

## Nernst Effect in Semimetals: The Effective Mass and the Figure of Merit

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(Received 6 November 2006; published 15 February 2007)

We present a study of electric, thermal, and thermoelectric transport in elemental bismuth, which presents a Nernst coefficient much larger than what was found in correlated metals. We argue that this is due to the combination of an exceptionally low carrier density with a very long electronic mean-free path. The low thermomagnetic figure of merit is traced to the lightness of electrons. Heavy-electron semimetals, which keep a metallic behavior in the presence of a magnetic field, emerge as promising candidates for thermomagnetic cooling at low temperatures.

DOI: 10.1103/PhysRevLett.98.076603

PACS numbers: 72.15.Jf, 65.40.-b, 72.15.Eb

In the presence of a magnetic field, the application of a thermal gradient to a solid may generate an electric field orthogonal to both of them. This is the Nernst effect that was discovered by Ettingshausen and Nernst 120 years ago in a study of elemental bismuth [1]. During the last few years, following the observation of a finite Nernst signal in the normal state of the underdoped cuprates [2], this effect was studied for the first time in metals host to correlated electrons. In several cases, a large Nernst signal was unexpectedly resolved [3–9]. Theoretically, the Nernst response of a simple metal is expected to vanish in the absence of electron-hole asymmetry [10,11]. An “ambipolar” Nernst effect is present when the metal is compensated [12], but the magnitude of the “giant” Nernst effect observed in correlated metals remained puzzling. In most cases, this signal emerged when the system was apparently out of the realm of the Fermi liquid picture. In CeCoIn<sub>5</sub>, the large Nernst signal was concomitant with anomalous behavior in various electronic properties of the system [4]. In the Bechgaard salts, it occurred when the field was oriented close to the magic Lebed angles [3,6]. In URu<sub>2</sub>Si<sub>2</sub> [5] and PrFe<sub>4</sub>P<sub>12</sub> [8], the giant signal emerged with the establishment of exotic electronic orders. These observations suggested a possible link between a large Nernst signal and non-Fermi liquid physics and raised a fundamental question: what sets the magnitude of the Nernst response of a Fermi liquid?

In this Letter, we present a study of thermal and thermoelectric transport in elemental bismuth down to 0.2 K. Our study confirms that in this semimetal the Nernst coefficient exceeds by an order of magnitude the largest signal observed in correlated metals. We argue that the Nernst coefficient of a Fermi liquid roughly tracks  $\omega_c \tau / \epsilon_F$ ; with  $\omega_c$ , the cyclotron frequency,  $\tau$ , the scattering time and  $\epsilon_F$ , the Fermi energy. The exceptionally low value of carrier density in bismuth combined to a very long electronic mean-free path in clean single crystals is a source of giant Nernst signal. However, because of the low effective mass of the quasiparticles, the electric conductivity is easily degraded by the application of a magnetic field. A remarkable dif-

ference between light- and heavy-electron semimetals is that only the latter continue to behave like a metal in the presence of a moderate magnetic field and could be used for constructing a cryogenic Ettingshausen refrigerator.

Figure 1 presents the thermal conductivity,  $\kappa$  and electric resistivity,  $\rho$ , of the Bi single crystal (dimensions:  $2.2 \times 1.1 \times 0.8$  mm<sup>3</sup>) used in this study. In all measurements, heat or charge was injected along the binary axis

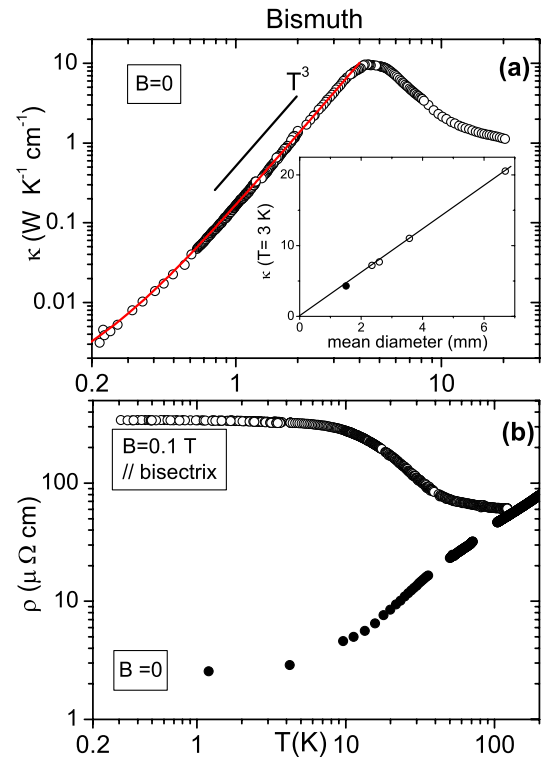


FIG. 1 (color online). (a) Thermal conductivity,  $\kappa$  of the Bi single crystal. Solid line represents a  $aT + bT^3$  fit (see text). Inset compares the magnitude of  $\kappa(3K)$  of the sample of this study (solid circle) with those reported in Ref. [15] (open circles) as a function of mean diameter. (b) Resistivity of the same sample at zero field and in presence of a field of 0.1 T.

and the magnetic field was oriented either along the trigonal or the bisectrix axes. As seen in the lower panel, the residual resistivity was  $\rho_0 \sim 2.5 \mu\Omega \text{ cm}$  (i.e., residual resistivity ratio = 47). The thermal conductivity,  $\kappa$ , displayed in the upper panel, presents a maximum at 4.1 K. Below this temperature,  $\kappa$  follows a  $T^3$  behavior characteristic of *ballistic* lattice thermal conductivity. The electronic contribution, which generates a small  $T$ -linear term becomes only visible below 0.5 K. The expression  $\kappa = aT + bT^3$  with  $a = 1 \text{ W K}^{-2} \text{ m}^{-1}$  and  $b = 158 \text{ W K}^{-2} \text{ m}^{-1}$  fits the data up to 3.6 K. The first term represents the electronic contribution and, as expected by the Wiedemann-Franz law:  $a \simeq L_0/\rho_0$  ( $L_0$  is the Lorenz number). The second term represents the lattice thermal conductivity. Since,  $\kappa_{\text{ph}} = \frac{1}{3} C_{\text{ph}} v_s \ell_{\text{ph}}$ , by taking the reported values for the sound velocity,  $v_s = 1100 \text{ m/s}$  [13], the lattice specific heat ( $C_{\text{ph}} = 35 \text{ T}^3 \text{ J m K}^{-1}$  [14]) and the measured value of  $b$ , one can estimate  $\ell_{\text{ph}} = 1.1 \text{ mm}$ . The closeness of this length to the sample's mean diameter (1.5 mm) validates the hypothesis of ballistic phonon transport. Our data should also be compared with a previous study of thermal conductivity (restricted to  $T > 2 \text{ K}$ ) on crystals of various dimensions [15]. Above 4 K, the phonon mean-free path drastically decreases as a function of temperature;  $\kappa$  is not set by the sample size and our data can be superposed on the results reported by Boxus *et al.* [15]. Below 4 K, and as seen in the inset of the figure which compares our data with the samples used in that study,  $\kappa$  at a given temperature (say 3 K) is simply proportional to the sample's mean diameter. This provides further evidence that the phonon mean-free path is set by the sample size.

The lower panel of Fig. 1 recalls the remarkably large magnetoresistance of bismuth. The application of a modest magnetic field of 0.1 T enhances the magnitude of resistivity by more than 2 orders of magnitude. In bismuth, as well as in graphite [16,17], the magnetic field induces an insulatinglike behavior. The ultimate criterion to qualify as a metal, however, is to have a Fermi surface and this is the case of the system under study in the zero-temperature limit. The giant magnetoresistance can be traced to the large value of  $\omega_c \tau$ . In bismuth, there are  $3 \times 10^{17}$  holes per  $\text{cm}^3$  and a same density of electrons. Therefore, the magnitude of  $\rho_0$  implies  $\omega_c \tau = \frac{eB\tau}{m^*} \simeq 42$  at 0.1 T and a 300-fold increase in resistivity is unsurprising [17]. The opening of an excitonic insulating gap at low applied magnetic fields has also been suggested [18].

We now turn to the Nernst coefficient. Figure 2 presents the temperature dependence of  $|\nu| = N/B = E_y/(B\nabla_x T)$ . As seen in the figure, we found that for two orientations of the magnetic field  $\nu$  peaks at 3.8 K to a value of 7 mV/K T. This large value falls in the range of magnitudes reported in studies published decades ago [19–21].

Since the contribution of electrons to heat transport is negligible and since bismuth is a compensated metal ( $n_e \simeq n_h$ ) with a Hall angle much smaller than  $\omega_c \tau$ , there is no surprise that we did not detect any measurable thermal Hall

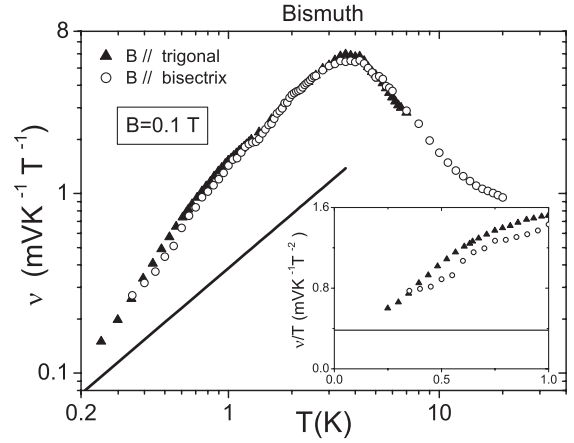


FIG. 2. The temperature dependence of the absolute value of the Nernst coefficient of the bismuth single crystal for two different orientations of the magnetic field. The solid line represents a linear function  $\alpha T$  with  $\alpha = 283 \frac{\omega_c \tau}{\epsilon_F B} = 0.38 \text{ mV K}^{-2} \text{ T}^{-1}$  (see text and Table I). Both this function and the low-temperature data are displayed in the inset as a  $\nu/T$  vs  $T$  plot.

effect. As heat current and temperature gradient vectors remain parallel in the presence of a magnetic field, the adiabatic and the isothermal Nernst coefficients are virtually identical in bismuth [19].

As seen in Fig. 3, the magnitude of the Nernst coefficient in bismuth is such that it dwarfs what is reported for other metals, even those subject to a generous attribution of the adjective giant. It is generally accepted that bismuth is a Fermi liquid. Why then is the magnitude of its Nernst coefficient so large? We will argue below that this is because of its unique electronic properties [22], namely, the combination of an exceptionally low-carrier density ( $10^{-5}$  carriers per atom) and a very long electronic mean-free path ( $40 \mu\text{m}$  in our sample).

Before this, let us briefly consider the role played by phonons. In bismuth, around 3 K, the typical phonon wave vector becomes comparable to  $2k_F$  [23]. Therefore, phonon drag should be the most important source for the Nernst signal at its peak temperature [19,20].

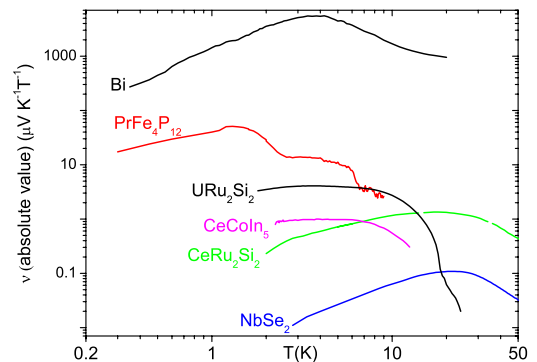


FIG. 3 (color online). The magnitude of the Nernst coefficient in bismuth compared to what is found in some other metals [4,5,7,8,12].

Conceptually, it is easier to picture this phenomenon [24] in an Ettingshausen geometry: when electrons lose their impulsion in a collision with phonons, the electric current gives rise to an entropy current of phononic origin, hence a finite Ettingshausen effect. Since the Bridgman relation ties the amplitudes of the Ettingshausen and Nernst effects [24], this implies that the Nernst effect should also be enhanced. In our case, below 4 K, electron-phonon scattering does not manifest itself either in charge or heat transport. Ballistic phonon conductivity means that the electrons do not scatter phonons in a visible way. As for charge conductivity, it changes by less than 10% below 4 K, which means that the electrons are also mostly scattered by defects. All this indicates that electron-phonon scattering events in this regime do not occur frequently. Even though, since the phonon lifetime is orders of magnitude longer than the inelastic lifetime of electrons, such rare events can drastically amplify the Nernst effect. The presence of this phonon-drag Nernst effect complicates the quantitative analysis of the purely electronic (often called diffusive) component of the Nernst effect. However, a finite  $\nu/T$  persists down to the lowest temperatures of this study (see the inset of the figure). Let us argue that the magnitude of this  $T$ -linear  $\nu$  is comparable to what is expected from the electronic properties of bismuth.

Within the Boltzmann picture, the Nernst coefficient of a metal is given by the following expression [25,26]:

$$\nu = \frac{\pi^2}{3} \frac{k_B^2 T}{Be} \frac{\partial \tan \theta_H}{\partial \epsilon} \Big|_{\epsilon_F} = \frac{\pi^2}{3} \frac{k_B^2 T}{m^*} \frac{\partial \tau(\epsilon)}{\partial \epsilon} \Big|_{\epsilon_F}, \quad (1)$$

which was first derived by Sondheimer [10]. The first expression links  $\nu$  to the Hall angle,  $\tan \theta_H$  and was discussed in detail in Ref. [26]. In the case of bismuth, because of the compensation between electrons and holes,  $\tan \theta_H$  is much smaller than  $\omega_c \tau$  of each type of carriers. In order to estimate the order of magnitude of the Nernst coefficient in a metal, let us replace  $\frac{\partial \tau}{\partial \epsilon} \Big|_{\epsilon_F}$  by  $\frac{\tau}{\epsilon_F}$  [5]. This leads to the following gross scale for the Nernst signal:

$$\nu \approx 283 \frac{\mu V}{K} \frac{\omega_c \tau}{B} \frac{k_B T}{\epsilon_F}. \quad (2)$$

Thus, there are three distinct ways of enlarging a  $T$ -linear  $\nu$ : increasing the scattering time, increasing the cyclotron frequency and reducing the Fermi energy. All these three routes are taken in bismuth. The samples are clean (enhancing  $\tau$ ), the effective mass is small (leading to a large  $\omega_c$ ) and finally (and most importantly) the carrier density is low (pushing down the Fermi energy in spite of the reduced effective mass). The solid line in Fig. 2 represents what is expected according to this expression taking  $\omega_c \tau / B = 420 \text{ T}^{-1}$  and  $\epsilon_F / k_B = 310 \text{ K}$  [27]. It appears to give a satisfactory account of the purely diffusive part of the Nernst signal.

Let us now compare bismuth with URu<sub>2</sub>Si<sub>2</sub> and PrFe<sub>4</sub>P<sub>12</sub>. In the two heavy-fermion metals, a large Nernst signal emerges below a temperature associated with an exotic phase transition. The case of bismuth suggests that the most likely source of the large Nernst signal in these two compounds is the semimetallic nature of the ordered system after the opening of a gap which destroys most of the Fermi surface. Table I gives a list of electronic properties of these three metals. The low level of the carrier density is one feature that they share. As seen in the table, the magnitude of the Nernst effect scales with  $\omega_c \tau / \epsilon_F$ . This conclusion implies that future experiments should resolve a large Nernst signal in heavy-fermion semimetals *without* any exotic order. While the case of bismuth shows that a giant Nernst effect cannot be considered as a solid signature of non-Fermi liquid physics, it also demonstrates that we still lack a precise quantitative understanding of the Nernst coefficient even in the zero-temperature limit.

The result has also an implication for applied research. In the quest for useful thermoelectricity [24,33], the figure of merit,  $ZT = \frac{S^2 \sigma T}{\kappa}$ , quantifies the adequacy of a given material for thermoelectric refrigeration. In metals, the Wiedemann-Franz law sets the magnitude of  $\frac{\kappa}{\sigma T} = L_0 = 2.44 \times 10^{-8} \text{ V}^2/\text{K}^2$ . Therefore, a thermopower of

TABLE I. A comparison of three semimetals.  $k_F$  and  $m^*$  are the radius and the effective mass of a Fermi surface (the hole ellipsoid in bismuth, the  $\tau$  and the  $\beta$  bands in the ordered states of PrFe<sub>4</sub>P<sub>12</sub> and URu<sub>2</sub>Si<sub>2</sub>).  $\gamma$  and  $n$  are electronic specific heat and carrier density. The electronic mean-free path,  $\ell_e$ , is estimated for samples used in the Nernst studies. The value for  $ZT_\epsilon$  is the highest obtained for  $B < 12 \text{ T}$ .

	Bi	PrFe <sub>4</sub> P <sub>12</sub>	URu <sub>2</sub> Si <sub>2</sub>	Ref.
$k_F$ (nm <sup>-1</sup> )	0.14	0.7	1.1	[22,28,29]
$m^*$ ( $m_e$ )	0.06	10	25	[27–29]
$\gamma$ (mJ K <sup>-1</sup> mol <sup>-1</sup> )	0.048	100	65	[14,30,31]
$n$ (per f.u.)	10 <sup>-5</sup>	(5–18) × 10 <sup>-3</sup>	(3–5) × 10 <sup>-2</sup>	[5,8,22,28]
$\ell_e$ ( $\mu\text{m}$ )	40	0.4	0.1	[5,8]
$\omega_c \tau$ ( $B = 1 \text{ T}$ )	420	0.85	0.08	
$\epsilon_F$ (K)	310	9	22	[27,30]
$283 \frac{\omega_c \tau}{\epsilon_F}$ ( $\mu\text{V}/\text{K}^2 \text{ T}$ )	383	27	1.1	
$\nu/T$ ( $\mu\text{V}/\text{K}^2 \text{ T}$ ) (0.3 K)	750	57	2.4	[5,8]
$ZT_\epsilon$ (1 K)	<0.001	0.19	~0.01	[5,8,32]

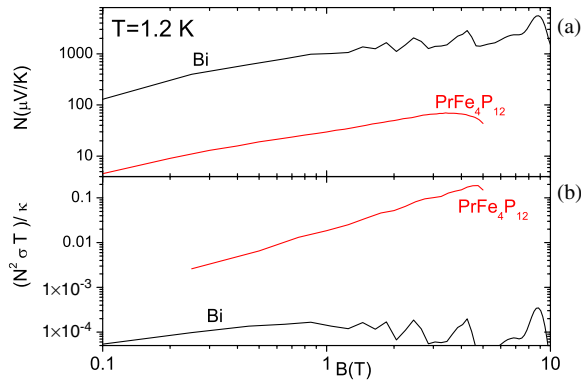


FIG. 4 (color online). The Nernst signal (a) and the thermomagnetic figure of merit (b) in Bi and in  $\text{PrFe}_4\text{P}_{12}$  as a function of magnetic field at  $T = 1.2$  K.

$S \approx \sqrt{L_0} = 155 \mu\text{V/K}$  would imply  $ZT \approx 1$ . Recently, Harutyunyan *et al.* [34] used  $\text{CeB}_6$  (with  $S \approx 120 \mu\text{V/K}$  around 6 K) to construct a Peltier cooler at cryogenic temperatures [34]. In the case of an Ettingshausen refrigerator, the relevant parameter is the thermomagnetic figure of merit  $ZT_\epsilon = \frac{N^2 \sigma T}{\kappa}$  [24] and  $\sqrt{L_0}$  sets a similar threshold for  $N$ . Therefore, its magnitude in  $\text{PrFe}_4\text{P}_{12}$  ( $\sim 100 \mu\text{V/K}$  at  $T = 1$  K and  $B = 4$  T) opens a possible route for thermomagnetic cooling at sub-Kelvin temperatures [8]. This is not the case of bismuth. In spite of its much larger Nernst coefficient, it does not qualify as a suitable thermomagnetic material. Since the magnetoresistance is large,  $ZT_\epsilon$  remains very small. This can be seen in Fig. 4, which compares the field-dependence of  $N$  and  $ZT_\epsilon$  in bismuth and in  $\text{PrFe}_4\text{P}_{12}$ . As a consequence of the lightness of carriers in bismuth,  $\omega_c = \frac{eB}{m^*}$  is large and the magnetic field induces a huge decrease in electric conductivity. Meanwhile, a large heat conductivity is maintained by phonons and the WF law is not relevant. In contrast with bismuth, the large Nernst coefficient of  $\text{PrFe}_4\text{P}_{12}$  is mostly due to the smallness of  $\epsilon_F$ . Electrons are heavy,  $\omega_c$  is not large and the system keeps its metallic behavior in a magnetic field. This is the fundamental reason behind its sizeable  $ZT_\epsilon$  ( $\approx 0.2$  at 4 T and 1 K). Such heavy-fermion semimetals emerge from our analysis as promising thermomagnetic materials at kelvin temperatures.

In comparison with its Peltier counterpart, Ettingshausen cooling presents the obvious drawback of requiring a magnetic field. However, there are reasons to suspect that it may prove to be promising. First, contrary to the Seebeck effect and as argued above, the Nernst effect is expected to scale with the mean-free-path. Therefore, the purification of the selected candidate can enhance its thermoelectric performance. Moreover, the geometry of the Ettingshausen effect allows the design of an infinite-stage refrigerator [35].

In summary, we studied the Nernst effect in bismuth and argued that the electrons present a large Nernst response

whenever their Fermi energy is low, their cyclotron frequency large and their scattering time long. Moreover, when they are heavy enough, a metallic behavior is maintained in presence of a magnetic field and thermomagnetic refrigeration at low temperatures becomes possible.

We thank Y. Nakajima, A. Pourret, and M. Nardone for precious assistance, C. Proust for useful discussions, and B. C. Sales for informing us on the large Nernst effect in bismuth. This work was supported in France by the ICENET project (ANR) and in Brazil by CNPq and FAPESP.

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