Ambipolar Nernst Effect in $NbSe_2$

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The first study of the Nernst effect in $NbSe_2$ reveals a large quasiparticle contribution with a magnitude comparable and a sign opposite to the vortex signal. Comparing the effect of the charge density wave (CDW) transition on Hall and Nernst coefficients, we argue that this large Nernst signal originates from the thermally induced counterflow of electrons and holes and indicates a drastic change in the electron scattering rate in the CDW state. The results provide new input for the debate on the origin of the anomalous Nernst signal in high-T_c cuprates.

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The Nernst effect in the normal state of high-T_c cuprates [1] has become a focus of renewed attention since the detection of an anomalous Nernst signal in the normal state of underdoped cuprates [2–4]. A well-established source of this less common thermoelectric coefficient is the movement of vortices induced by a thermal gradient in the vortex-liquid state of a type II superconductor [5]. In metals, on the other hand, the Nernst coefficient, while much less explored, is believed to be small. The fundamental reason behind this belief, recently recalled by Wang *et al.* [3] and dubbed the "Sondheimer cancellation," was first put forward in 1948 [6].

In this Letter, we present the case of $NbSe_2$. A large negative Nernst coefficient, persisting at temperatures well above $T_c = 7.2$ K, was found in this metal. The quasiparticle contribution to the Nernst signal attains a magnitude comparable to the vortex signal in the superconducting state. Comparing the evolution of Nernst and Hall coefficients, we observed that the maximum in the Nernst signal occurs when the contribution of holelike and electronlike carriers to the Hall conductivity cancel out. Moreover, we found that in the charge density wave (CDW) state, the Nernst signal becomes sublinear as a function of magnetic field. Our study recalls that the ambipolar flow of quasiparticles in the presence of a thermal gradient can lead to an enhancement of the Nernst signal in a multiband metal. The results open a new window on the driving mechanism of the CDW instability in $NbSe_2$ and establish that a large sublinear Nernst signal can arise in a metal in total absence of superconducting fluctuations.

Single crystals of $2H$-$NbSe_2$ were grown by the standard iodine vapor transport method. Stoichiometric amounts of 99.9% pure Nb wire and 99.999% pure Se shots were sealed in a quartz ampoule and then heated in a temperature gradient for a few weeks. On each sample, four longitudinal and two lateral electrodes were painted with silver epoxy in order to measure the resistivity (ρ_{xx}) and the Hall coefficient (R_H). The Nernst effect, thermopower, and thermal conductivity were measured using a one-heater two-thermometer setup which allowed us to measure all thermoelectric coefficients of the sample in the same conditions.

The temperature dependence of the Nernst signal in $NbSe_2$ at $H = 1$ T is displayed in Fig. 1. A sharp peak associated with the superconducting transition is superposed on a large negative signal which peaks at 20 K. As seen in the inset, the positive peak occurs in a temperature window closely related to the superconducting transition. The sharp resistive transition ($\Delta T_c \sim 0.1$ K) at $H = 1$ T indicates that the vortex-liquid state occurs only in a very narrow temperature-field window stretching along the $H_{c2}(T)$ line in the (H, T) plane. Since the vortex Nernst signal changes drastically in a very narrow temperature interval, the presence of a relatively large temperature gradient along the sample is expected to

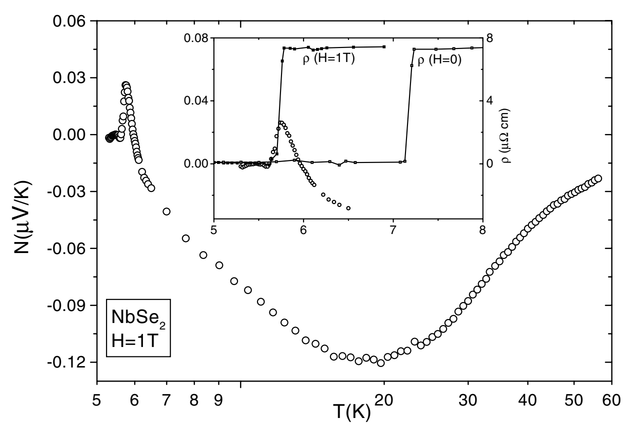

FIG. 1. The Nernst effect in $NbSe_2$ in a semilogarithmic plot. A sharp positive signal associated with thermally induced vortex movement is superposed on a large negative quasiparticle signal. The inset compares the behavior of the Nernst signal and resistivity near the superconducting transition.

broaden the peak. No systematic study of the variation of the signal with the magnitude of the temperature gradient was performed. The size of the peak (0.03 μV/K), observed in the presence of a temperature difference of about 0.2 K between the middle electrodes, underestimates the magnitude of the maximum vortex signal.

One striking feature of Fig. 1 and the main new result of this investigation is the presence of a large negative Nernst signal in the normal state which presents a broad maximum around 20 K. Like many other two-dimensional dichalcogenides, $NbSe_2$ undergoes a CDW transition at $T_{CDW} \sim 32$ K [7]. In order to explore a possible connection between the anomalously large Nernst signal and the CDW transition, we measured the temperature dependence of thermal conductivity (κ), thermopower (S), and Hall coefficient of the same sample.

Figure 2 displays the temperature dependence of longitudinal (thermal, electric, and thermoelectric) conductivities. Thermopower, slightly increasing with decreasing temperature for temperatures above T_{CDW}, presents a broad maximum and then, at temperatures well below T_{CDW}, displays a purely linear temperature dependence. This linear decrease is interrupted only with the superconducting transition. The application of a magnetic field of 5 T, strong enough to destroy superconductivity, restores the linear $S(T)$ without any detectable field-induced change in the magnitude of S. As seen in the lower panel, the effect of the CDW transition on charge and heat transport is far from spectacular. As reported in previous studies [8–10], the resistivity presents a barely noticeable anomaly at T_{CDW}. We observed a slight gradual enhancement of charge conductivity, σ, below T_{CDW}. A concomitant enhancement is also observable in the temperature dependence of κ/T. Multiplying σ by the Sommerfeld number ($L_0 = 24.5 \times 10^{-9}$ $W\Omega/K^2$) and comparing it with κ/T gives a rough estimate of the size of the electronic contribution to heat transport. Note, however, that sizable deviations from the Sommerfeld number are expected in a multiband metal at finite temperatures. As seen in the figure, this rough estimate implies that at 35 K, 35% of the heat is carried by electrons and this proportion rises to 80% at the onset of superconductivity.

The transverse transport coefficients plotted in Fig. 3 present more remarkable signatures of the CDW transition which contrasts with the behavior observed for σ and κ/T. Upon cooling from room temperature, the Hall coefficient remains virtually constant [8]. At $T = 32$ K, with the entry of the system into the CDW state, it begins

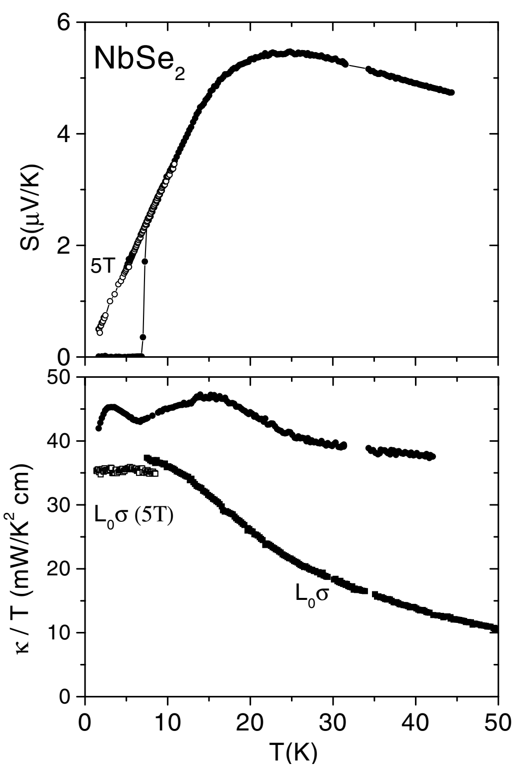

FIG. 2. Upper panel: thermopower (S) of $NbSe_2$ at $H = 0$ (solid circles) and $H = 5$ T (open circles). Lower panel: thermal conductivity divides by temperature (solid circles) as a function of temperature. Also shown is the charge conductivity (σ) at $H = 0$ (solid squares) and at $H = 5$ T (open squares) multiplied by the constant L_0 (see text).

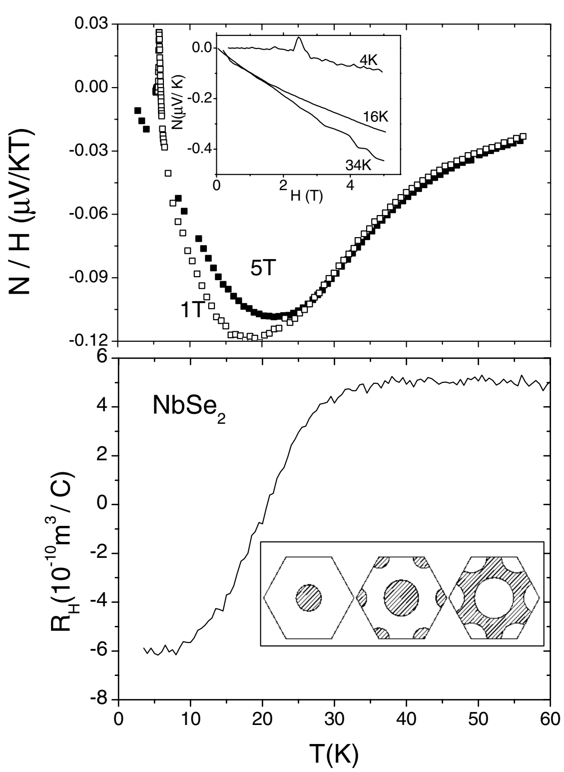

FIG. 3. Upper panel: the Nernst coefficient as a function of temperature at $H = 0$ and $H = 5$ T. The inset compares the field dependence of the Nernst signal at three different temperatures. Lower panel: the temperature dependence of the Hall coefficient measured at $H = 5$ T. Inset: a schematic plot of the three-band Fermi surface in $NBSe_2$ as observed by angular-resolved photoemission spectroscopy (ARPES) [11].

to deviate downward from this positive constant value ($+4.9 \times 10^{-10}$ m^3/C). The decrease of the Hall coefficient continues down to 8 K and then saturates to a constant negative value (-6.1×10^{-10} m^3/C). One can see in the upper panel of Fig. 3 that the Nernst coefficient ($\nu = N/H$), which remains negative above T_c in the whole temperature window investigated, presents a peak at $T = 21$ K. Remarkably, at this temperature R_H is almost zero. We argue below that this gives an important clue to the origin of the Nernst signal. A second feature of data is revealed by comparing the Nernst coefficient at two different fields ($H = 1$ T and $H = 5$ T). The two curves superpose for $T > 27$ K but become clearly distinct for lower temperatures. This suggests that the Nernst signal ceases to be field linear in the CDW state. As seen in the inset which compares the field dependence at three different temperatures, $N(H)$ is linear at 34 K but becomes clearly sublinear at 16 K. Also shown in the figure is the $T = 4$ K curve. Here, N is virtually zero up to $H \simeq 2.3$ T; then it becomes positive in a narrow field associated with vortex movement before attaining the normal-state negative regime.

Band calculations [10,12] have predicted a complex Fermi surfaces (FS) for $NbSe_2$ which consists of a small holelike closed pocket, two holelike cylinders, and two electronlike cylinders (see the inset in the lower panel of Fig. 3). While only the small holelike pocket was detected by de Haas–van Alphen measurements [10], more recent ARPES studies have led to the detection of all portions of the predicted FS [12,11].

Now, in presence of such a complicated FS, a finite Nernst signal is not unexpected. Following Wang *et al.* [3], we define the Peltier conductivity tensor $\overline{\alpha}$ with equations $\vec{J} = \overline{\sigma}\vec{E} - \overline{\alpha}\vec{\nabla}T$ and $\vec{J}_q = \overline{\alpha}T\vec{E} - \overline{\kappa}\vec{\nabla}T$. Here, $\vec{J}$ and $\vec{J}_q$ are charge and heat current densities. $\vec{E}$ and ∇T are the electric field and the thermal gradient. $\overline{\sigma}$ and $\overline{\kappa}$ are electric and thermal conductivity tensors. Assuming $\sigma_{xy} \ll \sigma_{xx}$ and neglecting the transverse thermal gradient produced by a finite κ_{xy}, the Nernst signal is easily obtained as [3]

$$N = \frac{E_y}{\frac{\partial T}{\partial x}} = S\left(\frac{\alpha_{xy}}{\alpha_{xx}} - \frac{\sigma_{xy}}{\sigma_{xx}}\right), \quad (1)$$

where $S = \frac{\alpha_{xx}}{\sigma_{xx}}$ is the thermopower. For a single band, and if $\overline{\sigma}$ is not energy dependent, one has

$$\frac{\sigma_{xy}}{\sigma_{xx}} = \frac{\alpha_{xy}}{\alpha_{xx}}, \quad (2)$$

and the two terms in Eq. (1) cancel out (“Sondheimer cancellation”) [3]. Now let us assume that the metal is not single band and there are two FS sheets with dominant carriers of opposite signs. Then Eq. (1) becomes

$$N = S\left(\frac{\alpha_{xy}^{+} + \alpha_{xy}^{-}}{\alpha_{xx}^{+} + \alpha_{xx}^{-}} - \frac{\sigma_{xy}^{+} + \sigma_{xy}^{-}}{\sigma_{xx}^{+} + \sigma_{xx}^{-}}\right), \quad (3)$$

where the superscript designates the sign of the dominant carriers and $S = \frac{\alpha_{xx}^{+} + \alpha_{xx}^{-}}{\sigma_{xx}^{+} + \sigma_{xx}^{-}}$. Now, obviously, the validity of Eq. (2) for each band does *not* lead to the cancellation of the two terms on the right side of Eq. (3). We can readily see that in a compensated two-band system, i.e., in the case of $\sigma_{xy}^{-} = -\sigma_{xy}^{+}$, the second term on the right side of Eq. (3) vanishes. But, since α_{xx}^{-} and α_{xx}^{+} are expected to have different signs, Eq. (2) implies the same sign for $\alpha_{xy}^{\pm}$. Therefore, the first term does not vanish and would yield a finite Nernst signal.

As recalled above, $NbSe_2$ is a multiband metal and becomes compensated at $T = 21$ K. Therefore, the finite size and the temperature dependence of the Nernst signal found in our study can safely be attributed to the counterflow of carriers with opposite sign. In semiconductors, this phenomenon, known as the ambipolar Nernst effect, has been known for a long time [13]. However, to our knowledge, this is the first case of a metal displaying the effect.

Using the experimental data and Eq. (1), one can compute the temperature dependence of the two components of the Peltier conductivity tensor $\overline{\alpha}$ [14]. Figure 4 compares the two ratios $\frac{\sigma_{xy}}{\sigma_{xx}}$ and $\frac{\alpha_{xy}}{\alpha_{xx}}$. As seen in the figure, at the onset of the CDW transition, the two angles display opposite signs and the absolute magnitude of $\frac{\alpha_{xy}}{\alpha_{xx}}$ is 5 times larger than $\frac{\sigma_{xy}}{\sigma_{xx}}$. Below 27 K, the two angles begin to gradually converge to a comparable negative magnitude. Now $\overline{\alpha} \propto \frac{\partial \overline{\sigma}}{\partial \epsilon}|_{\epsilon = E_f}$ for each band. Therefore, the contrasting behavior observed here indicates a different energy dependence of σ_{xy} and σ_{xx} on at least one of the bands or a substantial difference among various bands.

These results provide fresh input for the ongoing effort to identify the driving mechanism of the CDW instability in $NbSe_2$. Surprisingly, even the recent high-resolution ARPES study which successfully probed the anisotropy of the superconducting gap [11] failed to detect a CDW gap. Moreover, the slightly incommensurate CDW vector, revealed by neutron scattering [7], cannot be associated in any obvious way with a nesting vector of the known FS [12,15]. The observation of a FS in good agreement with the theoretically predicted one as well as the absence of any detectable gap indicates that the CDW transition is

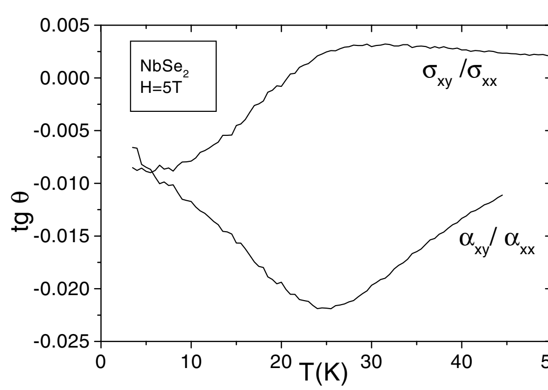

FIG. 4. The temperature dependence of two Hall-like angles (see text).

not accompanied by any substantial modification of the Fermi surface [12]. The temperature dependence of specific heat close to the CDW instability [9] confirms that the change in the density of states is small. The above-mentioned behavior of $\sigma(T)$ and $\kappa(T)$ point to the same conclusion.

But if the CDW transition leaves the FS almost intact, how does one account for the spectacular sign change of the Hall coefficient? One plausible scenario would be a drastic change in electronic mean-free path induced by the transition. To illustrate the point, let us use Ong's geometrical picture of two-dimensional Hall conductivity [16]. In a metal with a holelike and an electron FS with circular cross sections, one can write

$$R_H = \frac{2\pi d(\ell_+^2 - \ell_-^2)}{e[(k_F^+\ell_+)^2 + (k_F^-\ell_-)^2]}, \quad (4)$$

where $k_F^\mp$ and $\ell_\pm$ are the Fermi wave vector and mean-free path for electrons and holes. Here, the latter is assumed to be isotropic for each band (the "isotropic-l" approximation). A drastic increase in ℓ_- below T_{CDW} leads to a change of sign of R_H without any modification in the FS. The case for an unusually high mean-free path for the electronlike orbit is supported by another piece of experimental evidence which is the contrasting effect of the impurities on ρ_{xy} and ρ_{xx}. Improvement in sample quality leads to a small decrease of residual resistivity, but a much larger enhancement of the negative Hall signal at low temperatures [17,18]. The emergence of sublinearity in the field dependence of the Nernst signal can also be explained in this scenario. (A similar sublinearity is reported for the Hall coefficient in clean samples [17].) It indicates a negative coefficient for the H^3 term in the Zener-Jones expansion and can be related to a small electronlike portion of the FS with a long mean-free path [19].

Thus, it is tempting to conclude that the CDW transition is accompanied with a sharp change in the scattering rate on an electronlike orbit. We note that a drastic change in the scattering rate is naturally expected in the model proposed by Rice and Scott in which the existence of saddle points close to the Fermi surface drives the formation of the CDW [20]. While these saddle points have been detected by ARPES measurements, their separation in k space does not correspond to the CDW vector [12,15]. It would be interesting to explore the consequences of this scenario for the thermoelectric coefficients. Notably, the positive sign of the linear thermopower, which contrasts with the negative Hall coefficient of the CDW state, is yet to be explained.

This study presents an example of various possible origins for a large sublinear Nernst signal in a metal. It provides interesting information for the debate on the origin of the Nernst signal observed in cuprates. We recall that in electron-doped cuprates, the quasiparticle contribution to the Nernst signal is large and field linear and can be easily distinguished from the vortex contribution. The large magnitude of the latter (the Nernst coefficient attains a maximum of 0.1–0.2 μV/KT, close to the value found here for $NbSe_2$) has been attributed to the existence of a two-band FS [21,22]. In the hole-doped cuprates, a sublinear Nernst signal is present in temperatures well above T_c and cannot be distinguished from the vortex signal [2–4]. While strong superconducting fluctuations would provide a natural explanation for this signal, one should not disregard alternative scenarios connected with subtle changes in the electronic properties of the normal state.

In conclusion, we found that the ambipolar flow of quasiparticles large quasiparticle leads to a large contribution to the Nernst signal in $NbSe_2$. The results are compatible with a drastic change in the scattering induced by the CDW transition.

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[1] J. A. Clayhold *et al.*, Phys. Rev. B **50**, 4252 (1994); Phys. Rev. B **54**, 6103 (1996).
[2] Z. A. Xu *et al.*, Nature (London) **406**, 486 (2000).
[3] Y. Wang *et al.*, Phys. Rev. B **64**, 224519 (2001); Phys. Rev. Lett. **88**, 257003 (2002); Science **299**, 86 (2003).
[4] C. Capan *et al.*, Phys. Rev. Lett. **88**, 056601 (2002); Phys. Rev. B **67**, 100507 (2003).
[5] H. C. Ri *et al.*, Phys. Rev. B **50**, 3312 (1994).
[6] E. H. Sondheimer, Proc. R. Soc. London **193**, 484 (1948).
[7] D. E. Moncton, J. D. Axe, and F. J. Di Salvo, Phys. Rev. Lett. **34**, 734 (1975).
[8] H. N. S. Lee *et al.*, J. Appl. Phys. **40**, 602 (1969).
[9] J. M. E. Harper, T. H. Geballe, and F. J. Di Salvo, Phys. Lett. **54A**, 27 (1975).
[10] R. Corcoran *et al.*, J. Phys. Condens. Matter **6**, 4479 (1994).
[11] T. Yokoya *et al.*, Science **294**, 2518 (2001).
[12] K. Rossnagel *et al.*, Phys. Rev. B **64**, 235119 (2001).
[13] R. T. Delves, Rep. Prog. Phys. **28**, 249 (1965).
[14] Note that this procedure neglects the transverse thermal gradient which appears in our adiabatic setup in the presence of a finite κ_{xy}.
[15] Th. Straub *et al.*, Phys. Rev. Lett. **82**, 4504 (1999).
[16] N. P. Ong, Phys. Rev. B **43**, 193 (1991).
[17] D. J. Huntley and R. F. Frindt, Can. J. Phys. **52**, 861 (1974).
[18] T. W. Jing and N. P. Ong, Phys. Rev. B **42**, 10 781 (1990).
[19] A. P. Mackenzie *et al.*, Phys. Rev. B **54**, 7425 (1996).
[20] T. M. Rice and G. K. Scott, Phys. Rev. Lett. **35**, 120 (1975).
[21] P. Fournier *et al.*, Phys. Rev. B **56**, 14 149 (1997).
[22] F. Gollnik and M. Naito, Phys. Rev. B **58**, 11 734 (1998).