Dual electronic states in thermoelectric cobalt oxide

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We investigate the low temperature magnetic field dependence of the resistivity in the thermoelectric misfit cobalt oxide [Bi1.7Ca2O4]0.59CoO2 from 60 K down to 3 K. The scaling of the negative magnetoresistance demonstrates a spin dependent transport mechanism due to a strong Hund’s coupling. The inferred microscopic description implies dual electronic states which explain the coexistence between localized and itinerant electrons both contributing to the thermopower. By shedding a new light on the electronic states which lead to a high thermopower, this result likely provides a new potential way to optimize the thermoelectric properties.

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I. INTRODUCTION

By converting heat into voltage, thermoelectric materials are not only of major interest in both energy saving and cooling applications but they also bring a fundamental challenge in order to find the physical limits optimizing their performance. As stated by Mahan and Sofo,1 this problem can be formulated as follows: What is the best electronic structure a thermoelectric can have? In their answer they stress that the energy distribution of the charge carriers should be as narrow as possible,1 thus emphasizing the relevance of correlated materials to thermoelectricity as those in the vicinity of a Mott metal-insulator transition.2,3,4 In particular, layered cobaltates seem to belong to this class of materials2 they exhibit interesting properties,2 including superconductivity2 and both metallic like resistivity and large thermopower at room temperature. In particular, it has been recently pointed out that their large thermopower could both result from extended quasiparticles with an enhanced effective mass, and from an entropic contribution of localized spins.2 Indeed the room temperature thermopower is large in the whole series of cobalt misfits and does not depend on the nature of the separating layers.2 In misfits, it ranges from 75 µV/K in [Sr2O2−δ][0.53][CoO2] as observed by Ishiwata et al.12 to 350 µV/K in (CaOH)1.14CoO213 the former value being close to the expected value for an assembly of free spins 1/2. On the other hand, a lack of systematic trend has been shown for both resistivity and thermopower of these systems at low temperature.2 The low temperature thermopower exhibits a strong magnetic field dependence in BiCaCoO and in Na2CoO214 but not in BiBaCoO2.15 While for most cobaltates, there is a large temperature range where the thermopower is T-linear, this behavior does not extrapolate to zero at zero temperature in BiCaCoO, in contrast to, e.g., BiBaCoO2.14 Furthermore, it is known that the entropic contribution12,13,15,16 or the electronic correlations2,3,5,17,18,19 can increase thermopower, these two additive contributions further raise the aforementioned issue: what is the nature of the electronic states relevant to the transport?

To that aim we report in this paper on a crossed experimental investigation of the magnetoresistance and thermopower in single crystal cobalt oxide [Bi1.7Ca2O4]0.59CoO2, here used as a probe aimed at characterizing the coupling between itinerant and localized states. While a large negative magnetoresistance was already measured in sintered samples14 we demonstrate here that it follows a scaling behavior with both magnetic field and temperature. Originally introduced
in the context of the colossal magnetoresistance of the manganites, this scaling implies a spin dependent transport mechanism. Thus, we show that the analysis of the negative magnetoresistance allows to shed new light on the electronic states leading to high thermopower.

Similarly to Na$_2$CoO$_2$, the structure of the incommensurate cobalt oxide [Bi$_{1.7}$Ca$_2$O$_4$]$_{0.59}$CoO$_2$ (abbreviated thereafter BiCaCoO) contains single [CoO$_2$] layer of CdI$_2$ type stacked with rocksalt-type layers instead of a sodium deficient layer as displayed in Fig. 1. One of the in-plane sublattice parameters being different from one layer to the other, the cobaltate BiCaCoO has a misfit structure as in most related compounds. This system exhibits at room temperature a very large holelike thermopower $S \approx 138 \ \mu$V K$^{-1}$ and a rather low resistivity as in the so-called bad metals near a Mott metal-insulator transition.

II. TRANSPORT MEASUREMENTS

In order to investigate the transport properties and more specifically the magnetoresistance in BiCaCoO, we have measured the single crystal in-plane resistivity $\rho(H,T)$ using a standard four terminal method. The studied single crystals were grown using a standard flux method with typical sizes of the order of $4 \times 2 \times 0.02$ mm$^3$. As displayed in the inset of Fig. 2, the temperature dependence of the resistivity exhibits a transport crossover around 200 K from a high temperature metalliclike behavior to a low temperature insulatinglike one. While in the former regime the values of the resistivity remain rather low, Fig. 2 displays a large enhancement of $\rho$ at low temperature indicating thus an efficient localization process. We also observe that the latter behavior is strongly reduced by the application of an in-plane magnetic field suggesting an unconventional insulatinglike regime.

A. Magnetoresistance

In order to gain a better insight into this state, we have performed transport measurements as a function of an in-plane magnetic field $H$ at constant temperature $T$. The data reported in the inset of Fig. 3 spans the T-range from 60 K down to 3 K with a large negative magnetoresistance reaching at the lowest temperature 85 % at 9 T. Also, Fig. 3 demonstrates that the whole set of magnetoresistance data can be scaled onto a variable range hopping form (abbreviated thereafter VRH) which can be written as it follows.

$$\rho(H,T) = \rho_0(T)\exp\left(\frac{\tau_0(H/T)}{T}\right)^{\alpha}$$

While the two exponents $\alpha=1/2$ and $1/3$ lead to satisfactory scalings, it is worth noting that the value $\alpha=1/2$ provides the best collapse of the experimental points onto a single curve. Originally introduced by Mott to describe the electronic conduction in disordered materials, the VRH theory essentially leads to the exponents $\alpha=1/4$ or $1/3$ in three or two dimensions, and $\alpha=1/2$ in disordered systems with electron correlations.

More recently, the VRH mechanism has been extended to the case of magnetic disorder to explain the colossal negative magnetoresistance measured in manganites and also applied in the Chromium based spinel compounds. The main ideas which underlie this conducting process consist in a variable range spin dependent hopping (VRSDH) due to the Hund’s coupling...
25 with \( \Delta = 2J \). An applied magnetic field tends to align the localized spins and reduce the disorder, which implies a VRH conduction. Besides, an applied magnetic field tends to align the localized spins and thus lowers both \( \Delta_{ij} \) and the disorder, suggesting a negative magnetoresistance.

In order to give a deeper insight into the spin-dependent hopping that is more extensively developed in Ref. 21, an analogy can be performed with the conventional VRH process. In the latter case, the resistivity varies as \( \rho \propto \exp(T/T_0) \) with \( T_0 \propto 1/(\xi^3 g(E_F)) \), \( \xi \) being the localization length and \( g(E_F) \) the density of states at the Fermi level (DOS). Without any magnetic field, the VRSDH resistivity should thus depend on a parameter \( \tau_0 \propto 1/(\xi^3 n(\Delta_{ij})) \) as in Eq. (1), with \( n(\Delta_{ij}) \) the DOS of the magnetic potential barriers.

Within this framework, the latter DOS can then be deduced from the probability of finding an angle \( \theta_{ij} \) as \( n(\Delta_{ij}) \approx 1/\Delta \). Also, this constant DOS implies an average magnetic potential barrier \( \langle \Delta_{ij} \rangle = \Delta/2 \). The latter mean value is no longer valid when a magnetic field is applied because \( \langle \cos \theta_{ij} \rangle \neq 0 \), and it must be written as \( \langle \Delta_{ij} \rangle = \Delta(1 - \langle \cos \theta_{ij} \rangle)/2 \). In this case, the misorientation can be expressed from the local magnetizations \( \vec{M}_{i,j} \) at the two sites \( i \) and \( j \) as \( \vec{M}_{i} \cdot \vec{M}_{j} = M_S^2 \langle \cos \theta_{ij} \rangle \), with the saturation magnetization \( M_S \). Since there are no short range correlations in a paramagnet, the averaged magnetization is supposed to scale as the Brillouin function \( B_J(x) \) as discussed by Wagner et al. It is given by:

\[
B_J(x) = \frac{2J + 1}{2J} \coth ((2J + 1)x) - \frac{1}{2J} \coth(x)
\]

Here \( J \) is the angular momentum, \( x = (gh_B H)/(2k_B T) \), the Landé factor \( g = 2 \), \( k_B \) the Boltzmann constant, and \( \mu_B \) the Bohr magneton.

As a consequence, one deduces that \( \langle \cos \theta_{ij} \rangle = B_J(x)^2 \) and thus the averaged magnetic potential barrier is \( \langle \Delta_{ij} \rangle = \Delta \langle 1 - B_J(x)^2 \rangle/2 \). Since it is lowered from its value without magnetic field by the factor \( (1 - B_J(x)^2) \), one may infer that the new DOS is enhanced as \( n(\Delta_{ij}) \approx 1/\Delta(1 - B_J(x)^2) \) by assuming that it keeps constant over the whole range of potential. In this approximation, the temperature \( \tau_0(x) \) can be written following Eq. (3) with the unit cell volume \( v \).

\[
\tau_0(x) = (1 - B_J(x)^2) T_0^M \quad \text{and} \quad T_0^M \approx \frac{v \Delta}{\xi^3 \mu_B}
\]

The combination of both Eq. (1) and Eq. (2) leads to a complete analytic expression of the magnetoresistance with the only two parameters \( J \) and \( T_0^M \) that yields to the curves in Fig. 3 compared to the experimental data. The three tested sets of parameters with \( J = 1/2 \) (\( T_0^M = 24 \) K), \( J = 1 \) (\( T_0^M = 12 \) K) and \( J = 3/2 \) (\( T_0^M = 6 \) K) demonstrate unambiguously the agreement with \( J = 1/2 \) by also confirming the relevance of the analysis. One can here emphasize that the found rather low value of \( T_0^M \) is consistent with a VRH transport since it suggests as required a localization length exceeding the interatomic distances. Beyond these strong checks, this result implies that the localized spin involved here in the VRSDH mechanism in BiCaCoO is \( \sigma = 1/2 \) as previously inferred from the analysis of the magnetic field dependence of the thermopower and in agreement with the previously reported susceptibility measurements. As a consequence, it seems that both extended and localized states not only coexist but also give rise to unusual electronic properties as large negative magnetoresistance and high thermopower.

Let us now discuss the relevance of the electronic levels as sketched in Fig. 4 in BiCaCoO. By analogy with the crystallographic structure of Na\(_x\)CoO\(_2\) the [CoO\(_2\)] planes in the misfit cobaltates are assumed to be conducting and are stacked with the insulating rocksalt-type layers. These [CoO\(_2\)] layers consist in a 2D triangular lattice Co sheets octahedrally coordinated with O above and below the Co plane. As depicted in Fig. 4 the Co d levels are first crystal field split in the octahedral O environment into a lower lying \( t_{2g} \) and a upper lying \( e_g \) manifold. In this context, the six electrons of the Co\(^{3+} \) (d\(^6\)) occupy

FIG. 4: (color online). Schematic picture of the electronic energy levels involved in an elementary spin dependent hopping from the site \( i \) to the site \( j \). The magnetic potential barrier \( \Delta_{ij} \) results from the misorientation \( \theta_{ij} \) between the quasiparticle spin \( s_i \) and the localized spin \( \sigma_j \) as explained in the text.
Hund’s rule splitting, i.e. the $d_{xy}$ levels can become smaller than the spin down $d$ energy for sufficiently strong Hund’s coupling, the gap between the $d_{z^2}$ and the $d_{xy}$ levels respectively. (b) and (c): Spin dependent hopping mechanism between the Co$^{3+}$ and the Co$^{4+}$. The thin red arrow represents the quasiparticle spin and the bold black arrows the localized spin.

The $t_{2g}$ levels (see Fig. 5(a)). Second, the difference in energy between the $d_{z^2}$ and $d_{xy}$ levels can be reduced assuming a structural distortion of the octahedron following from a stretching of the the $z$ axis. Therefore, for sufficiently strong Hund’s coupling, the gap between the $d_{z^2}$ and the $d_{xy}$ levels can become smaller than the Hund’s rule splitting, i.e. the spin up $d_{z^2}$ energy can get smaller than the spin down $d_{xy}$ energy. As a result the scattering of itinerant $e_g$ electrons hopping from site to site by the localized $t_{2g}$ electrons, as illustrated in Fig. 5(b) and Fig. 5(c), leads to the same electronic background as in Fig. 4 and explains the above-mentioned negative magnetoresistance.

Even if this situation can be achieved from others scenarios, possibly involving others orbitals instead of the $d_{z^2}$ and the $d_{xy}$ ones, we emphasize that the aforementioned ingredients must remain to explain the magnetoresistance, namely a distorsion and a Hund’s splitting which reduce the $t_{2g}$-$e_g$ gap and spin polarization the electronic levels. Also, it is worth noting that a similar description with a strong coupling between the spin and the orbital degrees of freedom has been quite recently proposed in order to explain the magnetic properties in the parent compound Na$_2$CoO$_2$.

**B. Thermopower**

We now would like to address more specifically the connection between the electronic levels represented in Fig. 5(b) and 5(c) and the thermopower $S$ measured in BiCaCoO and reported in Fig. 6.

According to Fig. 5(b) and 5(c), the $t_{2g}$ electrons are localized ($\sigma=1/2$), while the lower $e_g$ electron ($\sigma=1/2$) is itinerant, preventing them from forming local triplet states on long time scales. Since the localized spins remain paramagnetic, they asymptotically give rise to a thermopower contribution $S_{\text{spin}}=k_B/e \ln(2)$ due to their spin entropy as displayed in Fig. 6 with $e$ the elementary electric charge. In order to provide a constant contribution over a wide temperature range, it is here assumed that their energy level is located in an energy width of a few tens of kelvin below the Fermi level and that it does not hybridize with the $e_g$ band. We stress that the latter interpretation is consistent with the fact that these spins are also responsible for a negative magnetothermopower.

On the other hand, the $e_g$ quasiparticles are expected to contribute to the thermopower as $S_{\text{QP}}\propto T/T_F$ at temperatures lower than the effective Fermi temperature $T_F\approx T_{F}\approx T_{F}/m^*$. Here $T_F$ is the bare Fermi temperature and $m^*$ is the effective mass which takes into account the electronic correlations. Note that, according to Pålsson and Kotliar, the thermopower does not depend on the scattering rate in the low temperature regime. Also, a rough estimate of the effective Fermi temperature inferred from the slope of $S$ leads to a very low value ($230 \, K < T_F < 260 \, K$) which implies an enhanced $m^*$ in agreement with the observed constant thermopower for $T>T_F$. In fact, at temperatures higher than $T_F$ the $e_g$ electronic excitations become incoherent and the related thermopower recovers a purely entropic form following Eq. (4). In this regime, the thermopower is temperature
with the degeneracy $N$ involving both spin and orbital degrees of freedom and the electronic filling factor $\delta$. Moreover, because of their spin polarized level the $e_g$ electrons have no more spin degeneracy, implying thus $N=1$ in Eq. (4). By adding the two aforementioned entropic contributions in Fig. 5, namely those originating from both the paramagnetic spins (the $t_{2g}$ electrons) and the quasiparticles (the $e_g$ electrons), one can therefore deduce the filling factor $\delta \approx 0.71$ corresponding to 0.29 hole. Let us finally discuss the electronic properties of the parent compound BiBaCoO. This cobaltate exhibits neither negative magnetoresistance nor negative magnetothermopower. The low temperature linear in $T$ dependence of $S$ extrapolates to zero in contrast to Fig. 6, suggesting the coexistence between localized and itinerant electrons that only extended states contribute to the thermopower. By shedding a new light on the electronic states leading to a high thermopower, this result likely provides a new potential way to optimize the thermoelectric properties.

### III. CONCLUSION

To conclude, we have investigated the low temperature magnetic field dependence of the resistivity in the thermoelectric misfit cobalt oxide BiBaCoO from 60 K down to 3 K. The scaling of the negative magnetoresistance demonstrates a spin dependent transport mechanism due to a strong Hund’s coupling. The inferred microscopic description implies dual electronic states which explain the coexistence between localized and itinerant electrons both contributing to the thermopower. Further experimental investigations are now needed in order to understand why these coexisting states are not observed in BiBaCoO in contrast to BiCaCoO.

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