Effect of Phonon Drag on the Electrical Resistivity of Metals*

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It is shown that the phonon-drag component ρ_g of the electrical resistivity and the phonon-drag component S_g of the thermoelectric power of a metal are related through the equation $\rho_g=S_g^2T/\kappa_L$, where T and κ_L are the absolute temperature and the lattice thermal conductivity, respectively. The relation is used to calculate the influence of phonon drag on the electrical resistivity of gold and platinum from the experimentally determined quantities S_g and κ_L. It is found that in gold and platinum phonon-drag effects reduce the electrical resistivity by less than 0.5 and 1.6%, respectively, above 20°K. The relation can serve to calculate the deviations from the Matthiessen rule in the lattice-defect electrical resistivity which are caused by changes in ρ_g due to the phonon scattering by the imperfections. Such deviations from the Matthiessen rule are estimated for lattice vacancies in gold and platinum and are found to be negligible.

INTRODUCTION

IN the Bloch theory of the electrical conductivity of metals it is assumed that the phonon system is in thermal equilibrium. If the phonon distribution departs sufficiently from equilibrium because of the presence of an electric field, agreement between the Bloch theory and the observed electrical conductivities could not be expected. Experimentally the Bloch theory appears to be confirmed in many metals down to temperatures of a few degrees Kelvin. At very low temperatures, say below 5°K, where phonon-drag effects on the electrical resistivity might become appreciable, deviations from the Bloch theory may be difficult to observe because of the electron scattering by lattice imperfections.

Whereas phonon-drag effects on the electrical resistivity are apparently negligible, deviations from thermal equilibrium in the phonon system have a very pronounced effect on the thermoelectric power.[1] The reason why phonon-drag effects are much more pronounced in the thermoelectric power than in the electrical resistivity lies in the fact that the phonon-drag thermopower is a first-order effect caused by the interaction between the phonon-current present in a temperature gradient and the electrons. The influence of phonon drag on the electrical resistivity is a second-order effect. The electron current, built up by an electric field, causes a current in the phonon system, which then acts back on the electrons.

It is the purpose of this paper to show that a relation exists between the effects of phonon drag on the electrical resistivity and on the thermoelectric power. This relation is derived from the results of Ziman's variational treatment[2] of the effects of nonequilibrium in the phonon system on the transport properties. The relation between the effects of phonon drag on the electrical resistivity and on the thermoelectric power is also derived using simple physical arguments. The relation is used for calculating the phonon-drag component of the electrical resistivity of gold and platinum from the experimentally determined phonon-drag component of the thermoelectric power. Finally, the deviations from the Matthiessen rule in the electrical resistivity of point defects, which may occur through the scattering of phonons by the lattice defects, are estimated.

RELATION BETWEEN THE EFFECTS OF PHONON DRAG ON THE ELECTRICAL RESISTIVITY AND ON THE THERMOELECTRIC POWER

We reproduce here the expressions for the various transport properties obtained by Ziman[2] with a variational method taking into account deviations from thermal equilibrium in both the electron and the phonon system. The variational principle used by Ziman requires the maximization of the rate of entropy production. For the electrical resistivity caused by the electron-phonon interaction Ziman obtained

$$\rho=\rho_L-\rho_g, \tag{1}$$

where

$$\rho_g=\rho_L(P_{1L}^2/P_{11}P_{LL}). \tag{2}$$

Here ρ_L is the electrical resistivity for the case that the phonon system is in complete thermal equilibrium. ρ_L is given by

$$\rho_L=P_{11}/J_1^2, \tag{3}$$

where J_1 is the generalized electron current. According to Eq. (1) the departure from equilibrium in the phonon system reduces the electrical resistivity by the "phonon-drag" component ρ_g.

The lattice thermal conductivity is given by

$$\kappa_L=(1/T)(U_L^2/P_{LL}), \tag{4}$$

where T is the absolute temperature and U_L is the lattice thermal flux. Apparently the lattice thermal conductivity is not affected by deviations from equilibrium in the electron system. The nonequilibrium in the phonon system causes an additional contribution to the thermoelectric power. According to Ziman, the phonon-

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.
[1] D. K. C. MacDonald, *Thermoelectricity* (John Wiley & Sons, Inc., New York, 1962).
[2] J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960); J. M. Ziman, Phil. Mag. 4, 371 (1959); J. G. Collins and J. M. Ziman, Proc. Roy. Soc. (London) **A264**, 60 (1961).

drag component of the thermoelectric power is

$$S_g=-(U_L/TJ_1)(P_{1L}/P_{LL}). \tag{5}$$

The scattering integrals P_{11}, P_{1L}, and P_{LL} are defined by

$$P_{11}=(k_BT)^{-1}\int\int\int(\phi_{k_1}-\phi_{k_1'})\times P_{k,q}{}^{k'}(\phi_{k_2}-\phi_{k_2'})\,d\mathbf{q}d\mathbf{k}'d\mathbf{k}, \tag{6a}$$

$$P_{1L}=(k_BT)^{-1}\int\int\int(\phi_{k_1}-\phi_{k_1'})P_{k,q}{}^{k'}\phi_L\,d\mathbf{q}d\mathbf{k}'d\mathbf{k}, \tag{6b}$$

$$P_{LL}=(k_BT)^{-1}\int\int\int\phi_L P_{k,q}{}^{k'}\phi_L\,d\mathbf{q}d\mathbf{k}'d\mathbf{k}. \tag{6c}$$

Here $P_{k,q}{}^{k'}$ is the probability for an electron transition from state $\mathbf{k}$ to $\mathbf{k}'$ by absorption of a phonon $\mathbf{q}$. k_B is Boltzmann's constant. The functions ϕ_{k_1}, ϕ_{k_2}, and ϕ_L are trial functions used in the variational method. They are given by

$$f_k=f_k{}^0-\Phi_k(df_k{}^0/dE_k), \tag{7a}$$

$$\Phi_k=\eta_1\phi_{k_1}+\eta_2\phi_{k_2}, \tag{7b}$$

and

$$n_q=n_q{}^0-\Phi_L(dn_q{}^0/dE_q), \tag{8a}$$

$$\Phi_L=\eta_L\phi_L, \tag{8b}$$

with

$$\phi_{k_1}=\mathbf{k}\cdot\mathbf{u};\quad \phi_{k_2}=(E_k-E_F)\mathbf{k}\cdot\mathbf{u};\quad \phi_L=\mathbf{q}\cdot\mathbf{u}. \tag{9}$$

Here $\mathbf{u}$ is a unit vector in the direction of the applied fields. f_k and n_q are the actual values of the electron and phonon distribution, respectively; $f_k{}^\circ$ and $n_q{}^0$ are the equilibrium values. E_k and E_q are the electron and phonon energy, respectively. E_F is the Fermi energy. The coefficients η_1, η_2, and η_L are determined by the maximization of the rate of entropy production.

Inserting Eqs. (3) to (5) into Eq. (2) we obtain the relation

$$\rho_g=S_g{}^2T/\kappa_L. \tag{10}$$

It is seen that the effects of phonon drag on the electrical resistivity and on the thermoelectric power are related through a simple equation. The appearance of the square of the phonon-drag thermopower in Eq. (10) reflects the fact that the phonon-drag effect on the electrical resistivity is a second-order phenomenon.

Whereas the derivation of Eq. (10) given above is based on Ziman's variational treatment of the transport problem, a direct physical derivation of Eq. (10) can be obtained in the following way. We consider a crystal through which the electrical current J is flowing. The current J will set up a heat current U_L in the phonon system which is given by

$$U_L=\Pi_gJ, \tag{11}$$

where Π_g is the phonon-drag component of the Peltier heat. On the other hand, a heat current in the phonon system causes the thermoelectric voltage

$$\Delta V=-S_g\Delta T \tag{12}$$

between both ends of the crystal. In order to talk about absolute values of the Peltier and Seebeck coefficient of the crystal, we imagine that the crystal is connected on each side with a conductor whose Peltier and Seebeck coefficient is zero. In Eq. (12) ΔT is the temperature difference between both ends of the crystal corresponding to the heat current U_L. The temperature difference ΔT is given by

$$\Delta T=(U_L/\kappa_L)(l/F), \tag{13}$$

where l and F are the length and the cross-sectional area of the crystal, respectively. The presence of the thermoelectric voltage ΔV is equivalent to an increase in the electrical resistivity by

$$-\rho_g=(\Delta V/J)(F/l). \tag{14}$$

In Eq. (14) the sign of ρ_g is consistent with Eq. (1). Inserting Eqs. (11) to (13) into Eq. (14) we find

$$\rho_g=S_g\Pi_g/\kappa_L. \tag{15}$$

With the Kelvin relation

$$\Pi_g=S_gT, \tag{16}$$

we finally obtain Eq. (10).

We note that ρ_g is always positive, independent of the sign of S_g. On the other hand, the phonon-drag thermopower can be positive or negative, depending on the shape of the Fermi surface and on whether normal or umklapp scattering is dominant in the electron-phonon interaction.[3] The reason why phonon-drag effects always reduce the electrical resistivity lies again in the fact that the basic interaction mechanism enters the effect twice.

PHONON-DRAG EFFECT ON THE ELECTRICAL RESISTIVITY OF GOLD AND PLATINUM

We may use Eq. (10) for calculating the phonon-drag component of the electrical resistivity (which is difficult to determine experimentally because of its smallness) from the quantities S_g and κ_L (which can be obtained from experiment relatively easily). In Table I we show

TABLE I. Phonon-drag component ρ_g of the electrical resistivity of gold calculated with Eq. (10) from the experimentally determined quantities S_g and κ_L for different temperatures.

T(°K)	20	40	60	80	100	120
S_g (μV/°K)[a]	0.93	0.82	0.53	0.33	0.20	0.12
κ_L (W/cm °K)[b]	0.30	0.20	0.13	0.10	0.08	0.07
ρ_g (10^{-12} Ω cm)	58	133	128	85	50	25
$(\rho_g/\rho)\times10^3$	4.6	1.1	0.45	0.18	0.079	0.031

[a] See Ref. 4. [b] See Ref. 5.

[3] M. Bailyn, Phys. Rev. **120**, 381 (1960).

TABLE II. Phonon-drag component ρ_g of the electrical resistivity of platinum calculated with Eq. (10) from the quantities S_g and κ_L for different temperatures.

T(°K)	20	40	60	80	100	150	200
S_g (μV/°K)[a]	3.14	5.86	6.97	6.78	6.18	3.79	2.07
κ_L (W/cm °K)[b]	0.28	0.35	0.43	0.40	0.40	0.37	0.35
ρ_g (10^{-9} Ω cm)	0.71	3.9	6.8	9.2	9.6	5.8	2.4
$(\rho_g/\rho)\times10^3$	16	9.6	6.1	4.7	3.4	1.2	0.34

[a] See Ref. 7. [b] Calculated from Eq. (17).

the phonon-drag component ρ_g of the electrical resistivity of gold calculated with Eq. (10) from the experimentally determined quantities S_g [4] and κ_L [5] for various temperatures. In the calculation of the ratio ρ_g/ρ given in Table I, ρ was obtained from electrical resistance measurements[4] with an annealed gold specimen at 4.2, 77.3, and 296°K by interpolation using the data of Burgers, Cath, and Onnes.[6]

In Table II we show the phonon-drag component ρ_g for platinum calculated with Eq. (10) from κ_L and the experimentally determined quantity S_g.[7] The lattice thermal conductivity of platinum given in Table II was calculated using the equation

$$\kappa_L \approx \tfrac{1}{3} C_L v \lambda. \tag{17}$$

Here C_L is the lattice component of the specific heat, v the sound velocity, and λ the phonon mean free path. In the calculation of κ_L the lattice specific heat of platinum was taken from Clusius *et al.*[8] The phonon mean free path was obtained from recent measurements[7] of the size effect on the phonon-drag thermopower of platinum. For the sound velocity in platinum the value $v=2.7\times10^5$ cm/sec was used.[9] In the calculation of the ratio ρ_g/ρ given in Table II ρ was taken from electrical resistance measurements[10] with an annealed platinum specimen carried out between 4.2 and 300°K. The platinum specimen used in these measurements had the resistivity ratio $\rho(296°K)/\rho(4.2°K)=4800$.

As seen from Tables I and II, above 20°K the electrical resistivity of gold and platinum is reduced by less than 0.5 and 1.6%, respectively, due to phonon-drag effects. The phonon-drag component of the electrical resistivity in gold and platinum has a maximum around 40 and 100°K, respectively. The ratio ρ_g/ρ decreases with increasing temperature above 20°K.

DEVIATIONS FROM THE MATTHIESSEN RULE

The change in the phonon-drag component of the electrical resistivity due to the phonon scattering by lattice defects acts as an additional contribution to the electrical resistivity of lattice imperfections in metals. Since this change in ρ_g is temperature-dependent, it will result in a deviation from the Matthiessen rule in the electrical resistivity of lattice defects. In the following we estimate the contribution to the electrical resistivity of lattice vacancies in gold and platinum, which is caused by the change in ρ_g due to the phonon scattering by the point defects. Indicating the transport properties of a specimen containing lattice defects by an asterisk, we have the equations

$$\rho_g^* = \rho_g + \Delta\rho_g, \tag{18a}$$

$$S_g^* = S_g - \Delta S_g, \tag{18b}$$

$$\kappa_L^* = \kappa_L - \Delta\kappa_L. \tag{18c}$$

Here $\Delta\rho_g$, ΔS_g, and $\Delta\kappa_L$ are the changes in the transport coefficients due to the presence of the lattice defects. With

$$\rho_g^* = S_g^{*2} T/\kappa_L^* \tag{19}$$

and for the case that $\Delta\kappa_L/\kappa_L \ll 1$ and $\Delta S_g/S_g \ll 1$ we obtain

$$\Delta\rho_g = -2(T/\kappa_L) S_g \Delta S_g + (T S_g^2/\kappa_L^2)\Delta\kappa_L. \tag{20}$$

With the rough approximation[11]

$$\Delta S_g/S_g = \Delta\kappa_L/\kappa_L, \tag{21}$$

we find

$$\Delta\rho_g = -(T S_g \Delta S_g/\kappa_L). \tag{22}$$

Since the product $S_g\Delta S_g$ is always positive,[4] Eq. (22) shows that the presence of lattice defects causes a reduction in the phonon-drag component of the electrical resistivity, which is equivalent to a positive contribution to the electrical resistivity of the lattice imperfections.

In Table III we show the change $\Delta\rho_g$ due to quenched-in lattice vacancies in gold calculated from Eq. (22) using experimental values of ΔS_g. The ΔS_g

TABLE III. Change $\Delta\rho_g$ in the phonon-drag component of the electrical resistivity of gold due to quenched-in lattice vacancies ($\Delta\rho=14.8\times10^{-9}$ Ω cm) calculated with Eq. (22).

T(°K)	20	40	60
ΔS^g (μV/°K)[a]	0.206	0.079	0.022
$\Delta\rho_g$ (10^{-12} Ω cm)	−12.8	−12.9	−5.3

[a] See Ref. 4.

[4] R. P. Huebener, Phys. Rev. **135**, A1281 (1964).
[5] G. K. White, S. B. Woods, and M. T. Elford, Phil. Mag. 4, 688 (1959).
[6] *International Critical Tables*, edited by E. W. Washburn (McGraw-Hill Book Company, Inc., New York, 1929), Vol. 6, p. 125.
[7] R. P. Huebener, Phys. Rev. **140**, A1834 (1965).
[8] K. Clusius, C. G. Losa, and P. Franzosini, Z. Naturforsch. **12a**, 34 (1957).
[9] Ref. 6, p. 465.
[10] R. P. Huebener and R. G. Stewart (to be published).
[11] F. J. Blatt, M. Garber, and B. W. Scott, Phys. Rev. **136**, A729 (1964).

TABLE IV. Change $\Delta\rho_g$ in the phonon-drag component of the electrical resistivity of platinum due to quenched-in lattice vacancies ($\Delta\rho=48.6\times10^{-9}$ Ω cm) calculated with Eq. (22).

T(°K)	20	40	60	80	100	150	200
ΔS^g (μV/°K)[a]	0.308	0.118	0.110	0.105	0.089	0.047	0.021
$\Delta\rho_g$ (10^{-12} Ω cm)	−69.1	−79.0	−107	−142	−137	−72.3	−25.2

[a] Ref. 12.

values given in Table III have been obtained[4] for a specimen with an electrical resistivity increment due to quenching of $\Delta\rho=14.8\times10^{-9}$ Ω cm. Table IV shows similar results for quenched-in vacancies in platinum. The ΔS^g values of Table IV were taken from recent thermoelectric measurements[12] with quenched platinum. They were obtained with a specimen whose electrical resistivity increment due to quenching was $\Delta\rho=48.6\times10^{-9}$ Ω cm. In the calculation of $\Delta\rho_g$ from Eq. (22) the quantities S_g and κ_L were taken from Tables I and II.

[12] R. P. Huebener, preceding paper, Phys. Rev. **146**, 490 (1966).

It is seen from Tables III and IV that the contribution to the electrical resistivity of lattice vacancies in gold and platinum due to changes in ρ_g is less than 0.1 and 0.3%, respectively, of the measured vacancy resistivity. The experimentally observed deviations from the Matthiessen rule in the electrical resistivity of lattice defects are usually about 10 to 25%.[4,12] It appears therefore, that in the electrical resistivity of lattice vacancies in gold and platinum the deviations from the Matthiessen rule caused by changes in ρ_g are negligible. It can be expected that these conclusions are generally valid for lattice defects in metals.

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Piezoresistance and Piezo-Hall Effects in *n*- and *p*-Type Aluminum Antimonide*†

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Measurements have been made between 77 and 362°K of the effect of uniaxial compression (up to 2×10^8 dyn/cm²) on the resistivity and Hall coefficient of oriented single-crystal samples of *n*- and *p*-type AlSb of nondegenerate carrier concentrations. Measurements were also made at 195 and 298°K employing hydrostatic pressures up to 4.5×10^9 dyn/cm². The piezoresistance results on *n*-type material indicate that the conduction band of AlSb is multivalleyed with valleys along ⟨100⟩ axes in **k** space. The temperature dependence of the piezoresistance coefficient π_{11} over most of the temperature range is explained by means of the deformation-potential theory for electron transfer with no intervalley (IV) scattering. The shear-deformation-potential constant, Ξ_u, is found to be given by $\Xi_u^\circ(1+\alpha T)$, where $\Xi_u^0=4.9\pm0.4$ eV and $\alpha=(1.0\pm0.4)\times10^{-3}$ °K^{-1}. Between 195 and 112°K, π_{11} is almost independent of temperature for unknown reasons, but this behavior does not seem to be due to IV scattering. For *p*-type material, only π_{44} is found to be large and, over much of the temperature range measured, to depend on temperature as predicted by deformation-potential theory. These results, when combined with magnetoresistance results of others, indicate that AlSb has a degenerate valence-band edge similar to germanium and other III-V semiconductors. Results of the piezo-Hall-effect measurements on both *n*- and *p*-type material are in qualitative accord with the type of extrema obtained from the piezoresistance measurements.

I. INTRODUCTION

SOME features of the conduction and valence-band structure of AlSb have been determined by various investigators. Thus, from the negative, silicon-like pressure coefficient associated with the optical absorption edge, Edwards and Drickamer[1] inferred that the conduction band of AlSb should be analogous to silicon, namely ⟨100⟩ valleys in **k** space. From the dependence of the energy gap on the composition of $(Ga_{1-y}Al_y)Sb$ alloys found by Burdiyan,[2] Ehrenreich[3] concluded that the next-to-lowest minimum in AlSb is at ⟨000⟩, lying 0.3 eV above the lowest ⟨100⟩ minima. Infrared-absorption experiments in Te- and Se-doped samples by Turner and Reese[4] indicated a more accurate value of 0.29 eV. Turner and Reese[4] also deduced a value of $0.3m_0$

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[2] I. I. Burdiyan, Fiz. Tverd. Tela **1**, 1360 (1959) [English transl.: Soviet Phys.—Solid State **1**, 1246 (1960)].
[3] H. Ehrenreich, J. Appl. Phys. **32**, 2155 (1961).
[4] W. J. Turner and W. E. Reese, Phys. Rev. **117**, 1003 (1960).