Brief Reports

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dc transport in metals

P. B. Allen, T. P. Beaulac, and F. S. Khan*
Department of Physics, State University of New York, Stony Brook, New York 11794

W. H. Butler, F. J. Pinski,† and J. C. Swihart‡
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830
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Ten years of evidence is summarized which supports and clarifies a simple scheme for analyzing dc resistivity of complex metals, namely, extraction of $(n/m)_{\rm eff}$ from band theory and estimation of the electron-phonon scattering rate $1/\tau_{e\text{-ph}}$ from the superconducting transition temperature. The accuracy of this procedure has now been tested by detailed microscopic calculations for Cu, Nb, Ta, and Pd.

This note updates a paper by Chakraborty, Pickett, and Allen,[1] which proposed a scheme for analysis of the phonon-limited electrical resistivity of crystalline metals which makes no simplifying approximations about the nature of the energy bands. The resistivity can be written as

$$\rho=[(n/m)_{\rm eff}e^2]^{-1}(1/\tau)\ , \tag{1}$$

$$(n/m)_{\rm eff}=\Omega^{-1}\sum_k v_{kx}^2\delta(\varepsilon_k)=\tfrac{1}{3}N(0)\langle v^2\rangle\ . \tag{2}$$

These equations essentially define the scattering rate $1/\tau$. However, a simple formula for the electron-phonon scattering rate $1/\tau_{e\text{-ph}}$ emerges in the lowest-order variational solution of the Bloch-Boltzmann equation.

$$\hbar/\tau=2\pi\lambda_{\rm tr}k_BT(1-\hbar^2\langle\omega^2\rangle_{\rm tr}/12k_B^2T^2+\cdots)\ . \tag{3}$$

This formula applies for $T\gtrsim\Theta_D$. The electron-phonon coupling parameter $\lambda_{\rm tr}$ is closely related to the mass enhancement λ which governs the superconducting T_c. The formula is

$$\lambda_w=\frac{N(0)\sum_{k,k'}w(k,k')\,|M(k,k')|^2(\hbar\omega_{k-k'})^{-1}\delta(\varepsilon_k)\delta(\varepsilon_{k'})}{\Omega^{-1}\sum_{k,k'}w(k,k')\delta(\varepsilon_k)\delta(\varepsilon_{k'})}\ , \tag{4}$$

where $N(0)$ is the electronic density of states of both spins per unit volume, and $M(k,k')$ is the electron-phonon matrix element to scatter from a state k of energy ε_k and group velocity v_k to a state k' by emission of a phonon of energy $\hbar\omega_{k-k'}$. The weight factor w equals 1 for λ and $(v_{kx}-v_{k'x})^2$ for $\lambda_{\rm tr}$. An accurate calculation of the coupling constant λ_w is very demanding. The simple scheme of Ref. 1 can be used in two versions.

Scheme I. Obtain $(n/m)_{\rm eff}$ from band theory, λ from the superconducting T_c, approximate $\lambda_{\rm tr}$ by λ, and estimate $\rho_{e\text{-ph}}$.

Scheme II. Obtain $(n/m)_{\rm eff}$ from band theory and use the experimental value of $\rho-\rho_0$ to extract an empirical value of $\lambda_{\rm tr}$. This should also approximately measure the value of λ.

Based on ten years of hindsight[2] we can confirm the validity of these schemes. The purposes of an update are to summarize the ways in which our understanding of this scheme has improved. Specifically, we discuss (a) the validity of the lowest-order variational approximation (LOVA) on which Eqs. (3) and (4) are based, (b) numerical evidence on the quantitative relationship between $\lambda_{\rm tr}$ and λ, (c) the sensitivity of $(n/m)_{\rm eff}$ to the accuracy of the energy bands, and (d) the limits of validity of the Bloch-Boltzmann theory.

In work on Cu (Ref. 3) and Nb and Pd (Ref. 4) we have solved the Bloch-Boltzmann integral equation to a high level of accuracy, including a complete treatment of corrections in higher powers of $\varepsilon-\mu$ and a partial treatment of angular anisotropy. We find that in the regime where Eq. (3) applies, LOVA is accurate to 1%. At lower temperatures ($T<\Theta_D/5$) the corrections can be a factor

TABLE I. Band structure and electron-phonon parameters.

	λ^{calc}	λ_{tr}^{calc}	λ_{tr}^{emp}	ρ_{295}^{expt} ($\mu\Omega$ cm)	Ω_p (eV)	$N(0)$ (states/Ry spin atom)	$\langle v^2\rangle^{1/2}$ (10^8 cm/s)	$\frac{\hbar^2\langle\omega^2\rangle_{tr}}{12k_B^2T_{295}^2}$	Refs.
Cu	0.111	0.116	0.107	1.69	8.5	1.89	1.08	0.050	3
Pd	0.41	0.46	0.41	10.55	6.6	15.5	0.33	0.037	4
Nb	1.12	1.07	0.99	14.5	8.9	9.9	0.61	0.037	4
Ta	0.88	0.57	0.58	13.1	7.1	8.03	0.55	0.021	5

of 2 or more. Thus while corrections to LOVA can be large and interesting in some cases, they do not affect the above scheme significantly.

Concerning point (b), careful numerical calculations[3-5] were made of both λ and λ_{tr} for Cu, Nb, Pd, and Ta. Table I shows these values in the first two columns. Except in the case of Ta, $(\lambda-\lambda_{tr})/\lambda$ is $\leq 10\%$, while for Ta the value is 35%. Apparently large values of $(v_{kx}-v_{k'x})^2$ tend to correlate with small values of $M_{kk'}^2/\hbar\omega_{k-k'}$ for Ta, while for the other metals there is no particular correlation. The complete numerical calculations of $\rho(T)$ for these four metals are shown in Fig. 1. Also shown in Table I is an empirical value of λ_{tr} found by scheme II. The close agreement between calculated and empirical λ_{tr} values simply reflects the good agreement between theory and experiment in Fig. 1.

Our calculations of $\rho(T)$, λ, and λ_{tr} used Korringa-Kohn-Rostoker (KKR) band structures with potentials

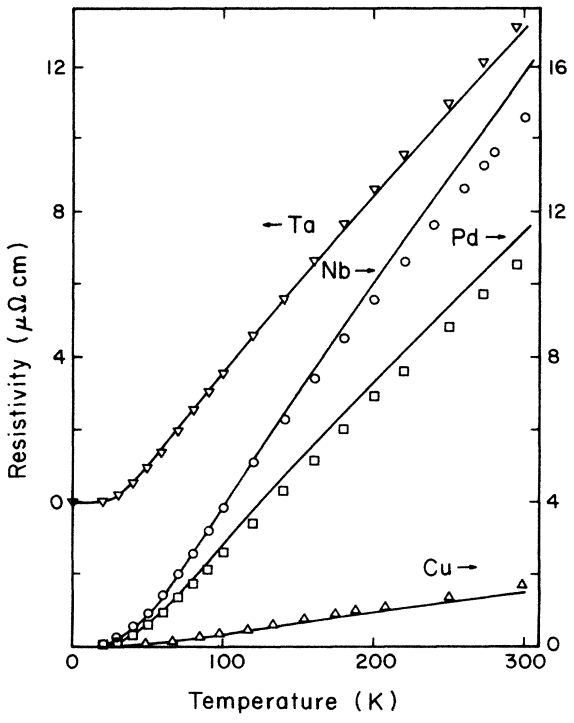

FIG. 1. Resistivity vs temperature. The solid lines are calculations. For Ta, the lowest-order variational solution of the Bloch-Boltzmann equations is used, while for the rest, higher-order corrections are included, but are negligible on the scale of this figure except below 100 K. Data are from Ref. 11.

fixed in several different ways. In the case of Ta, the potential came from a relativistic self-consistent $X\alpha$ calculation by Boyer, Papaconstantopoulos, and Klein.[6] For Nb, Pd, and Cu the potentials were derived from the Mattheiss prescription[7] starting with nonrelativistic $X\alpha$ atomic charge densities. In the case of Nb, a small alteration of the phase shifts $\delta_l(\varepsilon_F)$ was made to bring the Fermi surface shape into agreement with experiment. In the case of Cu, flexibility in the choice of the muffin-tin zero was exploited to find a set of phase shifts which gave a sensible forward-scattering matrix element.[8] These two adjustments were made prior to calculation of λ and λ_{tr}, which entitles us to a fair claim of using no adjustable parameters. The close agreement between theory and experiment suggests that the ingredients of our scheme are essentially sound. These ingredients are (a) Bloch-Boltzmann theory, (b) the use of band eigenvalues and eigenfunctions to describe quasiparticle behavior at the Fermi surface, and (c) the rigid muffin-tin model for electron-phonon coupling. Ingredient (c) is the weakest element, and we cannot argue that it is correct in all details. For example, if the long-wavelength deformation potential coupling were miscalculated, this would not show up in λ_{tr}. However, larger-Q matrix elements averaged on the Fermi surface seem to be very good.

These schemes would be of little use if band theory did not give reliable values of $(n/m)_{eff}$ or the Drude plasma frequency Ω_p defined by $\Omega_p^2=4\pi e^2(n/m)_{eff}$. Unfortunately, it is not easy to test this directly because optical (reflectivity or absorption) experiments measure a Drude plasma frequency Ω_p^* which has an electron-electron renormalization effect[1] which cancels out in ρ_{dc}. Also, experimental determination of Ω_p^* is very difficult, due in part to the large interband term which must be subtracted.

Fortunately, there is some evidence that Ω_p is less sensitive than other band structure quantities like $N(\varepsilon)$ and $\langle v^2(\varepsilon)\rangle^{1/2}$. Figure 4 of a paper by Klein, Papaconstantopoulos, and Boyer[9] shows the energy variation of all three quantities in Nb_3Sn; compared to $N(\varepsilon)$, and $\langle v^2(\varepsilon)\rangle^{1/2}$, $\Omega_p(\varepsilon)$ is more slowly varying and has smaller fluctuations, suggesting that band theory answers for Ω_p should be comparatively good. As a note of caution, however, our self-consistent relativistic KKR band structure of Ta gave $\Omega_p=7.1$ eV as shown in Table I, whereas the nonrelativistic augmented-plane-wave (APW) bands[10] used in Ref. 1 gave $\Omega_p=9.44$. This increase of 32% leads to an increase in λ_{tr}^{emp} of 74% above the value shown in Table I. Clearly, the sensitivity of Ω_p to the accuracy of band theory is significant, and in $5d$ materials relativistic effects need to be included.

We can learn quite a lot about the validity of Bloch-Boltzmann theory from these calculations. The accepted criterion demands that $k_F l$ or $\varepsilon_F \tau$ should be large, where l is a mean free path. Of course k_F and ε_F do not mean much for nonparabolic bands, but the criteria can be rewritten so that l/d or $\tau/\hbar N(0)$ become the parameters in question, where d is the interatomic spacing. The former seems more meaningful, and we can estimate it from the values of λ_{tr} and $\langle v^2\rangle^{1/2}$ in Table I. Using the definition $l = \langle v^2\rangle^{1/2}\tau_{e\text{-ph}}$, we find l/d equals 162, 12, 9, and 14 for Cu, Pd, Nb, and Ta, respectively, at 295 K. A typical quasiparticle crosses ten or more atomic planes before scattering, so it is not surprising that Bloch-Boltzmann theory should apply. However, at the melting temperatures, the results are $l/d = 35$, 1.9, 1.0, and 1.2. Bloch-Boltzmann theory should work all the way to the melting point for Cu, but not for the rest. Some experimental suggestion of a breakdown can be seen from the $\rho(T)$ curves.[11] The slope of $\rho(T)$ for Cu increases above the 295 K value near melting as might be expected from thermally activated vacancy formation. The other three metals all show reductions of $\sim 30\%$ in the slope of $\rho(T)$. It is perhaps surprising that such a small deviation from Bloch-Boltzmann behavior is seen considering the small value of l/d. The data suggest that Bloch-Boltzmann theory is accurate to at least 10–20% for $l/d \geq 5$, or alternately that the point $l/d \approx 5$ is where deviations start to be noticeable. Of course, it is notoriously hard to know exactly what Bloch-Boltzmann theory predicts at elevated temperatures because thermal expansion and Fermi smearing effects begin to invalidate the simple expression of Eqs. (1)–(3).

Much more dramatic deviations from Bloch-Boltzmann behavior[12] have been seen in many d-band compounds, especially $A15$-structure superconductors, where even at 300 K the slopes of $\rho(T)$ are always significantly reduced [a normal slope can be recognized because according to Bloch-Boltzmann theory the slope at $T \geq \Theta_D$ should extrapolate back at $T = 0$ to the value $\rho(T = 0) = \rho_0$]. The analysis of scheme I has been applied to these materials by Allen, Pickett and Cohen.[13] By using superconductivity to estimate λ_{tr} and band theory to get Ω_p, it was found that Bloch-Boltzmann theory predicts mean free paths of 5–6 Å and Nb_3Al and Nb_3Ge at 300 K. This distance is comparable to a unit-cell dimension; the electrons scatter just as they encounter the first evidence that their environment is periodic. Bloch-Boltzmann theory also predicts room temperature values of $\rho_{e\text{-ph}} = \rho(t) - \rho_0$ of order 150 $\mu\Omega$ cm, which is larger by about a factor of 4 than observed. This analysis clarified that the observed anomalous $\rho(T)$ was indeed a breakdown of Bloch-Boltzmann theory, and that the breakdown could be anticipated by invoking normal ideas of band theory and electron-phonon theory. Thus we disagree with the more recent proposal by Yu and Anderson[14] which is based on the premise that an extraordinarily large value of λ is needed to account for the breakdown of Bloch-Boltzmann theory in these materials.

We also wish to disagree with the suggestions of Glötzel, Rainer, and Schober,[15] who have evidence that band theory is not capable of accounting for superconducting transition temperatures, and blame this on the theory of electron-phonon interactions. Our work suggests that the electron-phonon interaction is well under control (Fig. 1 is perhaps the strongest evidence). Our ability[2] to explain T_c is far from perfect (although not as bad as in Ref. 15) and we suggest that much of the fault may lie in our understanding of the Coulomb interaction.

Finally, we repeat our message[1] of 1976, and urge theorists to compute $(n/m)_{\text{eff}}$ [Eq. (2)] whenever $N(0)$ is calculated, and to compute λ_{tr} whenever λ is calculated.

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*Permanent address: Department of Electrical Engineering, Ohio State University, Columbus, Ohio 43210.

†Permanent address: Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221.

‡Permanent address: Department of Physics, Indiana University, Bloomington, Indiana 47401.

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