PHYSICAL REVIEW B VOLUME 4, NUMBER 12 15 DECEMBER 1971

Comment on "Anomalous Electron-Phonon Transport Properties of Impure Metals"*

Henrik Smith†
Research Institute for Theoretical Physics, Siltavuorenpenger 20 *B*, *Helsinki* 17, *Finland*
(Received 12 March 1971)

The substantial deviations from additivity of electron-phonon and electron-impurity scattering [Phys. Rev. B 2, 3833 (1970)] are shown to result mainly from an unfortunate choice of a trial function in the variational calculation of the resistivity.

The purpose of this note is to comment on a recent paper by Rice and Bunce[1] on the anomalous electron-phonon transport properties of impure metals. The basic effect was outlined by Rice[2] and further elaborated on in Ref. 3. It was shown by the present author[4] that the treatment in Ref. 2 leads to a considerable overestimate of the deviation from additivity of the electron-phonon and electron-impurity scattering. In this note we point our that the same criticism applies to RB, in which the detailed account of the effect outlined in Refs. 2 and 3 is given.

In order to elucidate the general nature of the argument let us consider the transport properties of a system, in which two scattering mechanisms are present simultaneously. The linearized Boltzmann equation may be written in a symbolic fashion as

$$X = HQ = (H_1 + H_2)Q \ , \tag{1}$$

where H is the total collision operator, assumed equal to the sum of the collision operators associated with each scattering mechanism. The unknown deviation from equilibrium of the distribution function is Q, and X is the driving term.

The well-known variational principle, which was introduced in transport theory by Kohler,[5] leads to a lower bound on, say, the conductivity σ of a metal. If the conductivity is written as a scalar product[5] of Q and X, that is, $\sigma = (Q, X)$, then the resistivity $\rho = 1/\sigma$ may be bounded from above according to

$$\rho \leq (U, HU)/(U, X)^2 \ . \tag{2}$$

Here U is the trial function which one has to choose in order to determine the bound (2). The exact resistivities for each scattering mechanism considered separately are given by $1/\rho_1 = (Q_1, X)$ and $1/\rho_2 = (Q_2, X)$, where Q_1 and Q_2 are the exact solutions of the Boltzmann equation (1) with H replaced by H_1 and H_2, respectively.

Let us now consider the case where the first scattering mechanism dominates the resistivity, that is, $\rho_1 \gg \rho_2$. It is then natural to use $U = Q_1$ as the trial function in (2). We then obtain

$$\rho \leq \rho_1 + (Q_1, H_2 Q_1)/(Q_1, X)^2 \tag{3}$$

$$= \rho_1 + \rho_2 + \Delta_2 \ , \tag{3$'$}$$

where (3′) defines the positive quantity Δ_2. It is apparent that Δ_2 is an upper bound on the deviation from additivity

$$\Delta = \rho - (\rho_1 + \rho_2) \ , \tag{4}$$

which is the quantity of interest in RB. One might think that $\Delta = \Delta_2$ in the limit $\rho_1 \gg \rho_2$. This was in fact the (implicit) assumption made in Refs. 1–3. To see why this is not necessarily true, we need only consider the analogous bound obtained with $U = Q_2$:

$$\rho \leq \rho_1 + \Delta_1 + \rho_2 \ . \tag{5}$$

If Δ_1 is comparable to Δ_2, even though $\rho_1 \gg \rho_2$, then clearly the bound Δ_2 cannot be trusted as a reasonably accurate approximation to Δ. If $\Delta_1 \ll \Delta_2$, even though $\rho_1 \gg \rho_2$, then Δ_1 is obviously a much better upper bound than Δ_2, and the identification $\Delta = \Delta_2$ would be grossly misleading. These remarks are important not only for the absolute magnitude of the predicted Δ, but also for its dependence on temperature and other parameters of the system.

To see explicitly how these considerations apply to RB we shall consider the case (treated in Ref. 4) where only the linear term in the energy dependence of the impurity relaxation time is kept. Then RB's equation (3.7) becomes[6] (with $b_0 = 0$)

$$\rho_{\mathrm{imp}} = \rho_0 \frac{1 + a_0^2 A\left[X^2/(1+X)^2 - 2X/(1+X)^2\right]}{\{1 - a_0^2 A\left[X/(1+X)^2\right]\}^2} \ , \tag{6}$$

where for brevity $A = \frac{1}{3}\pi^2 (T^2/\Theta_D'^2)$ and $X = \rho_{\mathrm{ep}}^0/\rho_0$. (The notation of RB is followed except when otherwise indicated.) With the condition $a_0^2 A \ll 1$ [cf. Ref. 4 or RB's (2.19)] the result (6) becomes

$$\rho_{\mathrm{imp}} = \rho_0 \{1 + a_0^2 A[X^2/(1+X)^2]\} \ . \tag{7}$$

When this is added to ρ_{ep} as given by RB's (4.2) the following expression for $\Delta = \rho_{\mathrm{imp}} + \rho_{\mathrm{ep}} - (\rho_0 + \rho_{\mathrm{ep}}^0)$ results:

$$\Delta/a_0^2 \rho_0 = X/(1+X)^2 + A[X^2/(1+X)^2] \ . \tag{8}$$

This may now be compared with the result given in Eq. (7) of Ref. 4:

$$\Delta/a_0^2\rho_0 \leq (1/X + 1/A)^{-1} . \qquad (9)$$

Since $A = \frac{1}{3}\pi^2(T^2/\Theta_D'^2) \ll 1$, the bound (9) is much smaller than (8). When viewed as a function of X the right-hand side of (9) increases monotonically with increasing X, the maximum (asymptotic) value being $A(\ll 1)$, whereas (8) peaks at $X \sim 1$ with a peak value $\gtrsim \frac{1}{4}$. The expressions (8) and (9) are approximately equal only for $X \gg 1/A$ and $X \ll A$.

The reason for the difference between the results (8) and (9) lies solely in the choice of trial function. The result (9) was obtained[4] with a trial function, which was a variable linear combination of the solution of the impurity-only problem with the solution of the phonon-only problem. The trial function of RB (2.15), however, contains no variational parameter; it is an indication of how unfortunate this ansatz is, that the simplest conceivable trial function, namely, an energy-independent constant [say $\tau(\epsilon) = \tau_{ep}^0$] would do far better than the ansatz of RB (2.15). Such a constant trial function gives immediately

$$\Delta/a_0^2\rho_0 \leq A , \qquad (10)$$

which eliminates the peak exhibited by (8) when plotted as a function of X.

The connection with our discussion prior to Eq. (6) may now be made. The bound (9) is simply a combination in *parallel* of the resistivities Δ_1 and Δ_2 as defined by (3′) and (5), since $\Delta_1 = a_0^2\rho_{ep}^0$ and $\Delta_2 = a_0^2 A\rho_0$. Then (9) assumes the form

$$\Delta \leq (1/\Delta_1 + 1/\Delta_2)^{-1} . \qquad (11)$$

Clearly (11) is in accordance with the requirement that Δ should be less than or equal to the smaller of Δ_1 and Δ_2. It is also apparent that the relative magnitude of ρ_1 and ρ_2 is of no immediate relevance.

With the obvious identifications the result (8) due to RB is similarly written as

$$\Delta = \Delta_1[\rho_2^2/(\rho_1+\rho_2)^2] + \Delta_2[\rho_1^2/(\rho_1+\rho_2)^2] , \qquad (12)$$

which has the form of a *series* combination of the resistivities Δ_1 and Δ_2 after multiplication with weight factors involving the ratio ρ_1/ρ_2. From (12) one may recover the form (11) only by the replacement $\rho_1 \rightarrow \Delta_1$ and $\rho_2 \rightarrow \Delta_2$ in the weight factors. Once again, this demonstrates the relevance of the ratio Δ_1/Δ_2 rather than ρ_1/ρ_2.

The plots shown in RB's Fig. 1 were obtained by neglecting the second term in (8) compared to the first one, that is, by writing

$$\Delta = a_0^2\rho_0 \frac{X}{(1+X)^2} = a_0^2 \frac{\rho_{ep}^0}{(1+\rho_{ep}^0/\rho_0)^2} . \qquad (13)$$

This approximation corresponds to setting $A = 0$ in (9), which results in $\Delta = 0$. Therefore (13) should be interpreted as nothing more than an upper bound on the number zero.

We conclude that Refs. 1–3 seriously overestimate the deviations from additivity of the electron-phonon and electron-impurity scattering, and that the predicted peaks in $\Delta(T)$ (RB's Fig. 1) do not reflect any property of the model considered, but only the inadequacy of the chosen trial function.

---

*See Ref. 1.

†Permanent address: Fysisk Laboratorium I, H. C. Ørsted Institute, Universitetsparken 5, Copenhagen Ø, Denmark.

[1] M. J. Rice and O. Bunce, Phys. Rev. B 2, 3833 (1970), to be referred to as RB.

[2] M. J. Rice, Phys. Rev. Letters 23, 1108 (1969).

[3] M. J. Rice and O. Bunce, J. Appl. Phys. 41, 1009 (1970).

[4] H. Smith, Solid State Commun. 8, 1991 (1970).

[5] See, e. g., J. M. Ziman, *Electrons and Phonons* (Oxford U.P., Oxford, England, 1960), Chap. VII.

[6] When the steps leading from RB's (3.2) to (3.7) are reproduced, it appears that the factors of $(1+\rho_{ep}^0/\rho_0)$ occurring explicitly in RB's (3.7) and (3.8) should not be there.

PHYSICAL REVIEW B VOLUME 4, NUMBER 12 15 DECEMBER 1971

Existence of a Gap in the Electronic Density of States of a Disordered System*

P. L. Taylor
Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106

(Received 1 July 1971)

A recent calculation by Weaire is shown to be a special case of an older and more general theory.

In a recent letter,[1] Weaire investigated the energy density of states of a particular model of an amorphous group-IV semiconductor. The Hamiltonian used was based on the tight-binding approximation to the true Hamiltonian of an electron in a disordered tetrahedrally coordinated network of