Magnetothermoelectric effects in $(TMTSF)_2ClO_4$

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We have measured the thermopower and Nernst effects in the quasi-one-dimensional organic molecular metal $(TMTSF)_2ClO_4$ as a function of temperature and magnetic field strength and orientation. At 10 K this material exhibits a maximum Nernst coefficient of 12 μV/KT, one of the largest ever observed in a metal. The thermoelectric effects are very sensitive to the reconstruction of the band structure caused by the ClO_4 anion ordering.

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The charge transfer salts $(TMTSF)_2X$ exhibit a rich spectrum of phases [including metallic, superconducting, insulating, density wave, field induced spin-density wave (SDW), quantum Hall effect, and non-Fermi liquid],[1] depending on pressure, temperature, magnetic field, and in certain cases, cooling rate. At high temperatures, above the anion ordering temperature T_{AO}, the $X=ClO_4$ salt is a quasi-one-dimensional single-band metal with highly anisotropic bandwidths $4t_a:4t_b:4t_c=1\ \text{eV}:0.096\ \text{eV}:0.003\ \text{eV}$.[1,12] As it is cooled slowly (i.e., at a rate less than 100 mK/min)[2] through T_{AO} $\sim$24 K, the ordering doubles the real space periodicity along the b axis, i.e., the extent of the Brillouin zone is halved in the k_b direction. This creates two pairs of Fermi surfaces separated by an anion ordering gap $(4t_a:4t_b:4t_c=1\ \text{eV}:0.048\ \text{eV}:0.003\ \text{eV})$.[3] This low-temperature metallic phase supports superconductivity below 1.2 K. Rapid cooling prevents the anion ordering and the quenched material enters a spin-density-wave state below about 6 K.[1]

The Fermi surfaces of the low-temperature metallic states of the TMTSF salts have been studied extensively through the dependence of the magnetoresistance on the orientation of the applied magnetic field. It is found that when the magnetic field is aligned at a "magic angle" (i.e., along a real space lattice vector in the plane perpendicular to a) and the scattering time is long enough for quasiparticles to traverse several Brillouin zones, sharp minima in the magnetoresistance, known as "Lebed resonances", are observed.[4–7] In a recent study of the thermoelectric effects in the low-temperature metallic phase of a sister compound with $X=PF_6$, the Nernst effect was found to exhibit very anomalous behavior around the magic angles.[8] A similar effect was recently observed in the Nernst effect measured along the b axis in the $X=ClO_4$ salt, in both the metallic and SDW phases.[9] The motivation of this paper is to understand the thermoelectric effects related to the anion ordering transition and associated band structure changes at $T=T_{AO}$ as well as the angle dependence of thermoelectric coefficients in the metallic state.

A schematic diagram of the experimental setup is shown in the upper inset of Fig. 1(a). Q1 and Q2 are single crystal quartz blocks. RuO_2 thermometers ($T1$ and $T2$) and a thermocouple (TC) are used to monitor the temperature difference between the two quartz blocks. Each end (1 and 2) of the sample (S) is thermally connected to one of the quartz blocks with gold wire leads. Note that the two electrical leads from each block go to the upper and lower sample surface to measure the transport along the a and c directions. The thermal gradient (∇T_a) is applied parallel to a, the most conducting axis, using either heater $H1$ (∇T is from 1 to 2) or $H2$ (∇T is from 2 to 1). The temperature difference applied is between about 50 and 125 mK; heat is applied in short pulses, typically a few seconds long. The setup is mounted inside a thermally isolated vacuum can. More experimental details can be found in Ref. 10, on which the experiment is based.

S_{aa}, the Seebeck coefficient, is defined as $E_a/\nabla T_a$ where E_a is the thermoelectric field parallel to the thermal gradient ∇T_a. A magnetic field, B, applied perpendicular to ∇T gives rise to the Nernst effect, a thermoelectric field perpendicular to both B and ∇T.

Figure 1 shows the temperature dependence below 45 K of various transport coefficients in $(TMTSF)_2ClO_4$. Between 45 and 25 K, the thermopower, S_{aa}, is positive, indicating that the carriers are holes, and decreases linearly extrapolating through the origin with a slope of about 0.13 μV/K^2. This slope is independent of the applied magnetic field along the b axis. For a three-quarter-filled one-dimensional uncorrelated electron band with a constant scattering time, this corresponds to a total bandwidth of about 540 meV (Ref. 11). Although this value is smaller than the bandwidth obtained from optical measurements,[12] it is consistent with earlier thermopower measurements at zero magnetic field which gave bandwidths of 500 meV at low temperature ($T<80$ K) and 840 meV at higher temperatures (110 K $<T<$ 200 K).[13]

As the sample is cooled slowly through the anion ordering transition temperature, S_{aa} falls more rapidly, changing sign at about 16 K and peaking at a value of about -7 μV/K at 5 K. As the temperature decreases further, S_{aa} again becomes approximately proportional to temperature, with a significantly enhanced slope of 2.6 μV/K^2. This data is qualitatively similar to previous thermopower measurements on the title compound through the anion ordering transition.[14] The rather sharp change in the transport behavior of ther-

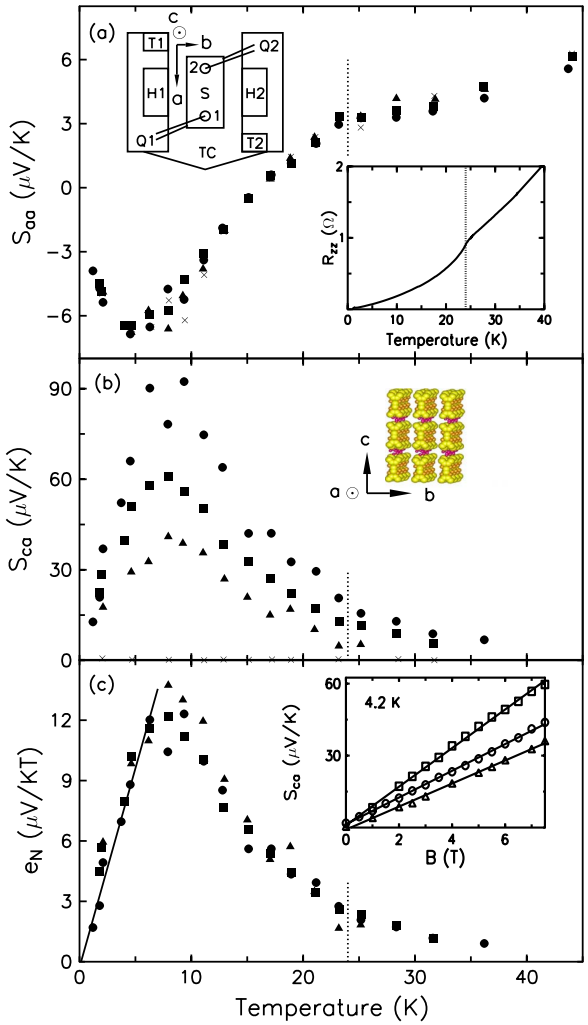

FIG. 1. (Color online) The temperature dependence of the (a) Seebeck coefficient, S_{aa}, (b) the Nernst signal, S_{ca}, and (c) the Nernst coefficient, e_N, at different magnetic fields along the crystalline b axis (circles: 7.5 T; squares: 5.0 T; triangles 3.0 T; crosses 0 T). The dotted isotherms indicate the anion ordering temperature, $T_{AO}\sim 24$ K. The inset to (a) shows the resistance R_{zz} during a typical slow cooling. The inset to (b) shows the real space molecular structure of $(TMTSF)_2ClO_4$. The inset to (c) shows the field dependence of S_{ca} for various magnetic field orientations [squares: B$\|b$; circles: $B\|\theta$=117°; triangles: $B\|\theta$=45° (the first Lebed angle)].

mopower, resistivity, and Nernst effect is expected from the reconstruction of the Fermi surface at the anion ordering temperature. The anion ordering transition appears as a kink or change in slope at 24 K. Below this temperature the temperature dependence of the transport coefficients is complicated by the reduction in scattering from the anion disorder as well as the opening of the anion ordering gap.

S_{aa} is largely independent of the magnetic field applied along the crystalline b axis (i.e., perpendicular to the temperature gradient but parallel to the most conducting plane). However, the applied magnetic field gives rise to a very large Nernst effect, S_{ca}, at low temperatures, shown in Fig. 1(b). Above the anion ordering temperature, S_{ca} is very small, as expected for a metal with a single carrier type.[15] Once the anion ordering occurs and two Fermi surfaces are stabilized,

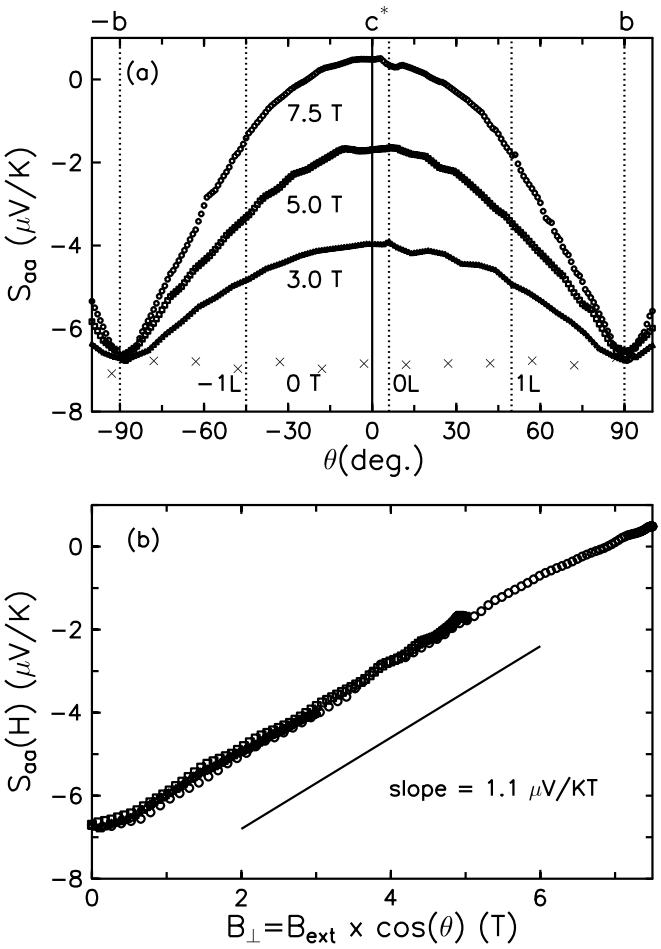

FIG. 2. (a) The angle dependence of S_{aa} at 4.2 K and 0 T, 3.0 T, 5.0 T, and 7.5 T. 0 L and ±1 L indicate the zeroth and first Lebed magic angles. The zeroth Lebed magic angle coincides with the c axis. (b) S_{aa} as a function of $B_\perp = B_{ext}\times\cos(\theta)$.

the Nernst effect increases sharply, peaking at around 8.5 K, and then dropping linearly with decreasing temperature to zero at 0 K (Refs. 15 and 16). S_{ca} is proportional to the applied magnetic field [see the inset to Fig. 1(c)]; the Nernst coefficient ($e_N \equiv S_{ca}/B$) is plotted in Fig. 1(c). Its peak value of about 12 μV/KT is extremely large. Boltzmann transport calculations for a similar band structure at a temperature of 1 K predict $e_N\sim 130$ nV/KT (Ref. 17), much closer to the values typically observed in metals. (Since the entropy of carriers is linear with temperature, but the scattering rate is superlinear, this value is expected to decrease with temperature.) A recent suggestion that large Nernst coefficients observed in high T_c and organic superconductors may be due to the presence of vortices[21] is unlikely to explain the present measurements; the superconducting T_c in the $X=ClO_4$ salt is 1.2 K, a factor of 20 less than the 24 K where we see a strong increase in Nernst effect.

Recently there have been reports[8,9] of strong anomalies in the thermoelectric coefficients at Lebed magic angles.[4] Figure 2 shows the dependence of S_{aa} on the orientation of the applied magnetic field, B_{ext}, as it is rotated in the b-c plane through the Lebed magic angles at 4.2 K (θ=90° corresponds to B_{ext} applied parallel to the crystalline b axis).[18]

When the magnetic field is applied along the b axis, the quasiparticle orbits traverse the Fermi surface in the direction of minimum bandwidth. This bandwidth is so small that S_{aa} exhibits no discernable dependence on the magnetic field applied in this orientation. As the magnetic field is rotated, we observe a slow variation of S_{aa}, but we find no distinct features at Lebed magic angles [see Fig. 2(a)] at the temperatures studied. At lower temperatures the Lebed magic angle effects are observed in this material.[9]

However, although no magic angle effects are evident, the thermopower has a strong monotonic dependence on the magnitude of the component of the magnetic field perpendicular to the highly conducting a-b plane. Figure 2(b) shows S_{aa} plotted as a function of this component, $B_\perp = B_{ext}\cos(\theta)$, for several different values of $|B_{ext}|$, where B_{ext} is the magnitude of the applied magnetic field. The data lie on a common line, confirming that S_{aa} is a function of the component of B_{ext} perpendicular to the a-b plane only [as opposed, for example, to the component along the crystalline c axis, which is coincident with the zeroth Lebed angle, marked "OL" in Fig. 2(b)].

Transport coefficients and particularly thermoelectric properties are often complex function of band structure, scattering rates, and their energy dependencies. However, by comparing with the behavior expected in a simple Drude-like model, we may get some idea of changes that occur around the anion ordering transition. A system with a single type of carrier has a thermopower that is linear in temperature and whose sign depends on the carrier type. The thermopower is independent of magnetic field, the Nernst coefficient is zero, and there is no magnetoresistance.[17] The measurements presented here and in Ref. 14 thus suggest that above the anion ordering transition there is a single holelike Fermi surface section. This is consistent with previous experiments and calculations.

If a system has two carriers with opposite sign or effective mass (i.e., a compensated system), the thermopower is small, the Nernst coefficient is large and linear in temperature, and there is a large magnetoresistance. A system which is partially compensated exhibits both thermopower and Nernst effects and both the thermopower and resistance depend on magnetic field.[14] Below the anion ordering transition our measurements and those in Ref. 14 are most easily interpreted as arising from an almost compensated system with a slightly larger electron contribution. In the anion-ordered state, S_{ca} is large, and a strong field dependence appears in S_{aa} and the resistance. While previous work suggests that the anion ordering results in two parts to the Fermi surface, in most scenarios both parts are holelike since they arise from the splitting of a one-quarter-filled tight binding band. It is possible that the combination of the anion-order-split band and strong Hubbard-like correlations could give rise to the near compensation hinted at by our data.

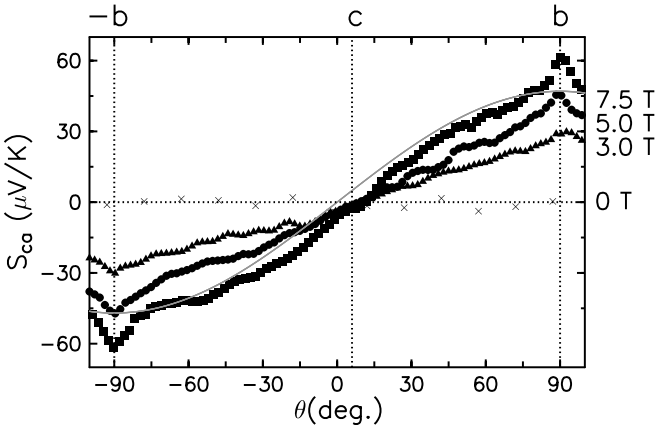

FIG. 3. Angle dependence of S_{ca} at various magnetic fields, 0 T (×), 3.0 T (▲), 5.0 T (●), and 7.5 T (■) and temperature at 4.2 K. The solid grey line shows the classically expected sinusoidal form for S_{ca} (though not the classical magnitude).

Figure 3 shows the dependence of the Nernst signal S_{ca} on the orientation of the magnetic field applied in the b-c plane, for various field magnitudes at 4.2 K. It compares favorably with classical behavior, with an approximately sinusoidal variation as the field is rotated away from the direction in which the transverse voltage is measured, except that the magnitude is extremely large. The sharp peaks near alignment with the b axis are also unusual.

In summary, we have studied the Seebeck and Nernst effects, S_{aa} and S_{ca}, in the metallic state of $(TMTSF)_2ClO_4$. We find that they are sensitive to the anion ordering transition and the accompanying electronic reconstruction, which gaps the Fermi surface and gives rise to two carrier types. At the temperatures studied here, there is no evidence for the dramatic effects seen at magic angles at lower temperature. While the large value of S_{aa} that we observe is consistent with the narrow bandwidth and a density of states that is enhanced at the Fermi energy by interactions, the giant Nernst effect, which reaches a maximum of $e_N = 12\ \mu V/KT$, is still unexplained. This result joins a small but increasing body of literature reporting very large Nernst effects in strongly correlated systems.[8,9,16,19,20] The magnitudes of the Nernst effect observed in these experiments dramatically exceed what could be expected from a simple Fermi liquid. In the present case they are unlikely to be due to superconducting vortex flow. These observations lead us to speculate that there are as yet unexplained mechanisms for large Nernst effects in strongly correlated electron systems.

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