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The Bipolar Righi-Leduc Effect

Recent measurements of the thermal conductivity of semiconductors have disclosed that, for PbTe,[1] InSb,[2, 3, 4] $Bi_2 Te_3$,[5, 6] and Germanium,[1, 7, 8] among others, an anomalous component, rapidly increasing with temperature, appears at the higher temperatures. Such an effect might be accounted for by the predicted bipolar contribution[10–16] to thermal conductivity; but there is only limited agreement between the theoretical formula for the latter and the experimental results so far available.[9] It appears, however, that the disagreements are such that the experimental values are in general the higher, and therefore consistent with the possibility of additional "anomalous" thermal conduction by other mechanisms, such as transport of energy by excitons.[1, 15]

A closer comparison of experiment and theory clearly depends on improvement of the measurements and on the reliability of the extrapolation, to the temperature range of the anomaly, of the lattice contribution to the thermal conductivity. In addition, the evaluation of the theoretical formula[17]

$$\kappa_{12}=(k/e)^2 T\sigma_1\rho\sigma_2\alpha^2 \tag{1}$$

for the bipolar contribution κ_{12} is limited in accuracy, at present for cases of interest, by uncertainties in the values of the component factors. In principle at least, these factors might be determined empirically, at each temperature, by measurements on a set of crystals spanning a sufficient range of doping for the position of the Fermi level to vary by an appreciable amount relative to the energy gap: the factor $\sigma_1\,\rho\sigma_2$ is known if the maximum resistivity, supposed determined in this way, is known; and similarly measurements of thermoelectric power,[18] or of Hall constant and Nernst coefficient,[19] will fix α.[20] Likewise, the variation of the total thermal conductivity κ with electrical conductivity σ, for a range of dopings at a fixed temperature, should determine κ_{12} (as well as the "extrinsic" contributions, κ_1 and κ_2, proportional to σ_1 and σ_2) empirically. However, apart from the practical appeal of simpler and more economical procedures, at the temperatures of interest the required impurity concentrations might be so large that the phenomenological formulas would be subject to large corrections.[21]

Thus the present situation is that, while the existence of the bipolar contribution to κ "cannot be denied,"[1] the extent of its contribution to the observed anomalies is not very well known or readily determined. On the other hand, little can be predicted, in practice, about the exciton contribution. There is, however, a transport effect connected with electronic thermal conduction, the Righi-Leduc Effect, for which it can be foreseen that there will be a bipolar contribution closely related to the bipolar contribution to thermal conduction. Furthermore, neither the lattice contribution nor an exciton contribution to κ should give corresponding components of the Righi-Leduc coefficient.[22] It appears possible, accordingly, that an estimate of κ_{12} might be obtainable from measurements of the latter.

The main purpose of this note is to derive the generalization of the theory of the bipolar contribution to κ so as to include the rotation of the energy-flux vector, relative to the temperature gradient, caused by a magnetic field: that is, the Righi-Leduc effect. It is useful, however, to go a little further in practice by extending the theory, of the bipolar contribution to κ, to the case where all the transport coefficients are dyadics of general form. The total energy flux may be written

$$\mathbf{W}=\mathbf{w}_1+\mathbf{w}_2-\boldsymbol{\kappa}_0\cdot\mathrm{grad}T\ , \tag{2}$$

where $\mathbf{w}_1$ and $\mathbf{w}_2$ are respectively the electron and hole contributions. These in turn are given by

$$\mathbf{w}_s=n_s[\pm\epsilon_{0s}\boldsymbol{\varepsilon}+kT\boldsymbol{\delta}_s]\cdot\mathbf{u}_s-\boldsymbol{\kappa}_s\cdot\mathrm{grad}T\ , \tag{3}$$

where $\boldsymbol{\varepsilon}$ is the unit dyadic, n_s, ϵ_{0s} and $\mathbf{u}_s$ are respectively the carrier concentrations, band-edge energies and carrier drift velocities (s = 1 for electrons, 2 for holes), and where the upper sign is for electrons and the lower sign is for holes. The corresponding equation for the drift velocity is

$$\mathbf{u}_s=\boldsymbol{\mu}_s\cdot\Big[\mp\Big(\mathbf{E}+\frac{1}{eT}\Big(\epsilon_{0s}-\zeta+T\frac{d\zeta}{dT}\Big)\mathrm{grad}T\Big) \\ -\Big(\frac{k}{e}\Big)\boldsymbol{\delta}_s^{\simeq}\cdot\,\mathrm{grad}T\Big]\ , \tag{4}$$

where ζ is the chemical potential of the electrons and $\mathbf{E}$ is the electric field. The significance of the $^{\simeq}$ notation introduced in (4) is:

$$\tau^{\simeq}{}_{ij}(\mathbf{H})\equiv\tau_{ji}(-\mathbf{H}) \tag{5}$$

for any dyadic $\boldsymbol{\tau}(\mathbf{H})$, where $\mathbf{H}$ is the magnetic field. The connection between the coefficients in (4) and those in (3) results from the Onsager reciprocal relations.[18, 23] The thermal conductivity is given by

$$\mathbf{W}=-\boldsymbol{\kappa}\cdot\mathrm{grad}T+(\mathrm{const.})\mathbf{J}$$

where $\mathbf{J}$ = e ($n_2\mathbf{u}_2$ − $n_1\mathbf{u}_1$) is the electric current density. On solving (4) for $\mathbf{E}$ as a function of $\mathbf{J}$ and grad T, and (2), (3) and (4) for $\mathbf{W}$ as a function of $\mathbf{E}$ and grad T, and combining the two solutions, one finds:

$$\boldsymbol{\kappa}=\boldsymbol{\kappa}_0+\boldsymbol{\kappa}_1+\boldsymbol{\kappa}_2+(k/e)^2T\boldsymbol{\alpha}\cdot(\boldsymbol{\sigma}_1\cdot\boldsymbol{\rho}\cdot\boldsymbol{\sigma}_2)\cdot\boldsymbol{\alpha}^{\simeq}\ , \tag{6}$$

where

$$\boldsymbol{\sigma}_s \equiv e n_s \boldsymbol{\mu}_s \ , \tag{7}$$

$$\boldsymbol{\rho} \equiv \boldsymbol{\sigma}^{-1} \equiv (\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2)^{-1} \ , \tag{8}$$

$$\boldsymbol{\alpha} \equiv [(\epsilon_{01} - \epsilon_{02})/kT]\boldsymbol{\varepsilon} + \boldsymbol{\delta}_1 + \boldsymbol{\delta}_2 \ . \tag{9}$$

(From the definition (8) of $\boldsymbol{\rho}$ follows an algebraic identity $\boldsymbol{\sigma}_1 \cdot \boldsymbol{\rho} \cdot \boldsymbol{\sigma}_2 = \boldsymbol{\sigma}_2 \cdot \boldsymbol{\rho} \cdot \boldsymbol{\sigma}_1$.)

In the absence of a magnetic field the dyadics summed on the right of (6) are all symmetric. To examine the Righi-Leduc effect for a *cubic* crystal, we expand the transport coefficients in powers of **H** up to the first power. For the thermal conductivity we have

$$\boldsymbol{\kappa} = \kappa(\boldsymbol{\varepsilon} + S\mathbf{H} \times \boldsymbol{\varepsilon}), \tag{10}$$

S being the Righi-Leduc coefficient. The corresponding expansions of the band coefficients are

$$\boldsymbol{\mu}_s = \mu_s(\boldsymbol{\varepsilon} \pm (\mu_s^H/c)\mathbf{H} \times \boldsymbol{\varepsilon}) \ , \tag{11}$$

$$\boldsymbol{\delta}_s = \delta_s(\boldsymbol{\varepsilon} \pm (eB_s/k)\mathbf{H} \times \boldsymbol{\varepsilon}) \ , \tag{12}$$

$$\boldsymbol{\kappa}_s = \kappa_s(\boldsymbol{\varepsilon} + S_s\mathbf{H} \times \boldsymbol{\varepsilon}) \ . \tag{13}$$

Here μ_1^H and μ_2^H are the band Hall mobilities, B_1 and B_2 the extrinsic Nernst coefficients. Then

$$\boldsymbol{\sigma}_1 \cdot \boldsymbol{\rho} \cdot \boldsymbol{\sigma}_2 = \sigma_1 \rho \sigma_2 (\boldsymbol{\varepsilon} + (\mu^{H*}/c)\mathbf{H} \times \boldsymbol{\varepsilon}) \ , \tag{14}$$

where

$$\mu^{H*} \equiv (\sigma_2 \mu_1^H - \sigma_1 \mu_2^H)/\sigma \tag{15}$$

and

$\sigma_1 = e n_1 \mu_1$, etc.;

$$\boldsymbol{\alpha} = \boldsymbol{\alpha}^{\sim} = \alpha \boldsymbol{\varepsilon} + eT(B_1 - B_2)\mathbf{H} \times \boldsymbol{\varepsilon} \ , \tag{16}$$

where

$$\alpha \equiv [(\epsilon_{01} - \epsilon_{02})/kT] + \delta_1 + \delta_2 \ . \tag{17}$$

Finally, on substituting (14) and (16) into (6), we have, for the coefficients in (10),

$$\kappa = \kappa_0 + \kappa_1 + \kappa_2 + \kappa_{12} \tag{18}$$

(where κ_{12} is given by (1)) and

$$S\kappa = S_1 \kappa_1 + S_2 \kappa_2 + S_{12} \kappa_{12} \tag{19}$$

where

$$S_{12} = \frac{\mu^{H*}}{c} + \frac{2}{\alpha} \frac{e}{k}(B_1 - B_2) \ . \tag{20}$$

The contribution $S_1\kappa_1 + S_2\kappa_2$ in (19) introduces band phenomenological constants peculiar to the Righi-Leduc effect. However, this contribution may be expected to be negligible compared with the final term $S_{12}\kappa_{12}$, for the conditions in which we are interested, since S_{12} should be of the same order of magnitude as S_1 and S_2. Furthermore the second term on the right of (20) should be of order of magnitude $1/\alpha$ times the first term; and so it should usually be legitimate to retain only the first term,within the accuracy that we may hope for.

Then

$$S\kappa \simeq \mu^{H*} \kappa_{12}/c \ . \tag{21}$$

Thus μ^{H*} is effectively the "Righi-Leduc mobility," giving the angle between the vectors ($\mathbf{W} + \kappa_0$ grad T) and grad T. The Hall mobility,[24]

$$\mu^H = (\sigma_2 \mu_2^H - \sigma_1 \mu_1^H)/\sigma \ , \tag{22}$$

is simply related to μ^{H*}:

$$\mu^H - \mu^{H*} = \mu_2^H - \mu_1^H \ . \tag{23}$$

The right-hand side of (23) is equal to twice the Hall mobility for the state of maximum resistivity, at the temperature in question, provided the μ_s^H are the same for this state as for the material to which the left-hand side refers (and provided the μ_s do not vary with doping near maximum resistivity). Where μ^{H*} may be determined, by the foregoing result, from a Dunlap ellipse, and where (21) applies, it is thus possible in principle to *deduce* κ_{12} from measurements of the total conductivity κ and of the angle between **W** and grad T. For temperatures where the doping required to shift the Fermi level appreciably (from its position for the intrinsic state) is too heavy for it to be possible to determine μ^{H*} directly from "Dunlap ellipse" data, one might perhaps, by extrapolation of mobility ratios from lower temperatures, still get estimates of μ^{H*} which are of tolerable accuracy for useful estimates of κ_{12}.

For the intrinsic state, μ^{H*} is proportional to

$$\frac{\mu_1^H}{\mu_1} - \frac{\mu_2^H}{\mu_2} \ .$$

According to the standard model of the bands, for which each of the two ratios of Hall to drift mobility is equal to $3\pi/8$, the first term of (20) therefore vanishes, and S_{12} should be small compared with μ^H/c. One should not expect the two ratios to be equal in practice, however. From experimental values of the mobilities for germanium,[25] we estimate $\mu^{H*} \simeq -1000$ cm²/volt sec. at 300°K. Linear extrapolations of the mobility data give $\mu^{H*} \sim -200$ cm²/volt sec. at 1000°K, but the extrapolation of μ_2^H/μ_2 especially seems dubious. (If μ_2^H/μ_2 does not increase much more above 300°, the true value of μ^{H*} at 1000° should be nearer -100.) It appears that, to obtain appreciable Righi-Leduc angles in the temperature range of the observed anomaly for germanium, very strong magnetic fields should be required.

References and footnotes

1. A. F. Ioffé, *Canad. J. Phys.* **34**, 1342 (1956).
2. G. Busch and M. Schneider, *Physica* **20**, 1084 (1954).
3. H. Weiss, Garmisch Conference, 1956 (to be published); H. P. R. Frederikse and E. Mielczarek, unpublished.
4. See also A. D. Stuckes, *Phys. Rev.* **107**, 427 (1957).
5. H. J. Goldsmid, *Proc. Phys. Soc.* B, **69**, 203 (1956).
6. C. B. Satterthwaite and R. W. Ure, Jr., *Phys. Rev.* **108**, 1164 (1957).

7. F. Kettel, Münster meeting of the German Physical Society, April 1957 (to be published). I am indebted to Dr. Kettel for a copy of his paper.
8. There is a substantial discrepancy between Kettel's measured values and those published by Ioffé. The values given by K. A. McCarthy and S. S. Ballard, *Phys. Rev.* **99**, 1104 (1955), for temperatures below the anomalous range, lie between Ioffé's and Kettel's.
9. For Bi_2Te_3, the agreement seems to be as good as would be plausible (references 6 and 15). For InSb and for Ge, the results of different experimenters disagree seriously. For PbTe, according to Ioffé (reference 1), the anomaly is already important at temperatures for which the bipolar contribution should still be negligible.
10. Davydov and Schmushkevich, *Uspekhi Fiz. Nauk* **24**, 21 (1940) (cited by Ioffé in reference 1). The name "bipolar," introduced by the Soviet physicists, seems better than (as well as prior to) the name "ambipolar" introduced by myself. It is proposed to adopt the former.
11. P. J. Price, *Phys. Rev.* **95**, 596 (1954) (Abstract); *Phil. Mag.* **46**, 1192 (1955).
12. H. Fröhlich and C. Kittel, *Physica* **20**, 1086 (1954).
13. J. M. Thuillier, *Comptes Rendus* **241**, 1121 (1955); **242**, 2633 (1956).
14. O. Madelung, *Zeits. f. Naturforschung* **11a**, 478 (1956); *Encyclopedia of Physics* **20**, 88, Springer 1957.
15. P. J. Price, *Proc. Phys. Soc.* B, **69**, 851 (1956).
16. P. J. Price, *IBM Journal* **1**, 147 (1957).
17. The notation is as given below. Eq. (1) is for a cubic crystal. The generalization for lower symmetries, indicated in reference 15, is given by Eq. (6) of the present paper.
18. P. J. Price, *Phys. Rev.* **104**, 1223 (1956).
19. P. J. Price, *Phys. Rev.* **102**, 1245 (1956).
20. This method should be inherently more accurate (except for the limitations noted in footnote 21) than those based on measurements for a single sample over a range of temperature, in that the latter involve the temperature dependence of the band transport coefficients and of the energy gap.
21. Heavy doping might change the lattice contribution to κ, and could change the forbidden gap and the band transport coefficients.
22. On the other hand, one might expect a contribution corresponding to the component of κ due to inhomogeneity of the sample (see Eq. (9) of reference 1).
23. The form of Eq. (4) allows for dependence of the ϵ_{0s} on temperature (reference 18; O. Madelung, *Zeits. f. Naturforschung*, **13a**, 22 (1958)).
24. It is convenient here to define the Hall mobility, in (22), so that it corresponds to the Hall angle in sign as well as in magnitude.
25. F. J. Morin and J. P. Maita, *Phys. Rev.* **94**, 1525 (1954).

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