Ambipolar Nernst effect in NbSe$_2$

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The first study of Nernst effect in NbSe$_2$ reveals a large quasi-particle 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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Since the report by Xu et al. [1] on the detection of a finite Nernst signal in the normal state of underdoped cuprates, this less common thermoelectric coefficient has become a focus of renewed attention [2, 3, 4]. A well-established source of Nernst signal 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. [2] and dubbed 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 quasi-particle 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 Nernst signal occurs when the contribution of hole-like and electron-like carriers to the Hall conductivity can cancel out. Moreover, we found that in the Charge Density Wave (CDW) state, Nernst coefficient becomes sublinear as a function of magnetic field. Our study recalls that the ambipolar flow of quasiparticles in presence of a thermal gradient can lead to an enhancement of the Nernst signal in a multi-band 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 standard iodine vapor transport method. Stoichiometric amounts of 99.9 percent pure Nb wire and 99.999 percent 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 ($\rho_{xx}$) and the Hall coefficient ($R_H$). Nernst coefficient, thermopower and thermal conductivity were measured using a one-heater-two-thermometer set-up which allowed us to measure all thermoelectric coefficients of the sample in the same conditions.

The temperature-dependence of the Nernst coefficient in NbSe$_2$ at $H=1T$ is displayed in Fig.1. A sharp peak associated with the superconducting transition is superposed on a large negative quasi-particle signal. The insert compares the behavior of Nernst coefficient and resistivity near the superconducting transition.
temperature gradient along the sample is expected to 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 \(\mu V/K\), observed in presence of a temperature difference of about 0.2K 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 20K. Like many other two-dimensional dichalcogenides, NbSe\(_2\) undergoes a CDW transition at \(T_{CDW} \sim 32K\). 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 (\(\kappa\)), thermopower (\(S\)) and Hall coefficient of the same sample.

Fig.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 only interrupted with the superconducting transition. The application of a magnetic field of 5T, 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 CDW transition on charge and heat transport is far from spectacular. As reported in previous studies \([8, 9, 10]\) the resistivity presents a barely noticeable anomaly at \(T_{CDW}\). We observed a slight gradual enhancement of charge conductivity, \(\sigma\) below \(T_{CDW}\). A concomitant enhancement is also observable in the temperature dependence of \(\kappa/T\). A rough estimate of the size of the electronic contribution to heat transport can be obtained by multiplying \(\sigma\) by the Sommerfeld number \((L_0=24.5 \times 10^{-9} W\Omega/K^2)\), and comparing it with \(\kappa/T\). As seen in the figure, the fraction of heat conductivity due to electrons increases from thirty percent at 35 K to eighty percent at the onset of superconductivity.

The diagonal thermoelectric coefficients, \(R_H\) and \(N\), plotted in Fig.3, present more remarkable signatures of the CDW transition which contrasts with the behavior observed for \(\sigma\) and \(\kappa/T\). Upon cooling from room temperature, the Hall coefficient remains virtually constant \([8]\). At \(T=32K\), with the entry of the system into the CDW state, it begins 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 8K and then saturates to a constant negative value \((-6.1 \times 10^{-10} m^3/C)\). One can see in the upper panel of Fig.3, that the Nernst coefficient, which remains negative above \(T_c\) in the whole temperature window investigated, presents a peak at \(T=21K\). Remarkably, at this temperature \(R_H\) is almost zero. We will 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 field-normalized Nernst signal \((N/H)\) at two different fields \((H=1T\) and \(H=5T)\). The two curves superpose for \(T > 27K\) but come clearly distinct for lower temperatures. This suggests that the Nernst signal ceases to be field-linear in the CDW state. As seen in the insert which compares the field dependence of \(N\) at three different temperatures, \(N(H)\) which is linear at 34K, becomes clearly sublinear at 16K. Also shown in the figure is the \(T=4K\) curve. Here \(N\) is virtually zero up to \(H \simeq 2.3T\), then it becomes positive in a narrow field associated with vortex movement before attaining the normal-state negative regime.

Band calculations \([10, 11]\) have predicted a complex Fermi Surface (FS) for NbSe\(_2\) which consists of a small hole-like closed pocket, two hole-like cylinders and two electron-like cylinders (see the insert in the lower panel of Fig. 3). While only the small hole-like pocket was detected by de Hass-van Alphen measurements \([10]\), more recent Angular-Resolved Photoemission Spectroscopy (ARPES) studies have led to the detection of all portions
Now, in presence of such a complicated FS, a finite Nernst signal is not unexpected. Following Wang et al., we define the Peltier conductivity tensor $\underline{\sigma}$ with equations $\underline{J} = \underline{\sigma} \underline{E} - \alpha T \nabla T$ and $\underline{J}_q = \underline{\sigma} T \underline{E} - \alpha T \nabla T$. Here, $\underline{J}$ and $\underline{J}_q$ are charge and heat current densities. $\underline{E}$ and $\nabla T$ are the electric field and the thermal gradient. $\underline{\sigma}$ and $\underline{\alpha}$ are electric and thermal conductivity tensors. Assuming $\sigma_{yy} \ll \sigma_{xx}$ and neglecting the transverse thermal gradient produced by a finite $\kappa_{yy}$, the Nernst coefficient is easily obtained as:

$$N = \frac{E_y}{\partial_x} = S \left( \frac{\sigma_{xy}}{\sigma_{xx}} - \frac{\sigma_{yy}}{\sigma_{xx}} \right)$$

Where $S = \frac{\sigma_{xx}}{\sigma_{yy}}$ is the thermopower. For a single band, and if $\underline{\sigma}$ is not energy-dependent, one has:

$$\frac{\sigma_{xy}}{\sigma_{xx}} = \frac{\alpha_{xy}}{\alpha_{xx}}$$

and the two terms in Eq.1 cancel out (“Sondheimer cancellation”). 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:

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

Where the superscript designates the sign of the dominant carriers. Now, obviously, the validity of Eq.2 for each band does not lead to the cancellation of the two terms in 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 $\alpha_{xx}^-$ and $\alpha_{xx}^+$ are expected to have different signs, Eq.2 implies the same sign for $\alpha_{xy}^+$. Therefore, the first term does not vanish and would yield a finite Nernst signal.

As recalled above, NbSe$_2$ is a multi-band 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 since a long time ago. 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 $\underline{\sigma}$. Fig. 4 compares the two ratios $\frac{\sigma_{xy}}{\sigma_{xx}}$ and $\frac{\sigma_{yy}}{\sigma_{xx}}$. As seen in the figure, at the onset of the CDW transition, the two angles display opposite signs and the absolute magnitude of $\frac{\sigma_{xy}}{\sigma_{xx}}$ is five times larger than $\frac{\sigma_{yy}}{\sigma_{xx}}$. Below $27$K, the two angles begin to gradually converge to a comparable negative magnitude. Now, $\underline{\sigma} \propto \frac{\partial \sigma}{\partial T} |_{T=E_f}$, for each band. Therefore, the contrasting behavior observed here indicates that the energy dependence of $\sigma_{xy}$ and $\sigma_{xx}$ is substantially different on 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 failed to detect a CDW gap. Moreover, the slightly incommensurate CDW vector, revealed by neutron scattering, can not be associated in any obvious way with a nesting vector of the known FS. 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 not accompanied by any substantial modification of the Fermi surface. The temperature dependence of specific heat close to the CDW instability 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 to 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 [13]. In a metal with a hole-like and an-electron FS with circular cross-sections, one can write:

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

where $k_F^+$ and $\ell_+$ are Fermi 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 $\ell_-$ 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 electron-like orbit is supported by another piece of experimental evidence which is the contrasting effect of the impurities on $\rho_{xy}$ and $\rho_{xx}$. 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 [14, 15].

The emergence of sublinearity in the field dependence of the Nernst coefficient can also be explained in this scenario. A similar sublinearity is reported for the Hall coefficient in clean samples [10]. We did not check the field-dependence of the Hall coefficient in our study. It indicates a negative coefficient for the $T^3$ term in the Zener-Jones expansion and can be related to a small electron-like portion of the FS with a long mean free path [10].

Thus, it is tempting to conclude that the CDW transition is accompanied with a sharp change in the scattering rate on an electron-like orbit. We note that a drastic change in 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 the $k$-space does not correspond to the CDW vector [11, 13]. It would be interesting to explore the consequences of this scenario for the thermoelectric coefficients.

This study presents an example of various possible origins for a large sublinear Nernst signal in a metal. It provides an interesting information for the debate on the origin of the Nernst signal observed in cuprates. We recall that in electron-doped cuprates, the quasi-particle 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 signal attains a maximum of 0.1-0.2 $\mu V/KT$; 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 smaller sublinear Nernst signal is present in temperatures well above $T_c$ and can not be distinguished from the vortex signal [1, 2, 3, 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 quasi-particles large quasi-particle leads to a large contribution to Nernst coefficient in NbSe$_2$. The behavior of the off-diagonal components of two conductivity tensors indicate a drastic change in electron scattering induced by the CDW transition.

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