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Electron-phonon effects in copper. II. Electrical and thermal resistivities and Hall coefficient

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The electrical and thermal resistivities (ρ and W) and Hall coefficient (R_H) of pure and impure Cu are calculated. Realistic Korringa-Kohn-Rostocker energy bands and wave functions, experimental phonon frequencies, and Born—von Kármán eigenvectors, and the rigid-muffin-tin model for electron-phonon scattering are used to generate the velocities and scattering probabilities in the Bloch-Boltzmann equation, on a mesh of nearly 24 000 points on the Fermi surface. The effect of impurities is approximated by an isotropic impurity scattering rate. Solutions for ρ, W, and R_H are exhibited at three levels of accuracy: (1) the lowest-order variational approximation (LOVA) where the Fermi surface displaces rigidly; (2) a fully inelastic calculation where the distribution function is allowed arbitrary variations with energy (normal to Fermi surface) to reflect the inelasticity of electron-phonon scattering; (3) inelasticity plus somewhat increased angular freedom in the distribution function. For ρ and W we find that above $T=100$ K the corrections to LOVA are negligible and that, except at the lowest temperatures $T\sim 20$ K, our angular corrections are negligible. For R_H the lowest-order approximation is temperature independent and the addition of both inelasticity and increased angular freedom are not negligible at any temperature. Agreement with experiment for all three quantities is good throughout the range $T=10$ to 300 K. The use of a phenomenological impurity relaxation time to study deviations from Matthiessen's rule in the electrical resistivity agrees qualitatively with experiment.

I. INTRODUCTION

A previous paper[1] described calculations of the electrical and thermal resistivities of pure Nb and Pd. We use the same techniques in the present work to calculate these quantities for pure and impure Cu and to extend the formalism to include the Hall coefficient. The objective is to make a realistic calculation of transport coefficients in a *d*-band metal without fitting parameters to experiment. This involves (1) the calculation of the electronic parameters of Cu, i.e., the energy bands and velocities, (2) the scattering amplitudes for electron-phonon scattering, and (3) combining these quantities into the Boltzmann equation which then needs to be solved.

A Korringa-Kohn-Rostocker band-structure program generates wave functions and velocities on the Fermi surface. To evaluate the scattering probabilities we used phonon-dispersion curves and polarization vectors obtained[2] from Born—von Kármán fits to experiment. These quantities are then used in the rigid muffin-tin model[3] of the electron-phonon interaction. To solve the Boltzmann equation we use the Fermi-surface harmonic and energy polynomial formalism developed by Allen[4] and Pinski.[5] This involves transforming the Boltzmann equation from an integral equation into a matrix equation which may then be readily solved. Overall we find good agreement between our calculations and experiment. The electrical and thermal resistivities are lower than experiment throughout the temperature range of 10 to 300 K, whereas the Hall coefficient tends to be higher than experiment for this same range of temperatures.

In Sec. II we describe our calculation of the electrical and thermal resistivities of pure Cu. We present the results of these calculations at various levels of approximation and compare our values to experimental values. Section III adds an isotropic impurity-relaxation time to our scattering matrices. We compare the electrical resistivity calculated with the new scattering matrix to experiment and display the expected behavior of the thermal resistivity as the impurity concentration rises. In Sec. IV a method of calculating the Hall coefficient is described using the techniques of Sec. II. The calculation is done for both pure and impure Cu. Section V describes the relation of our calculations to previous calculations, and summarizes our conclusions.

II. CONDUCTIVITIES OF PURE COPPER

A. Lowest order

The lowest-order variational approximation (LOVA) result for the electrical resistivity is[4]

$$\rho = \frac{Q_{X0,X0}}{2e^2}, \tag{1}$$

where the factor of 2 is for spin degeneracy, and $Q_{X0,X0}$ describes the scattering of electrons. The subscripts $X0$ are explained in Ref. 4; X refers to the "angular" variation of the distribution function in lowest order, i.e., proportional to v_{kx}, and 0 refers to the energy variation in lowest order, i.e., independent of energy. For electron-phonon interactions $Q_{X0,X0}$ is given by

$$Q_{X0,X0} = \frac{1}{N_\uparrow \langle v^2 \rangle} \frac{4\pi k_B T}{\hbar} \times \int_0^\infty \frac{d\Omega}{\Omega} \alpha_{\text{tr}}^2(\Omega) F(\Omega) \left[\frac{x}{\sinh x} \right]^2 . \tag{2}$$

Here Ω is a phonon frequency, x is $\hbar\Omega/2k_B T$, $N_\uparrow$ is the single-spin density of states per atom at the Fermi energy, and $\langle v^2 \rangle$ is the mean-square Fermi velocity. The spectral function $\alpha_{\text{tr}}^2(\Omega)F(\Omega)$ is given by

$$\alpha_{\text{tr}}^2(\Omega)F(\Omega) = N_\uparrow \frac{\sum_{k,k',\nu} (v_{kx} - v_{k'x})^2 \, | g_{k,k'}^{\nu} |^2 \delta(\epsilon_k) \delta(\epsilon_{k'}) \delta(\Omega_Q - \Omega)}{2 \sum_{p,p'} v_{px}^2 \delta(\epsilon_p) \delta(\epsilon_{p'})}, \tag{3}$$

where $\vec{v}_k$ is the velocity of the electron state ϵ_k, and k is short for $(\vec{k},n)$. The factor $g_{k,k'}^{\nu}$ is the matrix element for an electron to scatter from state k to k' by the absorption or emission of a phonon of branch ν. The modified potential for Cu is described in the Appendix of the preceding paper.[6] We use a mesh of 492 points in the irreducible $\frac{1}{48}$th of the Fermi surface. At these points the velocities and wave functions are also found. The Eliashberg spectral function $\alpha^2 F(\Omega)$ of superconductivity theory is closely related. In Fig. 1 we display $\alpha_{\text{tr}}^2(\Omega)F(\Omega)$, $\alpha^2(\Omega)F(\Omega)$, and the phonon density of states $F(\Omega)$.

In Fig. 2 we display the results of the LOVA calculation of ρ together with the experimental data of White and Woods[7] and the composite data of Matula.[8] The agreement with experiment is

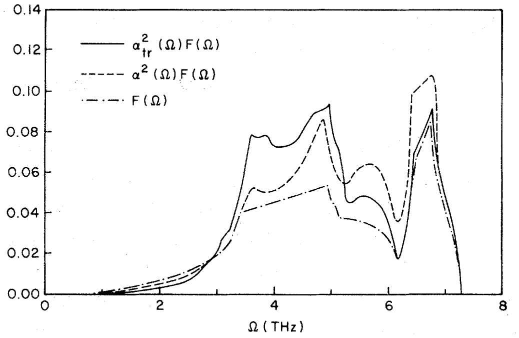

FIG. 1. Spectral functions for Cu. For reference, $F(\Omega)$ as calculated by Nicklow *et al.* (Ref. 2) is also included. Note that $F(\Omega)$ has an arbitrary scale.

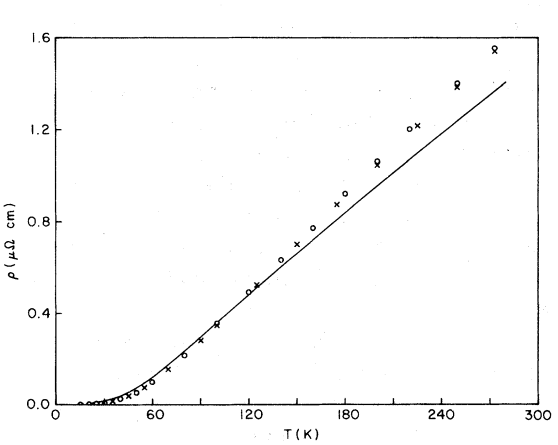

FIG. 2. Electrical resistivity of Cu. The solid curve was calculated in lowest order, using Eqs. (1)–(3). ×'s and ○'s are the experimental values from Matula (Ref. 8) and White and Woods (Ref. 7), respectively.

reasonable considering the simplicity of our distribution function. We find that the LOVA result is 20% low at 300 K and about 50% high at 30 K. Higher-order corrections to LOVA will substantially lower the low-temperature resistivity but will leave the high-temperature regime essentially unchanged.

So that we may compare our calculation of the resistivity to other calculations we also calculate the Bloch-Grüneisen (BG) resistivity,[9] i.e.,

$$\rho_{\mathrm{BG}}(T)=4\rho' T(T/\Theta)^4 J_5(\Theta/T)\;, \tag{4}$$

where

$$J_n(\Theta/T)=2^{n-1}\int_0^{\Theta/2T} dx\,\frac{x^n}{\sinh^2 x}\;. \tag{5}$$

We choose the parameters ρ' and Θ so that the BG and LOVA resistivities agree at high temperatures. This leads to the identification

$$\rho'=2\pi k_B\lambda_{\mathrm{tr}}/(2e^2N_{\uparrow}\langle v^2\rangle)$$

and

$$\Theta=\hbar\omega_D/k_B=\hbar(3\langle\Omega^2\rangle_{\mathrm{tr}}/2)^{1/2}/k_B\;,$$

λ_{tr} and $\langle\Omega^2\rangle_{\mathrm{tr}}$ being defined by

$$\lambda_{\mathrm{tr}}=2\int_0^\infty\frac{d\Omega}{\Omega}\alpha_{\mathrm{tr}}^2(\Omega)F(\Omega)\;, \tag{6}$$

and

$$\langle\Omega^2\rangle_{\mathrm{tr}}=\frac{2}{\lambda_{\mathrm{tr}}}\int_0^\infty\frac{d\Omega}{\Omega}\Omega^2\alpha_{\mathrm{tr}}^2(\Omega)F(\Omega)\;. \tag{7}$$

On the scale used in Fig. 2, the BG result and the LOVA result are virtually indistinguishable. The BG result agrees slightly better with experiment, being about 30% too high at low temperatures.

TABLE I. Calculated parameters of Cu. The single-spin density of states at the Fermi level $N_{\uparrow}$ and the root-mean-square Fermi velocity $(\langle v^2\rangle)^{1/2}$ were calculated from the band structures. λ_{tr} and $(\langle\Omega^2\rangle_{\mathrm{tr}})^{1/2}$ were calculated from the spectral function. The final three parameters give the Bloch-Grüneisen-Wilson fits of Eqs. (4) and (9).

$N_{\uparrow}$ (states/Ry spin atom)	1.89
$\langle v^2\rangle^{1/2}$ (cm/s)	1.08×10^8
λ	0.111
λ_{tr}	0.116
$(\langle\Omega^2\rangle_{\mathrm{tr}})^{1/2}$ (THz)	4.757
ρ' ($\mu\Omega$ cm/K)	0.00528
Θ (K)	279.6
k_F/q_D	0.582

The parameters used in the BG calculation appear in Table I, as well as the calculated value for λ,[6] which is similar to λ_{tr} except that $\alpha^2(\Omega)F(\Omega)$ is used in place of $\alpha_{\mathrm{tr}}^2(\Omega)F(\Omega)$. We find λ_{tr} to be about 4.5% larger than λ. Pinski *et al.*[1] found that for Nb λ_{tr} was about 4% smaller than λ, and that for Pd λ_{tr} was about 12% larger than λ. It therefore seems reasonable to assume that λ and λ_{tr} will differ by only ~10% for any of the transition metals.

The LOVA formula for the thermal resistivity is[4]

$$W=\frac{3}{\pi\hbar k_B N_{\uparrow}\langle v^2\rangle}\times\left[2\int_0^\infty\frac{d\Omega}{\Omega}\alpha_{\mathrm{tr}}^2(\Omega)F(\Omega)\left[\frac{x}{\sinh x.}\right]^2\left[1+\frac{x^2}{\pi^2}\right]+2\int_0^\infty\frac{d\Omega}{\Omega}\alpha_{-}^2(\Omega)F(\Omega)\left[\frac{x}{\sinh x}\right]^2\frac{3x^2}{\pi^2}\right]\;. \tag{8}$$

The spectral function $\alpha_{-}^2(\Omega)F(\Omega)$ is identical to $\alpha_{\mathrm{tr}}^2(\Omega)F(\Omega)$ except that $(v_{kx}-v_{k'x})^2$ has been replaced by $(v_{kx}+v_{k'x})^2$. Again we compare the LOVA calculation to the BG result, actually Wilson's result. The BG expression for the thermal resistivity is[9]

$$W_{\mathrm{BG}}(T)=(4\rho'/L_0)(T/\Theta)^4\times\{[1+(3/\pi)^2(k_F/q_D)^2(\Theta/T)^2]\times J_5(\Theta/T)-(1/2\pi^2)J_7(\Theta/T)\}\;, \tag{9}$$

where L_0 is the Lorenz number and k_F/q_D is a free parameter. In order to specify this parameter we again require that the high-temperature LOVA and BG results agree. This leads to the identification

$$\frac{k_F}{q_D}=\left[\frac{\lambda_{\mathrm{tr}}\langle\omega^2\rangle_{\mathrm{tr}}+\lambda_{-}\langle\omega^2\rangle_{-}}{3\lambda_{\mathrm{tr}}\langle\omega^2\rangle_{\mathrm{tr}}}\right]^{1/2}\;.$$

Here λ_{-} and $\langle\omega^2\rangle_{-}$ are calculated like λ_{tr} and $\langle\omega^2\rangle_{\mathrm{tr}}$ except that $\alpha_{-}^2(\Omega)F(\Omega)$ is used in place of $\alpha_{\mathrm{tr}}^2(\Omega)F(\Omega)$.

In Fig. 3 we display W_{LOVA} and W_{BG} together with the experimental values of White and Woods.[7] We note that at temperatures below 150 K the LOVA result is closer to the experiment, i.e., only a factor of 2 above experiment, while the BG result is as much as a factor of 4 too high. Thus in both the electrical and thermal resistivity we see the need to allow more flexibility in the distribu-

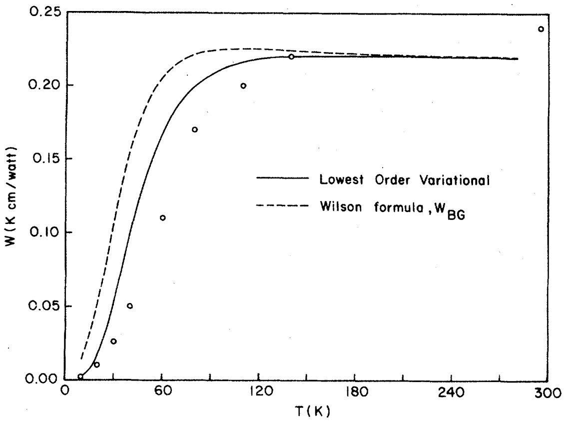

FIG. 3. Thermal resistivity of Cu. The solid curve is calculated from Eq. (8). The dashed curve is the BG result. ○'s are the experimental values of White and Woods (Ref. 7).

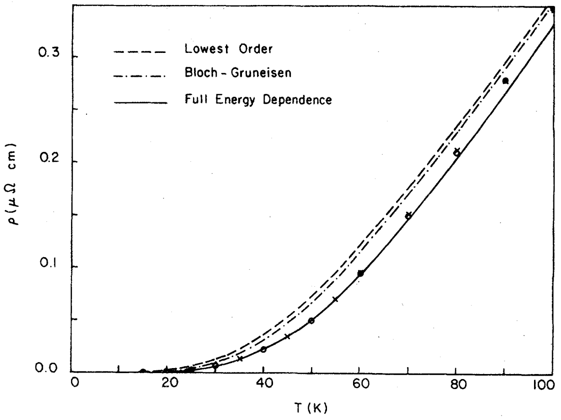

FIG. 4. Calculated electrical resistivity of Cu. ×'s and ○'s are the experimental points from Refs. 8 and 7.

tion function. We next discuss the effect of allowing energy dependence in the distribution function.

B. Energy dependence

By assuming that parameters like $N_\uparrow(\epsilon)$, the density of states, do not vary rapidly with energy, a tractable expression for the electron-phonon scattering matrix Q may be written out[4]

$$Q_{Xn,Xn'} \cong \frac{4\pi k_B T}{\hbar N_\uparrow \langle v^2 \rangle} \times \sum_{s=\pm} \int_0^\infty \frac{d\Omega}{\Omega} \alpha^2(s,X,X) F(\Omega) \times \left[\frac{x}{\sinh x} \right]^2 I^s_{nn'}(x) \,. \tag{10}$$

This omits angular anisotropy but contains full energy dependence. Here

$$\alpha^2(+XX)F(\Omega) = \alpha^2_{\text{tr}}(\Omega)F(\Omega) \,,$$

$$\alpha^2(-XX)F(\Omega) = \alpha^2_{-}(\Omega)F(\Omega) \,,$$

and $I^s_{nn'}(x)$ is zero if $n+n'$ is odd, and a polynomial in x of order $n+n'$ if $n+n'$ is even. The polynomials $I^s_{nn'}(x)$ have been exhibited by Pinski[5] and used by Pinski *et al.*[1] Note that $n=n'=0$ reproduces the LOVA scattering term as $I^{-}_{00}=0$ and $I^{+}_{00}=1$.

With the scattering operator now a matrix, the resistivity is given by

$$\rho = \frac{1}{2e^2}[Q^{-1}]_{X0,X0} \,. \tag{11}$$

From the variational principle on the resistivity we find that for Q truncated to some order N, we have an upper bound on the resistivity. Thus as we increase the order of Q we form a decreasing sequence of upper bounds on ρ which we may extrapolate to the $N \to \infty$ limit. We have found that calculating the first eight terms in the sequence (i.e., polynomials up to order 14) is sufficient to extrapolate to the $N \to \infty$ limit. This extrapolation is simple linear extrapolation in $1/N$. In Fig. 4 we show the results of this calculation for the resistivity together with the LOVA and BG results plus the experimental data. Only the region 10–100 K is displayed, as this is where the differences are most pronounced. Below 10 K the finite size of our mesh affects our results and above 200 K the

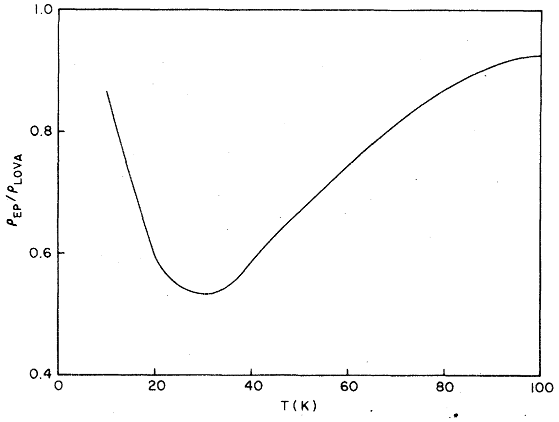

FIG. 5. Ratio of the electrical resistivity calculated with and without energy dependence of the distribution function.

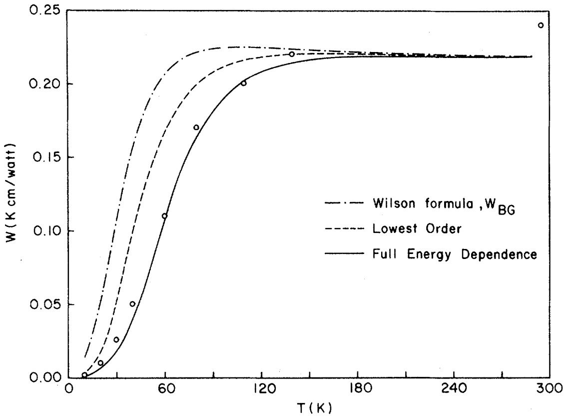

FIG. 6. Calculated thermal resistivity of Cu. O's are experimental data taken from Ref. 7.

differences between LOVA and the inclusion of energy polynomials is not noticeable. It is clear from Fig. 4 that the energy dependence of the distribution function is important if good agreement with experiment is desired. In Fig. 5 we display the ratio of the resistivity calculated using the energy polynomials to the LOVA result. Near 30 K the enhancement of the conductivity is in excess of 80%, clearly not a small effect.

For the thermal resistivity with energy polynomials we need to calculate

$$W=\frac{3}{2\pi^2 k_B^2 T}[Q^{-1}]_{X1,X1}\ . \tag{12}$$

Again we appeal to a variational principle which says that for Q truncated at any order N we have an upper bound on W, and that the sequence generating by taking increasing N is monotonic. As before we calculate the first eight terms in the sequence and then extrapolate N to ∞. In Fig. 6 we display this extrapolated curve together with the LOVA and BG curves and the experimental data of White and Woods.[7] Above 200 K the higher-order calculation and the LOVA calculation are identical but at lower temperatures the higher-order curve is much closer to experiment. In Fig. 7 we plot the ratio of the high-order calculation to the LOVA result. At 30 K this ratio is less than 0.4. As was the case for electrical resistivity, the addition of energy dependence to the distribution function brings about a large change in the thermal resistivity.

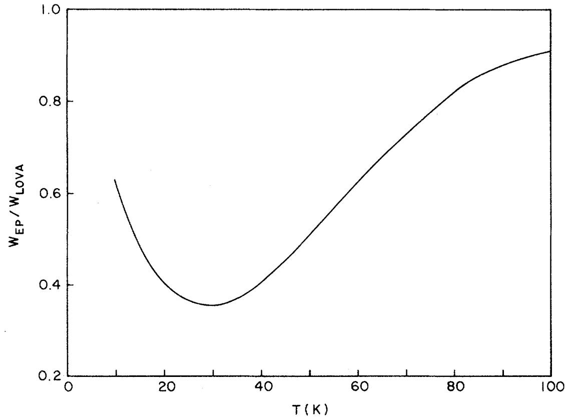

FIG. 7. Ratio of the thermal resistivity calculated with and without energy dependence of the distribution function.

C. Angular dependence

We may further generalize the scattering matrix by adding angular dependence to it. Lowest-order approximation assumes that the distribution function is a rigidly displaced Fermi distribution, having an angular variation proportional to $\vec{v}_k$. We now consider the addition of higher-order polynomials in $\vec{v}_k$. Symmetry requirements dictate that the polynomials have the same symmetry as $\vec{v}_k$, i.e., Γ_{15} or vector symmetry. The spectral function is written as[4]

$$\begin{aligned}\alpha^2(s,J,J')F(\Omega)\\ &=\frac{1}{2N_\uparrow}\sum_{k,k',\nu}|g^{\nu}_{k,k'}|^2[F_J(k)-sF_J(k')]\\ &\quad\times[F_{J'}(k)-sF_{J'}(k')]\\ &\quad\times\delta(\epsilon_{k'})\delta(\epsilon_{k'})\delta(\Omega_Q-\Omega)\ ,\end{aligned} \tag{13}$$

where the F_J's are polynomials orthogonal on the Fermi surface, referred to as Fermi surface harmonics (FSH). The scattering matrix is

$$\begin{aligned}Q_{Jn,J'n'}\cong\frac{4\pi k_B T}{\hbar N_\uparrow\langle v^2\rangle}\sum_{s=\pm}\int_0^\infty\frac{d\Omega}{\Omega}\alpha^2(s,J,J')F(\Omega)\\ \times\left[\frac{x}{\sinh x}\right]^2 I^s_{nn'}(x)\ .\end{aligned} \tag{14}$$

The formula for the calculation of the electrical and thermal resistivity is the same as in Sec. II B, i.e., Eqs. (11) and (12). We could now extrapolate $J\rightarrow\infty$ as we do n. In this calculation only the first three FSH are used, i.e., $\propto v_{kx}$, $v_k^2 v_{kx}$, and v_{kx}^3, and it would be unreasonable to extrapolate J to ∞.

The reduction of the resistivity in our calculation using three FSH's is less than 5% above 30 K, typically only 1%. Similarly for the thermal resistivity the results above 30 K are reduced by less than 3% and typically less than 0.1%. At 30 K and below the difference between the $J_{\max}=3$ and the $J_{\max}=1$ calculations for both the electrical and thermal resistivity rises rapidly. At 10 K, for example, the $J_{\max}=1$ calculation is about 20% larger than the $J_{\max}=3$ calculation for both resistivities. This is reasonable, as the thermally excited phonons present have small q, the scattering is more sensitive to the local Fermi surface topology, and thus a larger $J_{\max}$ is needed.

In the low-temperature region Khan *et al.*[6] have found that the quasiparticle lifetimes converge slowly in FSH's. They find for the range of temperatures 5–15 K that the first three FSH's represent only 80% of the quasiparticle lifetime. Similar disagreements would be expected for the Q matrices that we have used in our calculations. Thus it is not completely safe to conclude that anisotropy has a negligible effect above 30 K, even though our work shows that $J_{\max}=3$ gives a negligible improvement over $J_{\max}=1$.

III. CONDUCTIVITIES OF IMPURE COPPER

To investigate the effect of scattering by both phonons and impurities, we add a phenomenological impurity relaxation time τ to the scattering matrix, that is,

$$Q_{Jn,J'n'} \rightarrow Q_{Jn,J'n'} + \delta_{JJ'}\delta_{nn'}/N_{\uparrow}\langle v^2\rangle\tau . \qquad (15)$$

If $Q_{Jn,J'n'}$ is diagonal (as in LOVA), then the above equation is equivalent to Matthiessen's rule and the addition of impurities would be of little interest. The scattering matrix in Eq. (15) is taken to be a first approximation for studying deviations from Matthiesen's rule. We calculate the electrical resistivity as in the preceding section with $J_{\max}=3$ and extrapolating N to ∞. In Fig. 8 we display the results of our calculation together with the experimental results[10] of Dugdale and Basinski[11(a)] and Lengeler, Schilling, and Wenzl.[11(b)] For all of our curves $\rho-\rho_0$ saturates for large ρ_0 or equivalently for large $1/\tau$. For $1/\tau$ sufficiently large compared with phonon scattering rates, the Q matrix is dominated by impurity scattering and thus is diagonal. Therefore the value of $\rho-\rho_0$ saturates at ρ_{LOVA}. As the temperature increases, the experimental and

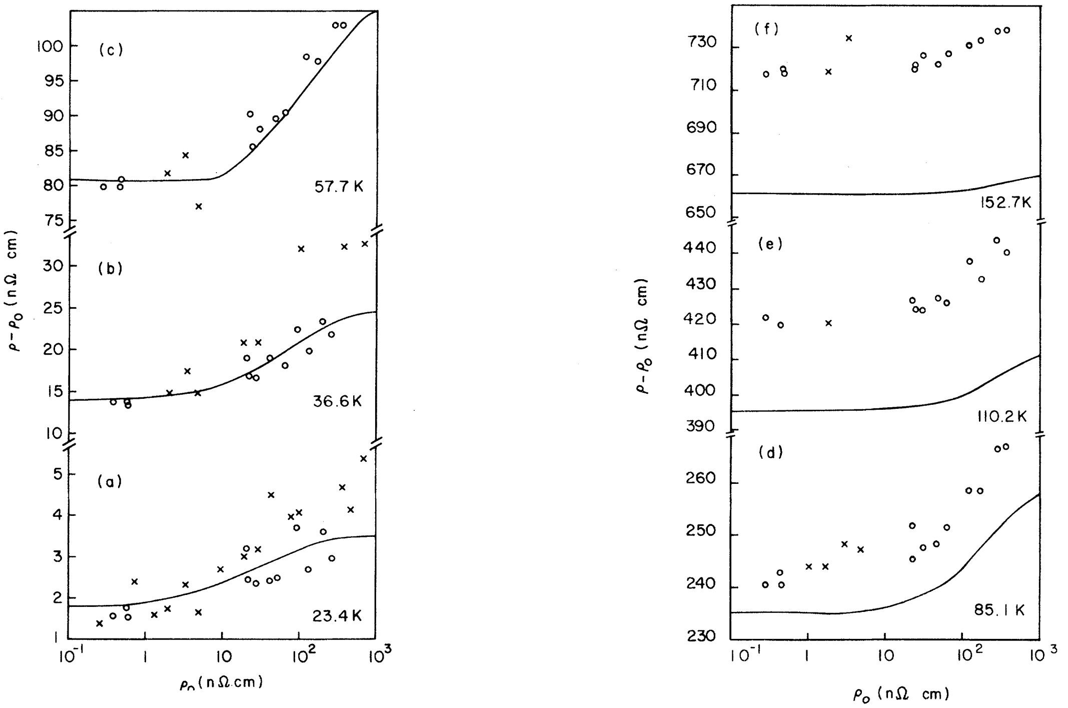

FIG. 8. Deviations from Matthiessen's rule plotted vs impurity resistivity for 6 temperatures. The solid lines are calculated results, ○'s are experimental results of Dugdale and Basinski [Ref. 11(a)] and ×'s are experimental values of Lengeler *et al.* [Ref. 11(b)].

theoretical results separate. This is, at least in part, due to our underestimate of the high-temperature resistivity. Taking this into account shows that qualitatively we have reproduced the experimental results. The curves in Fig. 8 are only altered slightly by using $J_{\max}=1$ instead of $J_{\max}=3$. The alteration consists of a slight increase of $\rho-\rho_0$ for small ρ_0, and no change at large ρ_0. The increase at 30 K is 7% as was found for pure Cu.

In Fig. 9 we display the effect of adding impurities to the thermal resistivity calculation. We see that the impurities cause the thermal conductivity to go to zero as T goes to zero. This is readily apparent from our model, in fact one sees that as T goes to zero $W^{-1}\sim T$.

IV. HALL COEFFICIENT

A. Formalism

We have previously reported[12] the high-temperature, $T\sim\Theta_D$, Hall coefficient R_H in Cu and Nb. The procedure used there yields no temperature dependence. We shall now derive a way of incorporating temperature dependence into R_H by allowing energy and angular dependence in the distribution function.

We start with the linearized Boltzmann equation

$$\left[-e\vec{v}_k\cdot\vec{E}+\frac{e}{\hbar c}\vec{H}\cdot(\vec{v}_k\times\vec{\nabla}_k\phi_k)\right]\left[-\frac{\partial f}{\partial\epsilon_k}\right]=\sum_{k'}Q_{kk'}\phi_{k'}\ . \qquad (16)$$

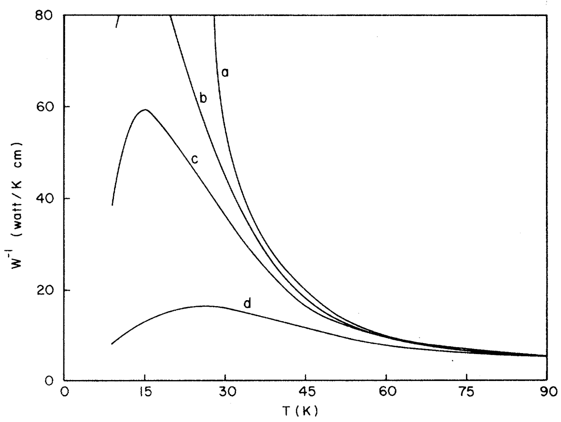

FIG. 9. Effect of impurities on the thermal conductivity. Curves $a-d$ represent residual resistivity ratios (RRR's) of 38 500 (pure), 15 612, 9825, and 2500. Here RRR equals ρ(300 K)/ρ(10 K).

Here $\phi_k(-\partial f/\partial\epsilon_k)$ represents the deviation of the distribution function from a Fermi function. It is then useful to pick directions for the electric and magnetic fields so as to simplify the notation. As the low-field Hall coefficient for a cubic metal is independent of the directions of the applied fields, the choice is not a restriction. Choose $\vec{E}=E\hat{x}$ and $\vec{H}=H\hat{z}$. The form of ϕ_k is assumed to be

$$\phi_k=\sum_{Jn}(\phi^0_{Jn}\chi^x_{Jn}E+\phi^1_{Jn}\chi^y_{Jn}EH)\ , \qquad (17)$$

where $\chi^\alpha_{Jn}(k,\epsilon)=F^\alpha_J(k)\sigma_n(\epsilon)/N_\uparrow\langle v^2\rangle^{1/2}$ and $\phi^{0(1)}_{Jn}$ is a constant to be determined. The function $F^\alpha_J(k)$ is a Fermi surface harmonic of vector symmetry in the αth direction, e.g., $F^x_1(k)\propto v_{kx}$, and $\sigma_n(\epsilon)$ is an energy polynomial. Inserting Eq. (17) in Eq. (16) and equating powers of H we find

$$ev_{kx}\left[\frac{\partial f}{\partial\epsilon_k}\right]=\sum_{\substack{k'\\Jn}}Q_{kk'}\chi^x_{Jn}\phi^0_{Jn}\ , \qquad (18)$$

$$\frac{e}{\hbar c}\sum_{Jn}\hat{z}\cdot(\vec{v}_k\times\vec{\nabla}_k\chi^x_{Jn})\left[-\frac{\partial f}{\partial\epsilon_k}\right]\phi^0_{Jn}=\sum_{\substack{k'\\Jn}}Q_{kk'}\chi^y_{Jn}\phi^1_{Jn}\ . \qquad (19)$$

Multiplying both of these equations by $\chi^\beta_{J'n'}(k,\epsilon)$ and summing over all k, noting that $Q_{kk'}$ has scalar symmetry, yields

$$-e\delta_{J,X}\delta_{n,0}=\sum_{J'n'}Q_{Jn,J'n'}\phi^0_{J'n'}\ , \qquad (20)$$

$$\frac{e}{\hbar c}\sum_{\substack{k\\J'n'}}\chi^y_{Jn}(\vec{v}_k\times\vec{\nabla}_k\chi^x_{J'n'})\cdot\hat{z}\left[-\frac{\partial f}{\partial\epsilon_k}\right]\phi^0_{J'n'}=\sum_{J'n'}Q_{Jn,J'n'}\phi^1_{J'n'}\ , \qquad (21)$$

where we have defined

$$Q^{\alpha\beta}_{Jn,J'n'}\equiv\sum_{kk'}\chi^\alpha_{Jn}(k)Q_{kk'}\chi^\beta_{J'n'}(k')=\delta_{\alpha\beta}Q_{Jn,J'n'}\ . \qquad (22)$$

Inversion of these two equations yields

$$\phi^0_{Jn}=-e[Q^{-1}]_{Jn,X0}\ , \qquad (23)$$

$$\phi^1_{Jn}=\frac{-e^2}{\hbar c}\sum_{\substack{J',J''\\n',n''}}[Q^{-1}]_{Jn,J'n'}M_{J'n',J''n''}[Q^{-1}]_{J''n'',X0}\ , \qquad (24)$$

where $M_{J'n',J''n''}$ is defined by

$$M^{\alpha\beta\gamma}_{Jn,J'n'} \equiv \sum_k \chi^{\beta}_{Jn}(\vec{v}_k \times \vec{\nabla}_k \chi^{\alpha}_{J'n'}) \cdot \hat{\gamma} \left[\frac{-\partial f}{\partial \epsilon_k} \right]$$

$$= M_{JJ'} \epsilon_{\alpha\beta\gamma} \delta_{nn'} , \tag{25}$$

and $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita symbol. Note that $M_{Jn,J'n'}$ is diagonal in n and n', and independent of n. To see this recall the definition of χ_{Jn} and that $\vec{v}_k \times \vec{\nabla}_k \sigma_n(\epsilon_k) = 0$. The orthonormality condition on the σ's, i.e.,

$$\int_{-\infty}^{\infty} \frac{-\partial f}{\partial \epsilon_k} \sigma_n(\epsilon_k) \sigma_{n'}(\epsilon_k) d\epsilon = \delta_{nn'} , \tag{26}$$

thus demands $n = n'$.

The current in the α direction is given by

$$j_\alpha = -2e \sum_k v_{k\alpha} \phi_k \left[\frac{-\partial f}{\partial \epsilon_k} \right] . \tag{27}$$

Thus for the electrical conductivity we have the form given in Eq. (11), and the Hall conductivity and Hall coefficient are

$$\sigma_H = \frac{2e^3}{\hbar c} \sum_{\substack{JJ' \\ n}} [Q^{-1}]_{X0,Jn} M_{JJ'} [Q^{-1}]_{J'n,X0} , \tag{28}$$

$$R_H = -(2e\hbar c)^{-1} \sum_{J,J',n} \frac{[Q^{-1}]_{X0,Jn} M_{JJ'} [Q^{-1}]_{J'n,X0}}{([Q^{-1}]_{X0,X0})^2} . \tag{29}$$

If we truncate Q to $Q_{X0,X0}$ we recover Eq. (2) of Ref. 12.

No variational principle exists to determine whether Eq. (29) is an upper or lower bound on R_H. However, we have found that for all temperatures the magnitude of R_H in pure Cu monotonically increases as $n_{\max}$ increases. We therefore extrapolate our results to $n_{\max} \rightarrow \infty$ as we did for the resistivities. $J_{\max}$ is again only 3 and we do not extrapolate $J_{\max}$ to ∞.

B. Hall coefficient of pure copper

For the case with $n_{\max} = 0$ and $J_{\max} = 1$ we reported[12] the value of R_H for Cu as being -5.30×10^{-11} m^3/C. The experimental value for R_H at room temperature is -5.17×10^{-11} m^3/C. If we then include energy polynomials in the calculation and extrapolate $n_{\max} \rightarrow \infty$ we find $R_H = -5.38 \times 10^{-11}$ m^3/C at $T = 300$ K and including the angular polynomials through cubic terms that $R_H = -5.58 \times 10^{-11}$ m^3/C. The inclusion of anisotropy and/or energy polynomials at 300 K is thus more important for the Hall-coefficient calculation than for the resistivities at high temperature. This is consistent with the absence of a variational principle.

In Fig. 10 we display the results of calculating R_H with $J_{\max} = 1$ and 3, where in both cases we have extrapolated $n_{\max} \rightarrow \infty$. We also present in Fig. 10 the experimental results of Love[13] and Barnard.[14] Barnard's experiment is especially interesting as he used a magnetic field of only 85 G which is some 200 times smaller than a typical Hall-experiment field. This enables him to remain in the low-field region, $\omega_c \tau \ll 1$, down to lower temperatures. Barnard should in fact satisfy the above inequality throughout the temperature range for which we perform the calculation.

Our $J_{\max} = 1$ result is in good agreement with both experiments. Love's high-temperature results are in disagreement with the majority of experiments, his value being too low, but his geometry is consistent with ours, and this should minimize the effects of his use of a larger field, $H \sim 10$ kG, than Barnard. The inclusion of two extra angular polynomials, i.e., increasing $J_{\max}$ from 1 to 3, moves the calculated value of R_H away from experimental values. Why this should happen is not clear. We remarked earlier that the Hall coefficient is not guaranteed to converge monotonically as $J_{\max}$ is increased, and perhaps increasing $J_{\max}$ would actually decrease the magnitude of R_H. In fact, we found that R_H always increased as $n_{\max}$ increased,

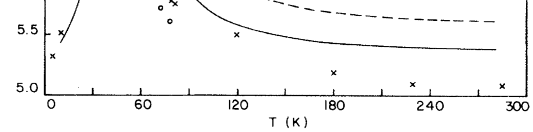

FIG. 10. Hall coefficient of pure Cu vs temperature. The solid line is calculated using energy polynomials, the dashed line is calculated using energy and angular polynomials. ○'s are the data of Barnard (Ref. 14) and ×'s are the data of Love (Ref. 13).

except for occasional decreases in impure Cu; these fluctuations were small and did not affect the convergence in energy of our results. Another point is that the Hall coefficient depends on derivatives of the velocities for $J_{\max}=1$ and on derivatives of velocity polynomials for $J_{\max}$ greater than one. Inaccuracies in the energy bands may then be more noticeable in a Hall-coefficient calculation. Still the agreement with experiment is good, qualitatively if not quantitatively.

An important point to note is the decrease in the magnitude of the Hall coefficient, which is seen experimentally at low temperatures and in low magnetic fields, is reproduced in our calculation even when $J_{\max}=1$. Recall that $J_{\max}=1$ corresponds to ϕ_k being proportional to v_k. The energy dependence alone of the distribution function will reproduce this feature of the experimental Hall coefficients. This was first pointed out by Engquist and Grimvall,[15] who did a model calculation of the Hall coefficient in alkali metals.

C. Hall coefficient for impure Cu

Proceeding as with the electrical and thermal resistivities, we add a phenomenological impurity scattering lifetime to the Q matrix. The Hall coefficients calculated with this new Q matrix are displayed in Fig. 11.

Dugdale and Firth[16] found that, in CuAu alloys, the peak in the Hall coefficient is moved to higher temperatures and reduced in magnitude as more Au is added. Unfortunately, the bulk of their data is not in the low-field region and thus not directly comparable with our calculations. We do see that the trends agree.

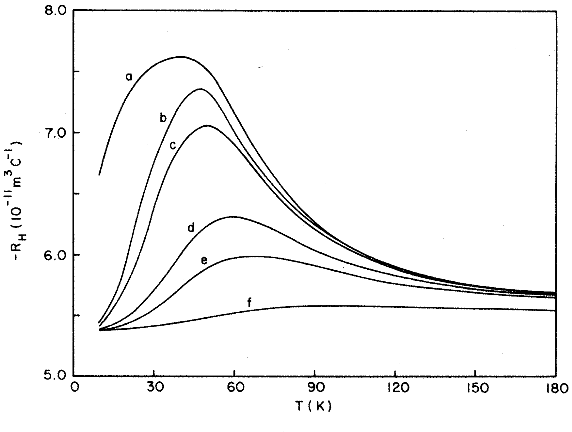

FIG. 11. Effect of impurities on the Hall coefficient of Cu. Curves $a-f$ represent RRR's of 38 500 (pure), 270, 135, 28, 15, and 4. $J_{\max}=3$ was used to calculate these curves.

V. RELATION TO PREVIOUS CALCULATIONS AND SUMMARY

Among the first realistic calculations of transport coefficients in metals were those of Hasegawa and Kasuya[17] for Cu. Using band theory to construct a Fermi surface, Bardeen's model for the electron-phonon interaction, experimental phonons, and assuming only angular dependence in the distribution function, they calculated the electrical resistivity, thermopower, and Hall coefficient. After adjusting the constants in Bardeen's formula to fit the measured electrical resistivity, their other calculations agreed well with experiment. Their Hall coefficient is higher than experiment by ~20% and they do not reproduce the decrease seen in experiments below ~40 K. This decrease was explained by Schmidt and Mann[18] on the basis of angular anisotropy.

Yamashita and Asano[19] used a model for the electron-phonon interaction similar to ours to calculate the electrical resistivity and thermopower of Cu. The difference between our calculation and theirs arises from a different choice of the family of phase shifts which fit the Fermi surface, as explained in the preceding paper.[6] At $T=300$ K, our value of ρ agrees with Ref. 19 to five percent.

Recently several other groups have realized the importance of the energy dependence in the distribution function. Kus[20] found for K that energy dependence of the distribution function was more important than angular anisotropy for thermal resistivity. Early work of Sondheimer[21] and Klemens[22] had shown the importance of energy dependence for thermal resistivity, but at that time it was not expected to influence electrical resistivity much. Recently Leavens[23] found for K that the electrical resistivity is more influenced by energy variations than by angular ones. Engquist and Grimvall then used a model energy-dependent scattering lifetime to account for deviations from Matthiessen's rule (DMR),[24] Hall coefficients, and Righi-Leduc coefficients[15] in the alkali metals. Zhernov[25] used both energy and angular variations in a calculation of the Hall coefficient of Na. He found that at high temperatures energy dependence dominated, but for $T \lesssim 30$ K angular variations dominated. Also in his calculations, contrary to ours, he finds that the effects of energy and angular variations tend to balance whereas we find that they are additive.

In summary we find that energy dependence alone can explain qualitatively and often quantitatively the transport coefficients in Cu. Our approximate treatment of angular dependence may omit as much as half of the angular effect. For $T \geq 100$ K this is a small correction, but increased angular freedom might lower the electrical and thermal resistivities by a further 20% at $T \sim 20$ K. Bergman *et al.*[26] have calculated DMR in Cu at temperatures below 10 K. They find that angular freedom is more important than energy dependence. At those temperatures we agree but for higher temperatures it appears that energy dependence alone is sufficient.

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