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HAL Id: hal-01870063
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Submitted on 7 Sep 2018

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Scaling Behavior in Thermoelectric Misfit Cobalt Oxides

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(Received 30 September 2005; published 25 July 2006)

We investigate both thermoelectric and thermodynamic properties of the misfit cobalt oxide [Bi1−xCo0.5Ca0.5O2]RS0.6CoO2. A large negative magnetothermopower is found to scale with both magnetic field and temperature, revealing a significant spin entropy contribution to thermoelectric properties giving rise to a constant $S_0 \approx 60 \mu V K^{-1}$. Specific heat measurements allow us to determine an enhanced electronic part with $\gamma \approx 50 mJ/(molK^2)$-1 attesting to strong correlations. Thereby, the comparison between cobaltites and other materials reveals a universal behavior of the thermopower slope as a function of $\gamma$, testifying to a purely electronic origin. This potentially generic scaling behavior suggests here that the high room temperature value of the thermopower in misfit cobalt oxides results from the addition of a spin entropy contribution to an enlarged electronic one.

DOI: 10.1103/PhysRevLett.97.046601 PACS numbers: 72.15.Jf, 65.40.+b, 71.27.+a

Since the discovery of large thermopower in metallic Na$_x$CoO$_2$ and superconductivity in its hydrated form [1,2], the layered cobalt oxides are at the heart of intense current research. Indeed, it was quickly realized that they exhibit striking properties at both low and high temperatures, with a large potential for applications. These properties are resulting from an unusual combination of what is conventionally interpreted as either metallic or insulating features. Even though their resistivity is metallic-like and exhibits a large thermopower (TEP) at room temperature (abbreviated CaCoO below). Consequently, the thermopower in this misfit cobalt oxide seems to consist mostly of two contributions: The first one results from a spin entropy part, and the second one originates likely from strongly renormalized quasiparticles.

Thermopower measurements were performed with an experimental setup described in Ref. [17] on a $2 \times 2 \times 10 mm^3$ polycrystalline sintered sample. Figure 1 presents the magnetic field (right inset) and the temperature (left inset) dependences of the thermopower $S$. As appears in the left inset in Fig. 1, three regimes can be distinguished when the temperature $T$ is varied from 300 down to 3 K. Qualitatively often observed in other misfit cobalt oxides [3,4], the thermopower remains first weakly temperature dependent from its room temperature value $S \approx 138 \mu V K^{-1}$ down to nearly 200 K. Next, $S$ exhibits a quite linear $T$ dependence down to approximately 20 K, followed finally by a strong decrease when the temperature is lowered down to 3 K. In the latter temperature range, namely, below 20 K, the thermopower shown in the right inset in Fig. 1 reveals a strong magnetic field dependence. A large negative magnetothermopower is observed at 3 K with a reduction of about 65% between the 0 and ±9 T values, while a weaker magnetic field effect is seen at higher temperatures, nearly vanishing above 20 K.

The combined influence of both magnetic field and temperature is demonstrated through the complete collapse of the data in Fig. 1 when plotted as a function of $H/T$. 

0031-9007/06/97(4)/046601(4) 046601-1 © 2006 The American Physical Society
Here \( x = (g\mu_B H)/(2k_B T) \), \( g \) is the Landé factor, \( k_B \) the Boltzmann constant, and \( \mu_B \) the Bohr magneton. It is worth noting that, whereas Eq. (1) accounts qualitatively for the measured magnetothermopower, the quantitative agreement with the experimental results is only efficient with \( g = 2.2 \) for moderate fields, i.e., when \(|\mu_0 H/T| < 1.5 \text{ TK}^{-1}\). Nevertheless, we emphasize that the ceramic structure of the studied sample with random orientations of crystallites could lower magnetic field effect without altering scaling properties.

Thermodynamic measurements have been performed on a classical specific heat option of a Quantum Design physical property measurement system on a sample of 34.7 mg, in order to determine the electronic contribution to the specific heat. Due to the occurrence of a Schottky anomaly, a direct extrapolation of \( C/T \) to zero temperature would overestimate the electronic coefficient \( \gamma \), as displayed in Fig. 2.

For \( T \gg T_{\text{Schott}} \) (\( T_{\text{Schott}} \) being the Schottky temperature), the contribution of the Schottky anomaly to the specific heat is given by \( C_{\text{Schott}} \sim k_B (T_{\text{Schott}}/2T)^2 \). Introducing this into the fitting procedure yields \( T_{\text{Schott}} = 0.696 \text{ K} \), and \( \gamma = 50 \text{ mJ (mol K}^{-2}\text{)}^{-1} \). Since a direct determination of \( \gamma \) from the \( T^2 \) behavior of \( C/T \) observed over a sizable temperature interval yields the same value within our range of accuracy, we confidently conclude that this rather high value suggests an enhanced electronic effective mass \( m^* \) which influence upon thermopower is checked below.

As previously mentioned, one can infer that the linear variation of \( S \) within the range 20–125 K in the left inset in Fig. 1 is likely to signal another thermoelectric regime compared to the low temperature regime dominated by a large spin entropy contribution. Theoretically, the electronic thermopower is expected to give rise to a linear temperature dependence contribution with a slope \( S/T \) proportional to the effective mass, namely, \( \gamma \) [8]. Thus, at a sufficiently low temperature compared to the Fermi energy, the ratio \( S/\gamma \) is predicted in this context to be independent of interactions even in a strongly correlated regime as emphasized in Refs. [8,9]. So, in order to check the electronic origin of the linear \( T \) dependence of the thermopower, its slope has been plotted in Fig. 3 as a function of \( \gamma \) in a wide range of materials [9,20,21] including the cobaltites as NaCoO [14], CaCoO [11], BiCaCoO, and even the rhodium misfit oxide BiBaRhO [22]. In analogy with the prototype compound NaCoO, the electronic specific heat coefficients have been considered for each cobaltite per CoO₂, with \( \gamma = 37 \text{ mJ (mol K}^{-2}\text{)}^{-1} \) for CaCoO.

As a matter of fact, the linear in \( T \) behavior of the thermopower is hardly observed in simple metals, where it is hindered by phononic contributions [23]. In contrast, for both misfit cobaltites, it turns out that its prefactor is
sufficiently strongly enhanced by the electronic correlations to yield a large temperature domain where the Fermi liquid behavior is observable. Thus, in this temperature range, the $T$ dependence of the thermopower is fully governed by the electronic effective mass and is renormalized by correlations.

In order to give some rather basic theoretical insight into the previous analysis, one may assume following the Landau’s Fermi liquid theory [24] that the main effect of the electronic correlations is to renormalize the effective mass. As a consequence, an effective Fermi temperature is defined as $T^* = T_F/m^*$ [5], with the bare Fermi temperature $T_F$. In this context, the electronic specific heat coefficient $\gamma^*$ is

$$\gamma^* = \left(\frac{\pi^2}{2}\right) \frac{\delta N_{Av} k_B}{T^*},$$

with the doping $\delta$ and the Avogadro number $N_{Av}$ [21]. Obviously, one recovers in Eq. (2) a proportionality between $\gamma^*$ and the effective mass through $1/T^*$ as expected. The electronic thermopower $S^*$ can be inferred in the framework of this basic approach for $T \ll T^*$ as:

$$S^* = \left(\frac{\pi^2}{6}\right) \frac{k_B T}{qT^*}.$$  

Since $S^*$ in Eq. (3) is also proportional to the effective mass, it results that the ratio $S^*/\gamma^* T$ in Eq. (4) is thereby independent of interactions as already noted in the context of the dynamical mean field theory of strongly correlated systems [5,7,8]

$$\frac{S^*}{\gamma^* T} = \frac{1}{3 \delta q N_{Av}}.$$  

Besides, it follows from Eq. (4) that most of the coefficients in Eq. (2) and (3) cancel out in the ratio $S^*/\gamma^* T$ that is only doping dependent. The latter dependence can thus explain the differences observed in Fig. 3 between experimental points and the straight line plotted following Eq. (4) with $\delta = 1/3$. In particular, the plotted dotted line with $\delta = 1$ accounts quite well for aluminum that is characterized by a quasispherical Fermi surface and one electron per atom. So this analysis suggests that the two misfit cobalt oxides CaCoO and BiCaCoO have a hole doping ($S > 0$) lying between nearly 0.13 and 0.33.

Because the relation (3) contains no free parameter besides $T^*$, its direct quantitative comparison with the experimental results should fully determine the effective Fermi temperature. In order to compare the thermopower kinetic component in both misfit cobaltites, one needs to subtract the asymptotic value of the spin entropy contribution $S_0$ to make the linear $T$ dependence vanishing with temperature.

So, one observes in Fig. 4 as a function of the reduced temperature $T/T^*$ a collapse of the different curves with the determined effective Fermi temperatures $T_{BiCaCoO} = 255 K$ and $T_{CaCoO} = 140 K$. Moreover, Fig. 4 clearly displays that the breakdown of the linear dependence of the thermopower seems to occur for the two compounds at the same reduced temperature of the order of $T^*/2$, indicating thus a possible crossover fully controlled by correlations. Finally, we emphasize that, while the thermopower is nearly constant above $T^*$, its asymptotic value differs from one cobaltite to the other one. We stress here that the high temperature regime $T > T^*$ involves likely incoherent electronic excitation, namely, of higher energy and is thus out of the scope of this low energy analysis. It is
worth noting that the temperature dependence of the spin entropy contribution $S_{\text{spin}}$ can also be extracted from the experimental thermopower subtracting the kinetic contribution defined with the corresponding $T^*$, as $S_{\text{spin}} = (S - S^*)$. Therefore, the spin entropy contribution in the inset in Fig. 4 yields the constant $S_0 = 20 \, \mu V \, K^{-1}$ for CaCoO and leads asymptotically to $S_0 = 60 \, \mu V \, K^{-1}$ for BiCaCoO. One must emphasize that the latter value agrees with the theoretical value $S_0 = k_B \ln(2)/q = 60 \, \mu V \, K^{-1}$ expected for one free spin 1/2 per Co site in the CoO$_2$ layers.

Let us mention that a similar coexistence between delocalized electrons and localized spins has already been evidenced in the context of the heavy electrons materials within the two fluid Kondo lattice model [25]. While the underlying physics of the latter results from distinct well identified energy scales (Kondo temperature, intersite coupling, crystal field effect splitting), here this coexistence may involve different competing effects. First, it is worth noting that the triangular arrangement of the cobalt sites in this quasi-two-dimensional structure makes the system naturally predisposed to magnetic frustration. As emphasized in Ref. [10], such a system with a strong Coulomb repulsion could be also characterized by charge frustration leading to a metallic state with a tendency for short-range charge ordering. In addition to this frustration effect, the misfit structure between the [CoO$_2$] and the RS layers may introduce disorder by distorting some of the CoO$_6$ octahedrons and lowering the local intersite coupling that could also localize electrons. So for now, in order to investigate both frustration and disorder effects, we believe that further x-ray and neutron scattering experiments are highly desirable.

To conclude, we have performed both thermopower and thermodynamic measurements in the misfit cobaltite BiCaCoO focusing on the identification of various regimes. Magnetothermopower experiments have demonstrated through a scaling behavior a spin entropy contribution, giving rise to a constant $S_0 = k_B \ln(2)/q$ above nearly 20 K. While specific heat measurements yield $\gamma = 50 \, \text{mJ} \, (\text{mol \ K}^2)^{-1}$, the thermopower $T$-linear dependence $|S/T|$ is found to scale with $\gamma$ in a wide range of materials including the cobaltites BiCaCoO, CaCoO, and NaCoO. Therefore, we conclude that the thermopower in these misfit cobaltite oxides behaves as if it were composed by two components, a kinetic one originating from quasiparticles renormalized by electronic correlations and a spin entropy contribution. Finally, we would like to address that the ratio $S/\gamma T$ seems to provide an efficient probe to check the influence of electronic correlations upon thermopower and should be put to experimental testing in other misfit cobaltites as well as in other strongly correlated systems.

We are grateful to D. Jérome, K. Behnia, G. Kotliar, and A. Georges for useful discussions.