

Some low-temperature-transport-coefficient relations in the alkali metals

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It is assumed that there exists a temperature range in which the transport coefficients in a Boltzmann-equation approximation are drag limited (i.e., the phonon-phonon collisions are negligible), and in which the electron-phonon interactions are dominated by phonons in one small pocket of the spectrum (the one-pocket approximation). Then it is shown that some relatively simple relations exist among the thermoelectric power, electrical resistivity, thermal resistivity, and specific heat. In the low-temperature limit, the ultimate behavior of the ideal thermoelectric power S is found to be $S = -|e|^{-1} (C_e + C_L/3)$ in the effective-mass approximation, where C_e is the electronic specific heat and C_L is the lattice specific heat.

I. INTRODUCTION

According to Wisner and Kaveh,¹ there exists a substantial (low) temperature range for the alkali metals in which the ideal (thermal) electrical resistivity ρ can be treated as "drag limited," on the one hand, and by the "one-pocket approximation," on the other hand. By "drag limited" I mean that the phonon-phonon relaxation channel for phonons can be neglected, whence an equation derived some years ago² should be valid for ρ ,

$$\rho = \frac{\Lambda}{T} \sum_{\vec{q}} \frac{dN}{dz} \left[\sum_{nn'} (\vec{K}_n - \vec{K}_{n'})^2 R_{nn'}(j\vec{q}) \right]. \quad (1)$$

This expression is the first (standard) term in the variational solution of the generalized-electron Boltzmann equation in the drag-limited limit, without computational approximations. A phonon is described by wave vector \vec{q} , polarization j , velocity \vec{v}_{jq} , frequency ω , and equilibrium distribution function $N = (e^z - 1)^{-1}$, where $z = \hbar\omega/k_B T$. In Eq. (1), R is a kind of reduced electron-phonon matrix element independent of temperature. The \vec{K}_n 's are reciprocal-lattice vectors, and the sum in the square brackets is over all the types of umklapp processes the phonon can enter, one of which could be the normal process $\vec{K} = 0$. If a phonon $j\vec{q}$ can engage in only normal processes, then $n = n'$, and the sum is zero. Thus the "only normal" phonons do not contribute to ρ in this limit. Λ is a constant.

The "one-pocket approximation" (OPA) consists in treating the $j\vec{q}$ sum in (1) as coming primarily from one small pocket of phonons in the lower transverse branch, allowing $R(j\vec{q})$ to be removed from the sum evaluated at the center of the pocket, $j\vec{q}_0$. [\vec{q}_0 may depend to some extent on temperature, but $R(j\vec{q}_0)$ could still be treated as constant.]

Equation (1) is not the equation Wisner and Kaveh worked with, but it is equivalent to the result they obtain. It contains directly the important factor $T^{-1} dN/dz$. Some discussion of the mechanism behind drag-limited resistivity is contained in Ref. 2.

Now there is a drag effect also in the thermo-

power.³ Some years ago attempts were made^{4,5} to fit the interesting behavior of this quantity at low temperatures. In one of these attempts,⁵ a kind of "two-pocket" approximation was used, one pocket for each of the transverse-phonon branches. The calculation was crude, and the thermopower drag effect is very difficult to estimate, since it is the result of a heavy cancellation between a large negative and a large positive term. The treatment of the pocket was different from that of Wisner and Kaveh. Also, in the thermopower calculation one must add on the diffusion term to get something to compare with experiment. Perhaps more importantly, there is an extra factor $(\hbar\omega/k_B T)^2$ in the corresponding thermopower term, and this factor tends to weaken the dominance and shape of the pocket. For all these reasons there need not be a contradiction between a one-pocket approximation in the electrical resistivity and a multipocket approximation in the drag term of the thermopower. However, it seems clear that at low enough temperatures a one-pocket approximation must be satisfactory in all such calculations, since the exponential factor must dominate.

In this paper I wish to show what happens if one adopts both a one-pocket approximation and the drag limit in the thermopower expressions. In particular, some relatively simple relations among the transport coefficients can be obtained. Whether or not the temperature range in which the approximations are valid is an interesting one will depend on future comparison with experiment. It should be kept in mind at the outset, however, that (i) the variational principle does not give a maximum or minimum to the thermopower, as it does for the resistivity, and the significance of the variational expression is not well established, and (ii) the drag term in the thermopower is much more sensitive to approximations than is ρ .

II. PHONON-DRAG THERMOPOWER

The starting point will be the drag term S_D of the thermopower given by Ref. 5,

$$S_D = S_D^{(-)} + S_D^{(+)} , \quad (2)$$

$$S_D^{(-)} = \frac{1}{3|e|} \sum_{\vec{q}_j} \hbar \vec{q} \cdot \vec{v}_q \frac{dN}{dT} = -\frac{C_L}{3|e|} , \quad (3)$$

$$S_D^{(+)} = \frac{k_B}{3|e|} \sum_{\vec{q}_j} \frac{\hbar q v_q}{k_B T} z \frac{dN}{dz} \left[\sum_{\vec{K}_n \neq 0} q^{-1} \hat{v}_q \cdot \vec{K}_n \alpha(j\vec{q}, \vec{q} + \vec{K}_n) \right] . \quad (4)$$

The sum in Eq. (3) is identified with the lattice specific heat⁶ C_L under the approximation

$$\hbar \vec{q} \cdot \vec{v}_q = \hbar \omega , \quad (5)$$

which is good for small q 's and hence is reasonably good at low enough temperatures, especially since the specific-heat contributions come from arbitrarily small q 's. However, it is still an approximation.

In Eq. (4), the reciprocal-lattice vectors are \vec{K}_n and $\alpha(j\vec{q}, \vec{q} + \vec{K}_n)$ is another quantity (defined in Ref. 5) depending on electron-phonon matrix elements. The \vec{K}_n sum does not contain $\vec{K} = 0$, meaning that phonons which can only engage in normal processes do not contribute.

The point now is to compare Eqs. (1) and (4). The restriction on the phonon sum is the same (only those phonons contribute which can engage in umklapp processes), the factor dN/dz which makes the anisotropy of the phonon spectrum so important is present in both expressions, and the large square brackets, containing the electron-phonon matrix elements, are relatively slowly varying and can be taken out from the sum sign at the value appropriate to the pocket \vec{q}_0 . If Eq. (5) is used in Eq. (4), the following relation emerges:

$$S_D^{(+)} = A\rho\langle\Theta^2\rangle/T , \quad (6)$$

where A is a constant,⁷

$$A = \frac{k_B}{3|e|\Lambda} \frac{[S_D^{(+)}]}{[\rho]} , \quad (7)$$

independent of temperature. Here $[S_D^{(+)}]$ means the large square brackets in Eq. (4), and $[\rho]$ means the large square brackets in Eq. (1). Phonon averages are defined as

$$\frac{\langle\Theta^2\rangle}{T^2} = \frac{\sum' z^2 dN/dz}{\sum' dN/dz} . \quad (8)$$

(\sum' excludes phonons which can only engage in normal processes.) The average will have contributions mainly from the center of the pocket. At low enough temperatures $k_B\langle\Theta\rangle = \hbar\omega(q_0)$, and $\langle\Theta\rangle$ is constant. However, at higher temperatures $\langle\Theta\rangle$ may vary as much as 20% over a range where ρ varies by a factor of 100.

Equations (6) and (3) substituted into Eq. (2) gives⁷

$$S_D = -C_L/3|e| + A\rho\langle\Theta^2\rangle/T . \quad (9)$$

This is the first of the desired relations. It seems to me that it should become exact as T approaches zero. The average in $\langle\Theta^2\rangle$ must still be computed, but it is well defined. The main defect of Eq. (9) is that it does not connect quantities that are actually measured. Not only is S_D not the entire thermopower, it is not even the entire ideal thermopower. This suggests looking at the other terms in the ideal thermopower.

III. DIFFUSION TERM OF THE THERMOPOWER

To do this, Eq. (95) of Ref. 2 is used,

$$S = S_D - \frac{\pi^2 k_B^2 T y}{2|e|E_F} \times \left[1 + \frac{\rho}{L_0 W T} \left(1 - \frac{2E_F}{\pi^2 y k_B^2 T^2} \frac{d_{01}}{d_{00}} \right) \right] . \quad (10)$$

Here E_F is the Fermi energy, and y and L_0 are constants

$$y = \frac{2}{3} E_F [d \ln(va)/dE]_{E=E_F} \cong 1 , \quad (11)$$

$$L_0 = \pi^2 k_B^2 / 3e^2 , \quad (12)$$

$v(E)$ being the average electron velocity on the energy surface E of area $a(E)$. The remaining factors in (10) are W , the ideal thermal resistivity, and d_{00} and d_{01} , two collision integrals, d_{00} being the one that enters the electrical resistivity and ends up proportional to Eq. (1).

The important point to note here is that the one term not evaluated in Eq. (10) is the last one, and it contains d_{00} and d_{01} , both of which contain drag effects [see Eqs. (A1) and (A2) in the Appendix] which cut out the q 's that can only engage in normal processes. In contrast, the drag effect in the collision integral d_{11} that enters the thermal resistivity does not cut out these q 's (see Ref. 2). Therefore it is reasonable to apply the one-pocket approximation to evaluate d_{01}/d_{00} . This is done in the Appendix. The answer is that most of the temperature dependence cancels out with the result

$$d_{01}/d_{00} = Bk_B\langle\Theta\rangle + Zk_B^2\langle\Theta^2\rangle/E_F + \pi^2 Zk_B^2 T^2/E_F , \quad (13)$$

where $\langle\Theta\rangle$ is an average defined as in Eq. (8) (it is T times the average of z), and where B and Z are two dimensionless constants which are probably of order of magnitude 1 [see Eqs. (A8) and (A9)]. Even if Z is two orders of magnitude larger than B , the Z terms in Eq. (13) are negligible. However, we shall retain them.

Substitution of Eqs. (13) and (9) into (10) gives⁷

$$S = -\frac{C_L}{3|e|} + A\rho \frac{\langle \Theta^2 \rangle}{T} - \frac{\pi^2 k_B^2 T}{2|e|E_F} y + \frac{k_B}{|e|} \frac{L}{L_0} \left(B' \frac{\langle \Theta \rangle}{T} + \pi^2 Z' \frac{k_B T}{E_F} \right), \quad (14)$$

where

$$L = \rho / WT, \quad (15)$$

$$B' = B + Z k_B^2 \langle \Theta^2 \rangle / (k_B \langle \Theta \rangle E_F) \cong B, \quad (16)$$

$$Z' = Z - \frac{1}{2} y. \quad (17)$$

Equation (14) is the main result of this paper. It connects the measurable ideal transport coefficients S , ρ , W , and the lattice specific heat C_L in terms of three constants, A , B , and Z (or two constants if Z is neglected, as seems reasonable) and the averages $\langle \Theta \rangle$ and $\langle \Theta^2 \rangle$, which can be computed from an independent knowledge of the phonon spectrum and the umklapp geometry. The first two terms on the right came from S_D , and approximations in those terms must be made with care. However, at low enough temperatures, Eq. (14) must be right, and experimental verification ought to be possible. Just where this low-temperature range should be is not completely clear, however. Ultimately, once the temperature dependence is verified, one can hope to compare the constants with calculated values.

IV. LOW-TEMPERATURE LIMIT

An interesting feature of this result is that if *very* low temperatures are considered, a much simpler result ensues. For, eventually, ρ cuts off exponentially with temperature, whereas W cuts off only as some power of T (since as mentioned above the drag effects do not cut out the phonons near $q=0$ in W). Thus the terms in L and ρ in Eq. (14) disappear faster than the others and we get

$$\lim_{T \rightarrow 0} S = -(|e|)^{-1} (\gamma C_e + \frac{1}{3} C_L), \quad (18)$$

where C_e is the electronic specific heat and is identified with

$$C_e = \frac{1}{3} \pi^2 k_B^2 T g(E_F), \quad (19)$$

where $g(E_F)$ is the density of electronic states (including spin) at the Fermi surface,

$$g(E_F) = \frac{V}{N_{e1ec}} \frac{1}{4\pi^3 \hbar} \left\langle \frac{1}{v} \right\rangle_{E_F} a(E_F) \cong \frac{3}{2} \frac{1}{E_F}. \quad (20)$$

Along with the definition of y from Eq. (11), this gives

$$\gamma = \frac{3y}{2E_F g(E_F)} \cong 1. \quad (21)$$

The reduction to $\gamma=1$ occurs in the effective-mass approximation.

The result in Eq. (18) is remarkably simple.

One does not have to write the electronic contribution ($\sim C_e$) in terms of the specific heat, of course, but if so written it suggests that perhaps a simple argument patterned after the one used for phonon drag (see Sec. 2 of Ref. 5) could be made.

V. DIRECT ARGUMENT

To do this consider a metal bar stretching from x_1 to $x_2 = x_1 + \Delta x$ in which the temperatures at the ends are maintained at T_1 and $T_2 = T_1 + (dT/dx)\Delta x$, with, say, $dT/dx < 0$. Consider now the \vec{k} electrons with energy $E(k) > E_F$, say, moving with velocity \vec{v}_k , v_{kx} in the positive x direction. Let Δt_k be the time it takes such an electron to traverse the bar ($\Delta t_k = \Delta x / v_{kx}$). The number of \vec{k} electrons entering unit cross section at x_1 in time Δt_k is $2f(\vec{k}, x_1) v_k \Delta t_k \times \hat{x} \cdot \hat{v}_k$, where the caret means unit vector. The number of \vec{k} electrons leaving unit cross section at x_2 is just the number in the truncated cylinder along the direction \vec{v}_k between x_1 and x_2 , namely, $2 \int_{x_1}^{x_2} f(\vec{k}, x) \hat{x} \cdot \hat{v}_k dx$. If we expand $f(x) = f_0(x_1) + (df_0/dx)(x - x_1)$, where f_0 is the equilibrium distribution, then the net number entering in time Δt_k in unit cross section is

$$-2 \frac{df_0}{dx} \hat{x} \cdot \hat{v}_k \int_{x_1}^{x_2} (x - x_1) dx = -\frac{df_0}{dx} \hat{x} \cdot \hat{v}_k (\Delta x)^2. \quad (22)$$

The volume associated with these electrons is $V_k = \Delta x \hat{x} \cdot \hat{v}_k$. Thus the number of \vec{k} electrons entering less the number leaving a unit volume in time Δt_k is

$$-\frac{df_0}{dx} \Delta x. \quad (23)$$

The momentum brought into unit volume per unit time by these electrons is

$$-\frac{df_0}{dx} (\Delta x / \Delta t_k) \hbar k_x \Rightarrow -\frac{2}{3} \frac{df_0}{dx} E(k). \quad (24)$$

A steady state implies that no net momentum accumulates in any volume. The variational-principle approximation in this problem is to allow only that there is no accumulation on the average, i. e., that the sum over k of Eq. (24) is zero,

$$\sum_{\vec{k}} E(k) \frac{df_0}{dx} = 0. \quad (25)$$

There are two external "forces" producing a df_0/dx . First, the temperature gradient gives $(df_0/dT)(dT/dx)$. Second, by forcing the current to be zero, one indirectly sets up an electric field \mathcal{E}_x in the bar by the electrons piling up at the ends. This provides an energy $-|e|\mathcal{E}_x x$ to be added to $E(k)$ in f_0 . Thus there will be a term $(df_0/dx) (= e\mathcal{E}_x)$,

$$\frac{df_0}{dx} = \frac{\partial f_0}{\partial T} \frac{dT}{dx} - |e| \mathcal{E}_x \frac{\partial f_0}{\partial E}. \quad (26)$$

The first term substituted into Eq. (25) gives essentially $C_e(dT/dx)$, the second term gives essen-

tially $|e|\mathcal{E}_x$. Solving for $\mathcal{E}_x/(dT/dx)$ gives the C_e contribution to S in Eq. (18).

There are a few points in this argument to mention. First, what was said in words here consists simply of multiplying the generalized Boltzmann equation including drag effects, Eq. (14) of Ref. 2, by k_x , neglecting the collision term L , and the phonon-drag term U and summing over \vec{k} . Second, the basic approximation was in allowing the electron-phonon interactions not to affect the behavior of the electrons as they wound their way through the bar, because of the drag limit and the freezing out of umklapp processes. At higher temperatures this is not the case, and the argument cannot be made. Or, in terms of Eq. (14) of Ref. 2, the collision terms cannot be neglected at higher temperatures. This means that a steady state cannot really be obtained by consideration only of electron-phonon processes in this temperature range, i. e., Eq. (14) of Ref. 2 has no solution if the collision term is neglected. Thus, in this "sub-drag-limit" region, a steady state is maintained by appeal to the impurity collisions. As regards the

thermopower, it is well known that it consists of a sum of the form $(W_{\text{ideal}}/W)S_{\text{ideal}} + (W_{\text{imp}}/W)S_{\text{imp}}$. The S_{ideal} is what Eq. (18) gives.

The solution in Eq. (18) indicates that the ultimate low-temperature behavior of the ideal thermopower is of the form $-(aT + bT^3)$, the sign being normal (negative) in both terms.

This completes the discussion of the results. The simple relations alluded to at the outset are Eqs. (9), (14), and (18). In the Appendix, the derivation (13) is made.

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APPENDIX

From Eqs. (81) and (82) of Ref. 2, with the \vec{k}' sum taken and E' replaced by $E + \hbar\omega$, and the \vec{k} sum converted to an energy times a surface ($\sim dS_k$) integral, the following are obtained:

$$d_{00} = \beta T^{-1} \sum_{j\vec{q}} [\hbar\omega(1 - e^{-z})]^{-1} \int dE f(E + \hbar\omega) [1 - f(E)] J_0, \quad (\text{A1})$$

$$d_{01} = \beta T^{-1} \sum_{j\vec{q}} [\hbar\omega(1 - e^{-z})]^{-1} \int dE f(E + \hbar\omega) [1 - f(E)] [\hbar\omega(J_0 + J_1) + (E - E_F)J_0]. \quad (\text{A2})$$

Here β is a constant ($\beta^{-1} = 24\pi^3 MN/V$, where M is the mass of the ion), $f(E)$ is the Fermi function, and the J 's are functions of E and of $j\vec{q}$,

$$J_0(E|j\vec{q}) = \sum_n \int_E dS_k (\vec{I}_{\vec{k}, \vec{k}+\vec{q}+\vec{k}_n} \cdot \hat{\xi})^2 |\nabla_k E|^{-1} (\vec{q} + \vec{k}_n) \cdot (\vec{q} + \vec{k}_n - \vec{Q}_0), \quad (\text{A3})$$

$$J_1(E|j\vec{q}) = \sum_n \int_E dS_k (\vec{I}_{\vec{k}, \vec{k}+\vec{q}+\vec{k}_n} \cdot \hat{\xi})^2 |\nabla_k E|^{-1} \vec{k} \cdot (\vec{q} + \vec{k}_n - \vec{Q}_0). \quad (\text{A4})$$

In this, I is the electron-phonon matrix element, $\hat{\xi}$ is the phonon-polarization unit vector, and

$$\vec{Q}_0(j\vec{q}) = \sum_n (\vec{q} + \vec{k}_n) \alpha(j\vec{q}, \vec{q} + \vec{k}_n). \quad (\text{A5})$$

\vec{Q}_0 was evaluated in Ref. 2, the α here being the same as in Eq. (4) above. If a phonon can engage in only one type of umklapp process, the normal one, then $\alpha = 1$, and $\vec{Q}_0 = \vec{q}$. Then the last brackets in Eqs. (A3) and (A4) are zero. This is the primary drag effect; it eliminates the small- q -phonon contribution.

The energy integrals can be evaluated by the usual expansion.⁸ If $J_0(E) = J_0(E_F) + (E - E_F)J'_0 + \dots$, then

$$d_{00} = -\beta T^{-1} \sum_{j\vec{q}} \frac{dN}{dz} J_0, \quad (\text{A6})$$

$$d_{01} = -\beta T^{-1} \sum_{j\vec{q}} \frac{dN}{dz} \times [\hbar\omega(\frac{1}{2}J_0 + J_1 + \frac{1}{3}\hbar\omega J'_0) + \frac{1}{3}\pi^2 k_B^2 T^2 J'_0]. \quad (\text{A7})$$

The one-pocket approximation rests on the idea that the $\vec{q}j$ sums in Eqs. (A6) and (A7) are dominated by contributions in one small pocket and that the slowly varying matrix elements such as J_0 and J_1 can be removed at some average value in the pocket. With this in mind, Eq. (13) results in

$$B = \frac{1}{2} + J_1/J_0, \quad (\text{A8})$$

$$Z = E_F J'_0 / (3J_0). \quad (\text{A9})$$

Although it does not look like it, Eq. (A6) is equivalent to Eq. (1) to within a constant (see Ref. 2, Sec. VII for a discussion).

- ¹M. Kaveh and N. Wiser, Phys. Rev. B 9, 4042 (1974); 9, 4053 (1974).
- ²M. Bailyn, Phys. Rev. 112, 1587 (1958).
- ³The original drag idea came from R. Peierls [Ann. Phys. (Leipz.) 4, 121 (1930)] in consideration of electrical resistivity. Peierls also proposed that umklapp processes are tied up with the equilibrium problem at low temperatures. L. Gurevich [J. Phys. USSR 10, 67 (1946)], explicitly used the idea in the thermopower to explain certain experiments.
- ⁴J. Ziman, Philos. Mag. 39, 371 (1959).
- ⁵M. Bailyn, Philos. Mag. 5, 1059 (1960), based on results in Ref. 2.
- ⁶The fact that the drag thermopower and specific heat are related has long been known. See, for example, D. K. C. MacDonald, Physica (Utr.) 20, 996 (1954).
- ⁷M. Wiser and N. Kaveh have pointed out in a private communication that, since the smallest frequencies at q_0 actually fall in the [110] direction, in which the cosine factors $[\hat{\xi} \cdot (\vec{k}' - \vec{k})]^2$ in R and α *vanish*, more care must be taken with the ratio A in the text. They point out that $[\rho]$, according to their Eqs. (3.5)–(3.7) of Ref. 1, is proportional to T , whereas an analogous argument applied to α gives $[S_D^*]$ independent of temperature. Thus the A in the text should be replaced by $A_0 T^{-1}$ where now A_0 is the constant. I am grateful for the permission of M. Kaveh and N. Wiser to include this note.
- ⁸See J. Ziman, *Electrons and Phonons* (Oxford U. P., London, England, 1960), p. 405.