Effects of two-stage drag of carriers by phonons on the electrical conductivity and maximum thermoelectric power of pure semimetals with a low density of carriers

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The effects of a two-stage drag on the electrical conductivity and maximum thermoelectric power of pure semimetals with a low carrier density are studied. It is shown that the maximum in the temperature dependence of the drag thermoelectric power need not be related to scattering of phonons from the surface of a sample. This maximum occurs when the two-stage drag begins to manifest itself in the conductivity. The thermoelectric power due to the two-stage drag decreases with decreasing temperature following the T^3 law, as in the case of the thermoelectric power of typical metals. The proposed theory can explain the observed absence of a plateau in the temperature dependence of the drag thermoelectric power of semimetals, which is predicted by the theory of a one-stage drag of the Herring type.
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A two-stage drag of electrons by phonons in semiconductors and in semimetals occurs because carriers are dragged by phonons of wavelength comparable with the electron wavelength and also because long-wavelength phonons are dragged by thermal phonons of much shorter wavelengths.[1] A two-stage electron-phonon drag in perfect crystals with a small number of free carriers can lead to an exponential growth of thermoelectric and ther-momagnetic coefficients at low temperatures $\sim \exp(\Theta/T)$, where Θ is a temperature of the order of the Debye temperature. Such temperature dependence cannot be obtained for the standard one-stage drag. The expected behavior of the aforementioned transport coefficients was observed in Refs. 2 and 3, for single crystals of bismuth of not very high purity. It is clear that such an exponential growth cannot continue down to the lowest temperatures because of the phonon scattering from, in particular, the surface of the sample, as in the case of the standard drag of the Herring type.[4, 5]

However, a maximum in the temperature dependence of the thermoelectric power due to the two-stage drag can be explained also by another mechanism rather than by the scattering of phonons from a surface. We can understand this mechanism qualitatively by analyzing the expression for the thermoelectric power on the basis of Kubo′s formulas

$$a = \frac{1}{T_\sigma} \int_0^\infty \left\langle \hat{q}; \hat{j}(t) \right\rangle dt, \quad \sigma = \frac{1}{T} \int_0^\infty \left\langle \hat{j}; \hat{j}(t) \right\rangle dt, \tag{1}$$

where $\hat{q}$ and $\hat{j}$ are heat and electric current operators. The following important conclusions can be obtained from equation (1). It is clear that a can depend exponentially on the temperature only when there are two characteristic decay times of the correlation functions $\left\langle \hat{q}; \hat{j}(t) \right\rangle$ and $\left\langle \hat{j}; \hat{j}(t) \right\rangle$, i.e., for carriers and phonons. In particular, such a situation is realized for the two-stage phonon-phonon drag when the characteristic relaxation time in the phonon system is determined by the umklapp scattering between phonons and, therefore, we obtain $\sim \exp(\Theta/T)$. The relaxation time of carriers, which determines the conductivity, is proportional to a power of the temperature since it is governed by the normal scattering of electrons from phonons. This result holds at temperatures when the number of phonons available for the interaction with electrons is large compared with the number of electrons in a semimetal or in a semiconductor. It follows that phonons play the role of a thermostat for electrons: they absorb the electron momentum but they do not "feel" effectively the reverse effect of electrons on phonon states.

However, it can be seen from equation (1) that, in the situation when the correlation functions $\left\langle \hat{j}; \hat{j}(t) \right\rangle$ and $\left\langle \hat{q}; \hat{j}(t) \right\rangle$ are determined by the same decay time τ, the quantity α is independent of this time. In fact, such a situation applies to metals and semimetals at very low temperatures when the number

of phonons is comparable with the number of electrons. The no equilibrium behavior of both phonon and electron subsystems is then determined by the same electron-phonon interaction. As a result, the thermoelectric power due to the two-stage drag should cease to grow exponentially with decreasing T when the phonon-phonon drag begins to influence strongly the conduction. The thermoelectric power should then decrease with decreasing temperature, as in the standard theory of drag in metals.[6] A maximum in the thermoelectric power independent of the dimensions of the sample should then manifest Itself in this temperature range.

These considerations apply to the situation when there is only one type of carrier. The effect should be then best observable in semimetals. However, since the electron and hole densities in perfect crystals are exactly equal to one another, the drag effect does not contribute to the thermoelectric power provided the scattering of quasiparticles is due only to the electron-phonon and phonon-phonon effects.[7] A nonzero contribution due to the two-stage drag appears only when there is an asymmetry in the scattering of electrons and holes, for example, diffuse scattering of carriers of one type from the surface of a sample and specula scattering of the other type of carrier. The thermoelectric power due to the drag effect then increases considerably.[7] The situation in the conduction is not so clear. On the one hand, enhancement of the scattering of carriers due to a new scattering mechanism should slow them down, i.e., the conductivity should decrease but, on the other hand, the presence of an oriented flux of phonons enhances the mobility of carriers. Only detailed calculations can predict the behavior of the conductivity.

We shall study the temperature dependence of the thermoelectric power due to the two-stage drag using a model of an isotropic semimetal with a small number of carriers, such as bismuth. We shall also calculate the temperature dependence of the conductivity. As already noted in Ref. 7, the transport equation used to study the effect of the two-stage drag on the conductivity and describing the motion of thermal phonons should include a collision integral for collisions of thermal phonons with long-wavelength phonons, i.e., with the phonons which interact with carriers and transfer the momentum received from carriers to thermal phonons. The corresponding system of transport equations for both groups of phonons and for carriers of both types assumes the form

$$s \nabla T \frac{\partial F_q}{\partial T} = I^N \left\{ F_q ; F_q \right\} + I^U \left\{ F_q ; F_q \right\} + I^N \left\{ F_q ; G_q \right\} \tag{2}$$

$$s \nabla T \frac{\partial G_q}{\partial T} = I^N \left\{ G_q ; F_q \right\} + \sum_{\pm} I^N \left\{ G_q ; f_p^{\pm} \right\} \tag{3}$$

$$e^{\pm} E \frac{\partial f_p^{\pm}}{\partial p} + v_p^{\pm} \nabla T \frac{\partial f_p^{\pm}}{\partial T} = I^N \left\{ f_p^{\pm} ; G_q \right\} + I \left\{ f_p^{\pm} ; D \right\} \tag{4}$$

where F_q and G_q are the distribution functions of thermal and long-wavelength phonons and $f_p^{\pm}$ is the distribution function of holes and electrons. The quantities $\hat{I}^N$ and $\hat{I}^U$ are the collision integrals describing the normal and umklapp scattering of quasiparticles; $I\{f_p^{\pm}; D\}$ are the collision integrals describing the scattering of carriers from long-wavelength objects, for example, from the surface of the sample; s is the velocity of sound; and e is the electronic charge.

We shall seek the solution of the system of equations (2)-(4) in the form

$$F_q = F_q^0 - qU \frac{\partial F_q^o}{\partial \omega_q}, \tag{5}$$

$$G_q = G_q^0 - qu \frac{\partial G_q^0}{\partial \omega_q}, \tag{6}$$

and

$$f_p^{\pm} = f_p^{0\pm} - pV_{\pm} \frac{\partial f_p^{0\pm}}{\partial \varepsilon_p}, \tag{7}$$

where $u(q)$, $U(q)$, and $V \pm (\varepsilon_p)$ are unknown vectors and the superscript 0 identifies the equilibrium parts of the corresponding distribution functions of quasiparticles.

The corresponding drift velocities can be obtained by the standard method of successive approximations subject to the condition that the normal scattering of quasiparticles is assumed to be more frequent than the umklapp scattering.[8] Substituting equations (5)-(7) in the law of conservation of the momentum,[9] we obtain a relationship between U and $V_{\pm}$

$$ div \left\{ \left\langle\!\left\langle q_i\ s_i\ F_q \right\rangle\!\right\rangle \right\} = \left\langle\!\left\langle q_i\ I^U \left\{ F_q;\ F_q \right\} \right\rangle\!\right\rangle + \sum_{\pm} \left\langle\!\left\langle p_i^{\pm}\ I \left\{ f_p^{\pm};\ D \right\} \right\rangle\!\right\rangle, \tag{8} $$

where the angular brackets indicate averages of the type

$$ \left\langle\!\left\langle \Phi(q) \right\rangle\!\right\rangle = \frac{1}{\hbar^3} \int \Phi(q)\, dq. $$

Equation (8) should be supplemented by a system of equations following from equation (4) in which the corresponding collision integrals of carriers with phonons include non-equilibrium corrections to the phonon distribution function (Ref. 10), i.e.,

$$ V^+ \left(1 - \gamma^+\right) - \gamma^+ \frac{l_f^+}{l_f^-} V^- = \frac{l^+}{l_f^+} U \left\langle \frac{L}{L_q} \right\rangle + \frac{l^+}{P_F} e^+ E - \frac{l^+}{l_f^+} \left\langle \frac{L}{L_q} \right\rangle \gamma\, \tau^U\, \nabla T, \tag{9} $$

$$ V^- \left(1 - \gamma^-\right) - \gamma^- \frac{l_f^-}{l_f^+} V^+ = \frac{l^-}{l_f^-} U \left\langle \frac{L}{L_q} \right\rangle + \frac{l^-}{P_F} e^- E - \frac{l^-}{l_f^-} \left\langle \frac{L}{L_q} \right\rangle \gamma\, \tau^U\, \nabla T \tag{10} $$

where

$$ \gamma^{\pm} = \frac{l^{\pm}}{4\, p_F^4\, l_f^{\pm}} \int_0^{2p_F} \frac{L}{L_q}\, q^3\, dq, \qquad \left\langle \frac{L}{L_q} \right\rangle = \frac{1}{4\, p_F^4} \int_0^{2p_F} \frac{L}{L_q}\, q^3\, dq, $$

p_F is the Fermi momentum; $L^{\pm}$ is the mean free path of long-wavelength phonons interacting with carriers due to their scattering from holes (electrons); L is the total mean free path of such phonons given by

$$ \frac{1}{L} = \frac{1}{L^+} + \frac{1}{L^-} + \frac{1}{L_q}; $$

L_q is the mean free path of long-wavelength phonons due to their normal scattering from thermal phonons; $l_f^{\pm}$ is the mean free path of holes (electron) due to their scattering from phonons; and $l^{\pm}$ is the total mean free path of carriers given by

$$ \frac{1}{l^{\pm}} = \frac{1}{l_f^{\pm}} + \frac{1}{l_d^{\pm}}, $$

where $l_d^{\pm} = \tau_d^{\pm} V_F$ is the mean free path of holes (electrons) due to their scattering from additional objects. The quantity γ in equations (9) and (10) is defined by

$$ \gamma = \frac{1}{T} \int qs\omega(q)\, \frac{\partial F_q^0}{\partial \omega q}\, dq \bigg/ \int q^2\, \frac{\partial F_q^0}{\partial \omega_q}\, dq. \tag{11} $$

For an isotropic phonon spectrum, it follows from equation (11) that $\gamma \approx s^2/T$.

The solution of equation (8) yields the following drift velocity U:

$$ U = m_+ n\, \beta_1\, \frac{\tau^U}{\tau_d^+}\, V_F^+ + m_-\, n\, \beta_1\, \frac{\tau^U}{\tau_d^-}\, V_F^- - \gamma\, \tau^U\, V T. \tag{12} $$

Here, $m_{\pm}$ is the effective mass of holes and electrons and n is the carrier density. The quantity β_1 is

defined by

$$\beta_1^{-1} = \int q^2 \, \frac{\partial F_q^0}{\partial \omega_q} \, dq. \tag{13}$$

For degenerate carriers, we find that the electric current is given by

$$j = n e^2 \left(V_F^+ - V_F^- \right), \tag{14}$$

where V_F^+ and V_F^- satisfy the system of equations (9), (10), and (12) subject to the assumption that the electron gas is completely degenerate.

We shall first discuss the conductivity y due to the two-stage drag. A general expression for σ_2 following from the system of equations (9)-(14) is rather complex and we shall not quote it. Simple physical results can be obtained only in certain limiting cases. However, the qualitative behavior remains unchanged. We shall study the case when one type of carrier, for example, holes, is scattered secularly from the surface and the scattering of electrons is of the diffuse type. Mathematically, this is equivalent to $\tau_d^+ \to \infty$. The corresponding conductivity σ_2 is then given by

$$\sigma_2 = \frac{n e^2}{p_F} \; \frac{\left(l_f^+ + l^- \right) - \left(l_f^+ + l_f^- \right) \left[\left(\gamma^- + \gamma^+ \, \dfrac{l_d^-}{l_d^- - l_f^-} \right) + \left\langle \dfrac{L}{L_q} \right\rangle n \beta_1 \, p_F \, \tau^U \Big/ \left(l_f^- + l_d^- \right) \right]}{\left(1 - \gamma^- - \gamma^+ \right) + \left\langle \dfrac{L}{L_q} \right\rangle n \beta_1 \, p_F \, \tau^U \Big/ \left(l_f^- + l_d^- \right)}. \tag{15}$$

In the absence of an additional scattering mechanism $\tau_d^- \to \infty$, $l^- = l_f^-$, it follows from Eq. (15) that the drag effect does not contribute to the total conductivity (as expected) and σ_2 is given by the standard expression

$$\sigma_2 = \frac{n e^2}{p_F} \left(l_f^- + l_f^+ \right). \tag{16}$$

When there is an asymmetry in the scattering of carriers, the drag effect can influence strongly the conductivity. Two limiting cases are of special interest. In the first case, when the terms proportional to τ^U in the numerator and denominator in equation (15) can be neglected, we obtain from equation (15) a result which agrees with the corresponding expression obtained in Ref. 10, i.e.,

$$\sigma_2 = \frac{n e^2}{p_F} \left(l_f^+ + l^- \right) \left(1 + \frac{\gamma^+ l_f^+ \left(l_f^- \right)^2}{\left(l_f^+ + l^- \right) \left(l_d^- + l_f^- \right)^2 \left(1 - \gamma^- - \gamma^+ \right)} \right). \tag{17}$$

In this limiting case, corresponding essentially to the absence of the two-stage drag, the drift of phonons does not influence the conductivity.

In the opposite limiting case when τ^U is large and the terms in the numerator and denominator in equation (15) not containing τ^U can be neglected, we again obtain from equation (15) a result for σ_2 which reduces to equation (16). However, in contrast to the case studied earlier, the conductivity y increases in the present context due to the electron-phonon drag since, in the absence of the drag, the expression for σ should involve τ_d^-. The effect of the drag is to increase the conductivity up to a value corresponding to the absence of additional scattering of carriers, i.e., approximately by a factor of $l_f^- \big/ l_f^+$. The temperature dependence of the total conductivity should be stronger than the temperature dependence corresponding to the scattering of electrons and holes from equilibrium phonons. When the ratio $l_f^- \big/ l_f^+$ is large, which corresponds to the experimental conditions for bismuth, the deviation of the temperature dependence of σ_2 due to the phonon-phonon drag from the value of y corresponding to equilibrium

phonons should be observable.

The thermoelectric power due to the phonon-phonon drag can be calculated from equations (9), (10), and (12) and from the condition j = 0. The corresponding result in the limit $\tau_d^+ \to \infty$ is given by

$$\alpha_2 = \frac{p_F}{e} \frac{\gamma\,\tau \left\langle \frac{L}{L_q} \right\rangle \left(l^-/l_f^- - 1 \right)}{\left(l_f^+ - l^- \right) - \left(l_f^+ + l_f^- \right) \left[\left(\gamma^- + \gamma^+ l_d^- \right) / \left(l_d^- + l_f^- \right) + \left\langle \frac{L}{L_q} \right\rangle n\,\beta_1 p_F\,\tau^U / \left(l_d^- + l_f^- \right) \right]} \tag{18}$$

In the limit when the phonon-phonon drag has only a weak effect on the conductivity, we have $s_\tau U / L_q \prec\prec 1$ and the last term in the denominator can be neglected; it then follows from equation (18) that the expression for α_2 reduces to the corresponding result of Ref. 7. In the opposite limit, using $n\,\beta_1 \approx s^2 / T \left(T/sp_F \right)^3$, we can transfer equation (18) to the form

$$\alpha_2 \approx \frac{1}{e} \left(T/sp_F \right)^3 l_f^- / \left(l_f^+ + l_f^- \right). \tag{19}$$

It follows from equation (19) that α_2 decreases with decreasing temperature as T^3. However, in contrast to typical metals with one type of carrier whose thermoelectric power due to the drag of electrons by phonons decreases at low temperatures T «Θ и following the law (T «Θ)^3 (see Ref. 6), we find that α due to the two-stage drag is proportional to the cube of a large parameter T/sp_F, i.e., to the principal parameter in the theory of the two-stage drag.

It follows from our results that the temperature dependence of the thermoelectric power due to the two-stage drag should exhibit a maximum even in the absence of the scattering of phonons from the surface of a sample. In fact, the finding that the thermoelectric power due to the phonon drag is proportional to $\left(L^U / l_f^\pm \right) \left(v_F / s \right)$ indicates that the aforementioned situation should occur in real crystals. Since $v_F\,s \approx 10^3$ holds for semimetals similar to bismuth, high thermoelectric emfs can occur even when the mean free path of carriers is longer than the phonon mean free path. Since the ratio $(T/sp_F)^3$ can be quite large at moderate temperatures, the maximum value of α_2 due to the two-stage drag can be much greater than k/e which represents the maximum attainable value of the thermoelectric power due to the standard drag of electrons by phonons.

The second important conclusion following from our theory is that there is no plateau in the temperature dependence of the thermoelectric power due to the two-stage drag. Such a plateau is typical of the one-stage drag of the Herring type in semimetals.[4] This result follows since the temperature T_0 at which long-wavelength phonons determine the scattering of carriers and the temperature T_1 corresponding to the conditions when the Fermi momentum is equal to the average momentum of thermal phonons differ from one another in semimetals similar to bismuth.[10] However, such a plateau has not been observed for typical semimetals such as bismuth, which supports our mechanism of the two-stage drag for the thermoelectric power of bismuth. In fact, the thermoelectric power α of pure and perfect bismuth single crystals was found to increase at temperatures to the right of the maximum.

Since the characteristic maximum in the temperature dependence of the drag thermoelectric power is usually attributed to the scattering of phonons from the sur-face of a sample, it would be desirable to carry out care-ful measurements of the temperature dependence of α at temperatures below its maximum. Our estimates indicate that the exponents in the power law governing the decay of α with temperature to the left of the maximum of the thermoelectric power differ at least by one for the mechanism studied in the present paper and for the mechanism corresponding to the scattering of phonons from the surface. Such a difference should be measurable. Naturally, the temperature corresponding to the maximum in the thermoelectric power due to the mechanism studied in the present paper is independent of the dimensions of the sample.

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