frac{\hbar\Omega N(\Omega)}{8k_B^2T^2}\int_{-\infty}^{\infty}d\epsilon\int_{-\infty}^{\infty}d\epsilon' f(\epsilon)[1-f(\epsilon')]\delta(\epsilon-\epsilon'+\hbar\Omega)\sigma_n(\epsilon)\sigma_{n'}(\epsilon')\,. \tag{A1}$$

By substituting the definitions of the Fermi and Bose factors, and by recognizing that

$$f(\epsilon)[1-f(\epsilon+\hbar\Omega)]=[N(\Omega)+1]\,[f(\epsilon+\hbar\Omega)-f(\epsilon)]\,, \tag{A2}$$

the integral $R_{nn'}$ can be written as

$$R_{nn'}(\Omega)=\frac{\hbar\Omega}{8k_B^2T^2}N(\Omega)[N(\Omega)+1]\int_{-\infty}^{\infty}d\epsilon[f(\epsilon+\hbar\Omega)-f(\epsilon)]\sigma_n(\epsilon)\sigma_{n'}(\epsilon+\hbar\Omega)\,. \tag{A3}$$

A simplification is made by evaluating the integral by parts and shifting the origin of the integral containing $f(\epsilon+\hbar\Omega)$. The simplified form is

$$R_{nn'}(\Omega)=\frac{\hbar\Omega}{32k_B^2T^2}\sinh^{-2}(\hbar\Omega/2kT)\int_{-\infty}^{\infty}d\epsilon\frac{\partial f}{\partial\epsilon}\int_{\epsilon-\hbar\Omega}^{\epsilon}d\eta\sigma_n(\eta)\sigma_{n'}(\eta+\hbar\Omega)\,. \tag{A4}$$

By defining $x=\hbar\Omega/2k_BT=\pi z$, $s=\epsilon/2\pi k_BT$, and $\eta'=\eta/2\pi k_BT$, the integral $R_{nn'}$ can be written as

$$R_{nn'}(\Omega)=\left(\frac{x}{\sinh x}\right)^2\frac{\pi}{16z}\int_{-\infty}^{\infty}ds\cosh^{-2}\pi s\int_{s-z}^{s}d\eta'\sigma_n(2\pi k_BT\eta')\sigma_{n'}(2\pi k_BT\eta'+2\pi k_BTz)\,, \tag{A5}$$

which can easily be seen to be

$$R_{nn'}(\Omega)=\left(\frac{x}{\sinh x}\right)^2 h_{nn'}(z)/16\,. \tag{A6}$$

By using Eqs. (2.14) and (2.15), the other seven parts of the integral can be evaluated in a similar manner.

APPENDIX B

In this section expressions for $\alpha^2F(\Omega)$ and $\alpha^2(\pm xx)F(\Omega)$ are found for the isotropic models considered in this paper. These models consist of a spherical Fermi surface (radius k_F) and a Debye spectrum defined by a Debye cutoff frequency ω_D and wave vector q_D. Defining $\vec{Q}=\vec{k}-\vec{k}'$, the functions $\alpha^2F(\Omega)$ and $\alpha^2(\pm xx)F(\Omega)$ can be written as

$$\left.\begin{matrix}\alpha^2F(\Omega)\\ \\ \alpha^2(\pm xx)F(\Omega)\end{matrix}\right\}=[N_\uparrow(0)]^{-1}\sum_{kk'\nu}|M_{k,k'}^{\nu}|^2 \times\delta(\epsilon_k)\delta(\epsilon_{k'})\delta(\Omega-\Omega_Q^{\nu}) \times\begin{cases}1\\ \\ 1\mp\cos\phi\end{cases}, \tag{B1}$$

where ϕ is the angle between $\vec{k}$ and $\vec{k}'$. This expression can be further simplified by using $\Omega=cQ$ (c is the speed of sound) and $\cos\phi=1-Q^2/2k_F^2$. The matrix element is assumed to be proportional to Q. The simplified expressions are

$$\alpha^2F(\Omega)=K_0\Omega^2\Theta(\Omega_c-\Omega)\,, \tag{B2}$$

$$\alpha^2(+xx)F(\Omega)=K_1\Omega^4\Theta(\Omega_c-\Omega)\,, \tag{B3}$$

$$\alpha^2(-xx)F(\Omega)=(K_2\Omega^2+K_3\Omega^4)\Theta(\Omega_c-\Omega)\,, \tag{B4}$$

where the difference between Ω_c and ω_D was discussed in Sec. IV. The constants $\{K_i\}$ can be expressed in terms of λ, $\lambda_\pm$ [Eqs. (4.1) and (4.2)]. Since $K_1=-K_3$ and $K_2=2K_0$, Eqs. (B3) and (B4) can be transformed into Eqs. (4.3) and (4.4).

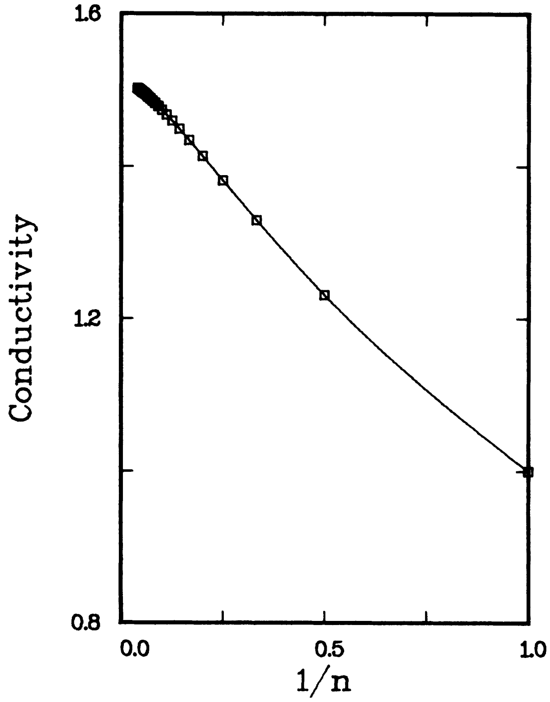

FIG. 3. Convergence of the thermal conductivity at low temperature. The thermal conductivity including n energy polynomials is plotted as a function of $1/n$. The conductivities are normalized to Wilson's formula, i.e., using only one energy polynomial. The curve is inserted as a guide to the eye.

APPENDIX C

At low temperatures ($\sim 0.1\,\Theta_D$), the series expansion for the thermal conductivity converges very slowly. A continued-fraction extrapolation of the sequence of results as presented by Baker[20] is a good method to speed up the convergence. The sequence of numbers is $\{S_n\} = \{1.00, 1.23, 1.33, 1.38, \ldots,\}$ as plotted in Fig. 3 as a function of $1/n$, n being the index in the sequence. The continued-fraction extrapolation of this sequence is 1.51 and is only changed by 0.5% after five terms. This is consistent with the results of the Legendre expansions and is slightly higher than the Klemens result[5] (~1%).

The curve determined by the continued-fraction representation goes through the points $(1/n, S_n)$. The value of the continued fraction evaluated at zero is the extrapolated value of the sequence. For the continued fraction f which can be written as

$$f(x) = \cfrac{b_0}{1 + \cfrac{b_1(x-1)}{1 + \cfrac{b_2(x-\frac{1}{2})}{1 + b_3(x-\frac{1}{3})}}} \qquad \begin{matrix} \cdot \\ \cdot \\ \cdot, \end{matrix} \tag{C1}$$

the coefficients are determined uniquely by the conditions that $f(1/n) = S_n$. As a result,

$$\begin{aligned} b_0 &= S_1, \\ b_1 &= 2 - 2S_1/S_2 . \end{aligned} \tag{C2}$$

Baker[20] has a convenient method for calculating these coefficients.

---

[1] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960), p. 257.

[2] B. Hayman and J. P. Carbotte, J. Phys. F 2, 915 (1972); F. Kus and J. P. Carbotte, *ibid.* 3, 1828 (1973).

[3] P. G. Tomlinson and J. C. Swihart, Phys. Rev. B 19, 1867 (1979).

[4] W. D. Jumper and W. E. Lawrence, Phys. Rev. B 16, 3314 (1977).

[5] P. G. Klemens, Proc. Phys. Soc., London A67, 194 (1954).

[6] E. H. Sondheimer, Proc. R. Soc., London A203, 75 (1950); C. P. Leavens, J. Phys. F 7, 1297 (1977).

[7] F. J. Pinski, P. B. Allen, and W. H. Butler, Phys. Rev. Lett. 41, 431 (1978).

[8] F. J. Pinski, P. B. Allen, and W. H. Butler (unpublished).

[9] P. B. Allen, Phys. Rev. B 17, 3725 (1978).

[10] F. W. Kus, J. Phys. F 6, 59 (1976).

[11] P. B. Allen, Phys. Rev. B 13, 1416 (1976).

[12] G. M. Eliashberg, Zh. Eksp. Teor. Fiz., 38, 966 (1960) [Sov. Phys.—JETP] 11, 696 (1960).

[13] D. J. Scalapino, in *Superconductivity*, edited by R. D. Parks (Deccer, New York, 1969), Vol. 1, p. 488.

[14] A. H. Wilson, Proc. Cambr. Philos. Soc. 33, 371 (1937); *The Theory of Metals*, (Cambridge University Press, London, 1954).

[15] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[16] B. Chakraborty, W. E. Pickett, and P. B. Allen, Phys. Rev. B 14, 3227 (1976).

[17] F. Bloch, Z. Phys. 52, 555 (1928).

[18] F. Bloch, Z. Phys. 59, 208 (1930).

[19] P. Rhodes, Proc. R. Soc., London A160, 207 (1950).

[20] G. A. Baker, *Essentials of Padé Approximants* (Academic, New York, 1975), p. 105.

[21] G. D. Gaspari and B. L. Gyorffy, Phys. Rev. Lett. 28, 801 (1972); R. Evans, G. D. Gaspari, and B. L. Gyorffy, J. Phys. F 3, 39 (1973).

[22] H.-L. Engquist, Phys. Rev. B 21, 2067 (1980).

[23] H.-L. Engquist and G. Grimvall, Phys. Rev. B 21, 2072 (1980).