

## Electron-Phonon Mass Enhancement in Thermoelectricity\*

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We consider the role of electron-phonon mass enhancement in impurity-dominated dc electronic transport and conclude that such mass enhancement should be observed in the thermoelectric effects. We also present new experimental evidence in support of this conclusion.

On the basis of statements made by Prange and Kadanoff<sup>1</sup> it has been believed for more than a decade that effects of electron-phonon mass enhancement are unobservable in dc electronic transport in metals. This was proved rigorously for electrical conductivity by Holstein,<sup>2</sup> but has not been demonstrated with comparable rigor for either thermal conductivity or thermoelectric effects. In this Letter we argue that while this belief is essentially correct for thermal conductivity, it is not correct for thermopower under conditions where electrons are scattered primarily by impurities. We show for elastic impurity scattering that if all the properties of the electrons are consistently renormalized, then this renormalization cancels out of the electrical resistivity and the thermal conductivity, but *not* out of the thermopower. That is, *only* the thermopower is enhanced. We also provide new experimental evidence in support of this thermopower enhancement. An independent examination from a microscopic point of view of the role of electron-phonon mass enhancement in dc transport is in progress,<sup>3</sup> and preliminary results are compatible with the conclusions reached in the present paper.

We begin by considering an ideal system of electrons (renormalized by the electron-phonon interaction) which at low temperatures are scattered elastically by a random distribution of fixed impurities. The dc transport properties of elastically scattered electrons are describable in terms of a vector mean free path  $\vec{l}_{\vec{k}}$ , which is related to the renormalized relaxation time  $\tau_{\vec{k}}$  by  $\vec{l}_{\vec{k}} = \vec{v}_{\vec{k}} \tau_{\vec{k}}$ . Here  $\vec{v}_{\vec{k}}$  is the renormalized velocity of an electron in state  $\vec{k}$ . (From here on, in the interests of notational simplicity we drop the subscripts  $\vec{k}$  from  $l$ ,  $\tau$ , and  $v$ , and the arrows from vectors except where essential for clarity. The derivations however are appropriate to the generalized quantities.)

For energies near the Fermi energy  $\epsilon_F$ ,  $v$  is related to the unrenormalized velocity  $v_u$  by  $v = v_u/(1 + \lambda)$ , where  $\lambda$  is the mass enhancement for

the electron in state  $K$ . In addition, it can be shown by a perturbation treatment of the impurity scattering between renormalized electron states (neglecting the vertex correction) that  $\tau = \tau_u(1 + \lambda)$ . Therefore  $l = v\tau = v_u\tau_u$  is the same for both renormalized and unrenormalized electrons. Physically this means that the average distance between collisions for a renormalized electron is the same as for the same electron when unrenormalized, a plausible result for scattering from impurities.

In the absence of any external fields the system is characterized by the equilibrium distribution  $f_0(\vec{k}) = \{\exp[(\epsilon(\vec{k}) - \epsilon_F)/k_B T]\}^{-1}$ , where  $\epsilon(\vec{k})$  is the renormalized energy of an electron having wave vector  $\vec{k}$ ,  $k_B$  is Boltzmann's constant, and  $T$  is the temperature. We note that  $\epsilon_F$  is unaffected by the renormalization. Upon application of a small electric field  $\vec{E}$ , the system can be characterized by a nonequilibrium distribution  $f$  which deviates from the local equilibrium distribution  $f_0$  by  $f - f_0 = (-\partial f_0/\partial \epsilon)\varphi$ , where  $\varphi$  is the solution of the linearized Boltzmann equation

$$\partial \varphi / \partial t + e\vec{E} \cdot \vec{v} = \varphi / \tau. \quad (1)$$

In Eq. (1),  $e$  is the electron's charge. Expressing Eq. (1) in terms of unrenormalized variables gives

$$(1 + \lambda)\partial \varphi / \partial t + e\vec{E} \cdot \vec{v}_u = \varphi / \tau_u. \quad (2)$$

In steady state,  $\partial \varphi / \partial t = 0$ , and the solution  $\varphi$  is the same as in the unrenormalized case,  $\varphi = e\tau_u \vec{v}_u \cdot \vec{E}$ . Using the expression for the current density,  $\vec{J} = e \sum_{\vec{k}} (-\partial f_0 / \partial \epsilon) \varphi(\vec{k}) \vec{v}(\vec{k})$ , we obtain for the conductivity as a function of energy

$$\sigma(\epsilon) = \frac{e^2}{4\pi^3 \hbar} \int \frac{ds}{v} \vec{v} \tau \vec{v} = \frac{e^2}{4\pi^3 \hbar} \int \frac{ds}{v_u} \vec{v}_u \tau_u \vec{v}_u, \quad (3)$$

where the integral is over the surfaces of constant energy  $\epsilon$ . Because the constant-energy surfaces are determined by the dispersion relation  $\epsilon(\vec{k})$ , and because  $\epsilon(\vec{k})$  for renormalized electrons differs from  $\epsilon_u(\vec{k})$  for unrenormalized electrons (except at  $\epsilon = \epsilon_F$ ), the constant-energy

surfaces for renormalized and unrenormalized electrons will be different (except at  $\epsilon = \epsilon_F$ ). This means that Eq. (3) differs from the unrenormalized conductivity function  $\sigma_u(\epsilon)$ , because the surfaces of integration are different. Therefore, the energy derivatives of  $\sigma(\epsilon)$  and  $\sigma_u(\epsilon)$  will be different, a fact which has ramifications for the thermopower, as we discuss below. On the other hand, the dc conductivity is simply  $\sigma(\epsilon_F)$  and is therefore unaffected by the renormalization. Similarly, we find that the thermal conductivity  $\kappa$  is also unchanged by the renormalization,<sup>4</sup>  $\kappa = \sigma T L_0$ , where  $L_0$  is the ideal Lorenz ratio,  $L_0 = \pi^2 k_B^2 / 3e^2$ .

We now consider the diffusion thermopower  $S_d$  which we find for renormalized electrons is given by the Mott expression<sup>5</sup>

$$S_d = eL_0 T (d \ln \sigma / d\epsilon)_{\epsilon_F}. \quad (4)$$

By applying the divergence theorem to Eq. (3) we find for the derivative

$$\begin{aligned} \left. \frac{d\sigma}{d\epsilon} \right|_{\epsilon_F} &= \frac{e^2}{12\pi^3 \hbar} \int \frac{ds}{\hbar v} \nabla \cdot (\tau_u \vec{v}_u) \\ &= (1 + \lambda) \frac{e^2}{12\pi^3 \hbar} \int \frac{ds}{\hbar v_u} \nabla \cdot (\tau_u \vec{v}_u), \end{aligned}$$

where, for simplicity, we have assumed cubic symmetry and an isotropic  $\lambda$ . Therefore, the thermopower is affected by the renormalization; i.e.,  $S_d = (1 + \lambda)S_d^u$ , where  $S_d^u$  is the diffusion thermopower for the unrenormalized electron system. Noncubic symmetry introduces tensor quantities, and an anisotropic  $\lambda_{\vec{x}}$  leads to an appropriately averaged enhancement factor in the relation between  $S$  and  $S_u$ , neither of which affect the essential features of our argument.

Using the semiclassical equation of motion for Bloch electrons in a magnetic field  $\vec{H}$ ,  $d\vec{K}/dt = e[\vec{E} + (\vec{v}/c) \times \vec{H}]/\hbar$ , we find that the form of the Boltzmann equation for steady-state transport in a magnetic field is also not affected by the renormalization. Therefore, the magnetotransport coefficients are affected by the renormalization in the same way as are the zero-field transport coefficients;  $\sigma(H)$  and  $\kappa(H)$  remain unchanged and  $S_d(H) = (1 + \lambda)S_d^u(H)$ .

We now turn to an examination of the experimental evidence concerning the effect of mass enhancement in dc transport. As we have indicated, only thermoelectric properties are of interest. However, most thermoelectric properties are notorious for their complexity and for their sensitivity to details of the processes by

which electrons are scattered. Therefore we must concentrate upon thermoelectric properties which are insensitive to the details of such scattering processes. Two such properties exist: the Nernst-Ettingshausen effect; and the difference between the high- and low-field electron-diffusion thermopowers in a noncompensated metal. Nernst-Ettingshausen-effect measurements have been made in a few systems, but for several reasons have been unable to establish whether or not thermoelectric effects are enhanced.<sup>6-8</sup> We therefore turn to magnetothermopower measurements on aluminum and dilute aluminum alloys.

Aluminum is nearly ideal for our purposes: Its Fermi surface is well established and simple in form<sup>9</sup>; the magnitude of the electron-phonon mass enhancement is known and is large<sup>10-12</sup> ( $\sim 40-50\%$ ); and the Debye temperature is high ( $\Theta_D \approx 430$  K), so that at low temperatures phonon-drag effects in the thermopower are small and can be eliminated with reasonable confidence.

Averback and Wagner<sup>13</sup> and Averback, Stephan, and Bass<sup>14</sup> recently found that for dilute polycrystalline aluminum alloys between 1 and 5 K, the difference between the high- and low-field electron diffusion thermopowers,  $\Delta S_d = S_d(H \rightarrow \infty) - S_d(H = 0)$ , was very nearly independent of impurity, varying by only 20% for a series of different impurities. The values ranged from  $(2.1$  to  $2.6) \times 10^{-8} T$  in units of volts/kelvin, with an average of  $2.3 \times 10^{-8} T$ .

Using semiclassical transport theory, Averback and Wagner<sup>13</sup> derived a general expression for  $\Delta S_d$  appropriate to a single crystal of a noncompensated metal with no open orbits, when the magnetic field  $H$  is aligned along a crystal axis having twofold or higher symmetry. The expression consisted of two terms,

$$\Delta S_d = \frac{2\gamma T}{(n_e - n_h)e} - eL_0 T \left( \frac{d \ln[\sigma_{yy}(H)\sigma_{xx}(0)]}{d\epsilon} \right)_{\epsilon_F}. \quad (5)$$

In Eq. (5),  $\gamma$  is the coefficient of electronic specific heat,  $n_e$  and  $n_h$  are, respectively, the number of electrons and holes contained within the surfaces of constant energy  $\epsilon_F$ , and  $\sigma_{yy}(H)$  and  $\sigma_{xx}(H=0)$  are energy-dependent conductivities, the derivatives of which are evaluated at  $\epsilon = \epsilon_F$ . Averback and Wagner evaluated the specific-heat term in the one-orthogonalized-plane-wave (OPW) approximation, using  $\epsilon_F = 11.6$  eV for Al and neglecting electron-phonon enhancement, and ob-

tained

$$2\gamma T / (n_e - n_h)e = +1.9 \times 10^{-8} T. \quad (6)$$

This value is, by itself, about 80% of the average of the experimental values. The effects of scattering on  $\Delta S_d$  appear only in the last term of Eq. (5), and on the basis of experiment must be small. If the two conductivities are evaluated in the relaxation-time approximation, and the high- and low-field relaxation times have the same energy dependence, then the relaxation times cancel out of the last term in Eq. (5), and  $\Delta S_d$  is independent of the scattering. Averbach and Wagner evaluated this term approximately for  $H$  along a fourfold symmetric axis, assuming a one-OPW Fermi surface for Al. They found

$$eL_0 T \left( \frac{d \ln[\sigma_{yy}(H)\sigma_{xx}(0)]}{d\epsilon} \right)_{\epsilon_F} = +0.3 \times 10^{-8} T. \quad (7)$$

Subtracting (7) from (6) yields  $\Delta S_d = 1.6 \times 10^{-8} T$ , a value about 30% smaller than experiment.

Three possible explanations exist for this discrepancy. (1) The experimental data, taken on polycrystalline samples containing impurities with unknown scattering anisotropies, are inappropriate for comparison with the calculation. (2) The calculation is inadequate, particularly in its use of a one-OPW Fermi surface for Al. (3) The mass enhancement must be taken into account—this would give a value  $\Delta S_d = 2.3 \times 10^{-8} T$ , right in the middle of the experimental data. We have examined each of these possibilities.

We began by measuring  $\Delta S_d$  for a single-crystal sample of Al containing a small amount of gallium, an impurity which according to recent calculations by Sorbello<sup>15</sup> should scatter electrons very nearly isotropically in Al. We measured  $\Delta S_d$  for  $H$  along a fourfold symmetry axis and obtained the value

$$\Delta S_d = (+2.23 \pm 0.25) \times 10^{-8} T. \quad (8)$$

The excellent agreement of this value with the polycrystalline data seems to rule out possibility (1). The details of this experiment will be published elsewhere.<sup>16</sup>

This experimental result led to a reexamination of Averbach and Wagner's one-OPW calculation, and to the discovery that some terms which they had only approximated could be evaluated exactly. This revised calculation<sup>17</sup> yielded a new one-OPW value for the second term in Eq. (5),

$$eL_0 T \left( \frac{d \ln[\sigma_{yy}(H)\sigma_{xx}(0)]}{d\epsilon} \right)_{\epsilon} = +0.9 \times 10^{-8} T, \quad (9)$$

which moves the calculation away from the experimental data. The effects of using a four-OPW Fermi surface for Al can be estimated, with the result

$$eL_0 T \left( \frac{d \ln[\sigma_{yy}(H)\sigma_{xx}(0)]}{d\epsilon} \right)_{\epsilon} = +0.5 \times 10^{-8} T. \quad (10)$$

Using a four-OPW Fermi surface to calculate the specific-heat term in Eq. (5) yields<sup>10</sup>

$$2\gamma T / (n_e - n_h)e = +2.0 \times 10^{-8} T. \quad (11)$$

Subtracting (10) from (11), a substantial disagreement with experiment still remains. To test the adequacy of our four-OPW analysis, one of us<sup>18</sup> used the same assumptions to evaluate the normalized magnetoresistivity  $r_\rho = \rho(H \rightarrow \infty) / \rho(H = 0)$  for Al. The results came out in quantitative agreement with experiment (e.g., for the present sample, the experimental  $r_\rho$  of 2.59 was in excellent agreement with the calculated  $r_\rho$  of 2.6) thereby resolving an existing 30% discrepancy.<sup>19,20</sup>

We therefore conclude that the most likely source of the disagreement between theory and experiment for  $\Delta S_d$  is the neglect of electron-phonon mass enhancement. If we include a mass enhancement of 45% in both Eqs. (10) and (11), we find

$$\Delta S_d = +2.2 \times 10^{-8} T, \quad (12)$$

in excellent agreement with both the single-crystal data and the average of the polycrystalline data. We attribute the residual variation of  $\Delta S_d$  for different impurities to the presence of anisotropy in the scattering of electrons.

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## Time-Resolved Optical Detection of Coherent Spin Motion for Organic-Radical-Ion Pairs in Solution

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The evolution of the singlet character of correlated ion radical pairs, prepared by high-energy impact in alkane solutions, is monitored by nanosecond-time-resolved solute-recombination fluorescence. Results obtained in the presence and absence of magnetic fields ( $B \leq 4$  kG) show evidence for damped periodic modulations ( $\omega \approx 10$  MHz) of fluorescence intensity. They are explained in terms of hyperfine-interaction-induced coherent singlet-triplet mixing, and of field-dependent spin-lattice relaxation.

Direct observation of time-dependent quantum-interference effects, using optical detection, has been mainly limited to gaseous atomic systems, where pulse excitation of coherent superpositions of fine- or hyperfine-structure levels initiates quantum beats with modulations of fluorescence intensity.<sup>1</sup> In this Letter, we report the observation of coherent motion, together with relaxation, of nonstationary quantum states in *condensed* organic matter, by means of nanosecond-time-resolved fluorescence measurements. The systems considered are dilute solutions of a fluorescent organic compound, where high-energy impact excitation creates correlated solute-radical-ion pairs in a singlet electronic spin state.<sup>2</sup> By recombination, these ion pairs produce fluorescing solute excited states provided they are singlet at the neutralization time. Recombination luminescence may thus be used to monitor the time development of the singlet character of the solute-ion-pair states between initial sudden preparation and final recombination.

The principle of the experimental approach is based on the influence of a magnetic field on the slowly decaying component of the luminescence excited in dilute alkane solutions by fast electrons. This radioluminescence component is known to arise from geminate recombination of

solute-ion pairs<sup>3</sup> which under nanosecond-resolution conditions may be regarded as impulsively formed in a singlet spin state.<sup>2</sup> The luminescence rate determining process is the migration of the correlated ions toward one another to form a closely spaced solute charge-transfer complex, which by spin-conserving recombination yields an excited solute molecule. Denoting by  $n(t)$  the concentration of such recombination complexes and by  $\rho_s(t)$  their probability to be singlet at time  $t$  after the  $\delta(t)$  impact creation of the spatially separated ion pairs, we can express the recombination fluorescence intensity as  $I(t) = q_f k_r n(t) \times \rho_s(t)$ , if  $t \gg \tau_f$ .  $\tau_f$  and  $q_f$  are the decay constant and quantum yield of solute fluorescence, and  $k_r$  is the recombination rate constant. The only magnetic-field-dependent factor in the expression of  $I(t)$  is  $\rho_s(t)$ ; the relative variation of luminescence intensity,  $\Delta_B I/I = [I^B(t) - I^0(t)]/I^0(t)$ , observed upon application of a field  $B$ , therefore measures the relative variation,  $\Delta_B \rho_s/\rho_s = [\rho_s^B(t) - \rho_s^0(t)]/\rho_s^0(t)$ , of the time-dependent singlet character of the ion-pair states.

The measurements were made at room temperature with degassed cyclohexane solutions of a scintillator solute denoted by 2b PPD [bis(butyl-4 phenyl)-2,5 oxadiazole-1,3,4 (cf. inset in Fig. 1)] with known fluorescence properties ( $\tau_f = 1.5$