

Large thermopower in a metallic cobaltite: The layered Tl-Sr-Co-O misfit

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The magnetic, transport, and thermoelectric properties of a Tl-based misfit cobaltite have been investigated. Although this material exhibits a metallic behavior, the thermopower (Seebeck) is large, with room temperature values close to $+90 \mu\text{V/K}$. Compared to previously studied misfit cobalt oxides $[\text{Ca}_3\text{Co}_4\text{O}_9, (\text{Bi}, \text{Pb})\text{SrCoO}]$ this Tl-based misfit is the only compound of this family which remains metallic and paramagnetic down to 2 K. On the one hand, this behavior emphasizes the importance of the edge-shared octahedra in the CoO_2 layer for the thermoelectric properties of these materials. On the other hand, the absence of a magnetically ordered state at low temperature explains the absence of low temperature negative magnetoresistance. It gives support to a mechanism based on quantum fluctuations stabilizing the paramagnetic state rather than a magnetically ordered state.

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Materials with a large thermopower (TEP) are potential candidates for applications to convert heat into energy. In this respect, transition metal oxides have been the focus of recent investigations after the discovery of high figure of merit Z in NaCo_2O_4 single crystals¹ ($Z = S^2\sigma/\kappa$ where S , σ , and κ are for Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively). The NaCo_2O_4 structure consists of the stacking of CoO_2 layers with the CdI_2 type structure, in which the edge-shared CoO_6 octahedra form a layer of triangular cobalt.² In the separating sodium layer the occupation of the crystallographic site is only 50% and random. Several explanations have been proposed to interpret the large figure of merit of NaCo_2O_4 .³⁻⁶ First, the random and partial filling of the Na site may help in the reduction of the thermal conductivity, necessary to obtain large Z , by analogy with the so-called “phonon glass.”³ Second, the thermopower is unusually large for a metal and several mechanisms have been proposed as the origin of such a large S . The degeneracy of the Co^{3+} and Co^{4+} low-spin (LS) electronic states, induced by the competition of Hund’s rule coupling and crystalline field, together with strong electron correlation could be responsible for the large S .⁴ Thermopower should also be enhanced in these cobalt oxides because of the triangular geometry of the CoO_2 planes which favors magnetic frustration, as emphasized by Merino *et al.*⁵ Lastly, by using density functional calculations within the local density approximation (LDA), the electronic structure of NaCo_2O_4 has been proposed.⁶ The three t_{2g} of LS cobalt species orbitals are further splitted by the rhombohedral crystal field in one a_{1g} and two e'_g orbitals and by applying the TEP formula to this band structure, realistic values of S are obtained.

Interestingly, the misfit-layered cobaltites are also built of similar CdI_2 type layers as in NaCo_2O_4 , but they are stacked with rock-salt type separating layers and the structural discordance of their two kinds of sublattices make them composite crystals.⁷⁻⁹ This class of cobalt oxides exhibits also high Seebeck values and low thermal conductivity, but, in contrast to NaCo_2O_4 , much lower electrical conductivities. This behavior is illustrated by the misfits $\text{Ca}_3\text{Co}_4\text{O}_9$ (Refs. 9 and 10) and $\text{Bi}_{3/4}\text{Pb}_{1/4}[\text{SrO}]_{1.06}\text{CoO}_2$.¹¹ This misfit cobaltites

(although their separating rock-salt type layers are of very different chemical natures Ca/Co/O or Bi/Pb/Sr/O), exhibit very similar transport properties, with a reentrant increasing resistivity at low temperatures along the conducting CoO_2 planes together with a large negative magnetoresistance, $\text{MR} = 100 \times ([\rho(H) - \rho(O)]/\rho(O))$, reaching $\sim -60\%$ in 8 T at 2 K.¹²

Consequently in both NaCo_2O_4 and misfit cobaltites, the CoO_2 layer plays a major role for the large TEP values but exhibits very different transport properties. In order to extend this conclusion and to search for other misfit oxide with large thermopower, we have reinvestigated the properties of Tl-based misfit of formula $\text{Tl}_{0.4}[\text{Sr}_{0.9}\text{O}]_{1.12}\text{CoO}_2$ for which only resistivity data have been published.⁷ In the present Brief Report, we report on the thermal, electronic, and magnetic properties of this Tl based misfit cobaltite. In contrast to other known misfit cobaltites CaCoO and $(\text{Bi}, \text{Pb})\text{SrCoO}$, this oxide remains metallic down to 2 K and does not exhibit negative magnetoresistance. The existence of a paramagnetic state, even at the lowest temperatures, is shown to be connected with the lack of upturn in the resistivity at low temperature in this Tl-misfit cobaltite. Despite these differences in the low temperature background state, its thermopower is also characterized by a large value at 300 K. This result gives support to the model based on a mixture of low-spin Co^{3+} and Co^{4+} species, characteristic of the edge-shared CoO_6 octahedra of the triangular lattice of cobalt: the corresponding narrow a_{1g} bandwidth yields a high value of the density of states at the Fermi level⁶ thought to be responsible for the Seebeck values.

The chemical preparation of the polycrystalline Tl-based misfit cobaltite was previously reported.⁷ Polycrystalline samples in the Tl-Sr-Co-O system were prepared with two steps. A precursor was firstly synthesized using a mixture of Co_3O_4 and SrCO_3 . The reactants were weighted according to a molar ratio Sr/Co of one. The mixture was ground in an agate mortar and heated in air at 950°C for 24 h, for decarbonation. Secondly, the thallium oxide Tl_2O_3 was added according to the relative ratio Tl/Sr equal to 0.6. The powder was pressed in the form of bars, packed in an alumina finger and sealed in an evacuated silica tube. The samples were

heated at 880 °C during 24 h and then slowly cooled (50 h). Magnetization data were collected with a commercial dc SQUID magnetometer (1.8–400 K; $0 \leq \mu_0 H \leq 5$ T). A physical properties measurements system (PPMS from Quantum Design) was used to measure resistivity (ρ), thermopower (Seebeck, S), and thermal conductivity (κ). Electrical contacts were made of ultrasonic deposited indium on $2 \times 2 \times 10$ mm³ bars of ceramic for the four-probe technique. The sample holder used for thermopower and thermal conductivity has been previously described.¹³

The x-ray diffraction pattern and transition electron microscopy observations of the as-prepared ceramic are compatible with a monoclinic symmetry. EDS analyses carried out on numerous crystallites lead to the cationic composition “Tl_{0.4}SrCo” and in the following, for sake of clarity, this phase will be written TlSrCoO. It should be pointed out that the cationic distribution is very homogeneous from part to part of the bar. Moreover, within these preparation conditions, the chemical reaction is very reproducible leading to constant 0.4:1:1 ratios for Tl:Sr:Co. All attempts to increase the oxygen content by postannealing treatments under oxygen pressure (150 atm, $400 \leq T \leq 600$ °C) were unsuccessful, if one judges by the absence of change in the T dependent resistivity. In fact, the synthesis of these materials is very sensitive to the internal oxygen pressure in the sealed tube during the reaction. The Tl₂O₃ decomposition in Tl₂O and O₂ controls the oxygen partial pressure. Consequently, by keeping constant the Tl₂O₃ quantity in the tube, the experiments are very reproducible. By changing this internal pressure via the use of different precursors, the thallium content can, however, be modified. This chemical aspect is outside of the scope of this paper and will be published separately. Powder x-ray diffraction pattern can be described with the coexistence of two C centered sublattices with common a , c , and β parameters (4.94 Å, 11.38 Å, and 97.8°, respectively) but with two different incommensurate related b parameters (5.01 Å and 2.80 Å). A first structural model was already proposed.⁷ There is also a great analogy between the lattices parameters for the present compound and those of the thallium free compound of general formula Ca₃Co₄O₉ which exhibits close structural parameters (4.83 Å, 10.76 Å, $\beta = 98^\circ$).^{9,14} A structural study involving the aperiodic character of the structure is in progress. Both models imply the alternation along c of a rock salt type subsystem (sublattice 1) and of [CoO₂] layers (sublattice 2) displaying a distorted pseudo hexagonal CdI₂ type structure ($a_2 \approx b_2 \sqrt{3}$). Similarities in the structural parameters of TlSrCoO and CaCoO indicate that the thicknesses of their sublattice 1 are close. The block of rocksalt type layers is thicker in the (Bi/Pb)SrCoO misfit cobaltite if one refers to the structural parameters ($a = 4.92$ Å, $c = 15.05$ Å, $\beta = 93.55^\circ$) showing a larger c value.^{8,15}

The T -dependent ρ of TlSrCoO shows that this compound exhibits a metallic behavior down to the lowest T of 2 K, ρ decreasing from 20 mΩ cm at 300 K down to 2.5 mΩ cm at 2 K (Fig. 1). This room temperature value is close to the $\rho_{ab}(300\text{ K})$ values reported for other (Bi, Pb)SrCoO (Ref. 11) and CaCoO (Ref. 9) misfit cobaltites, $\rho_{ab}(300\text{ K}) \sim 10$ mΩ cm. However, resistivity values of the latter go

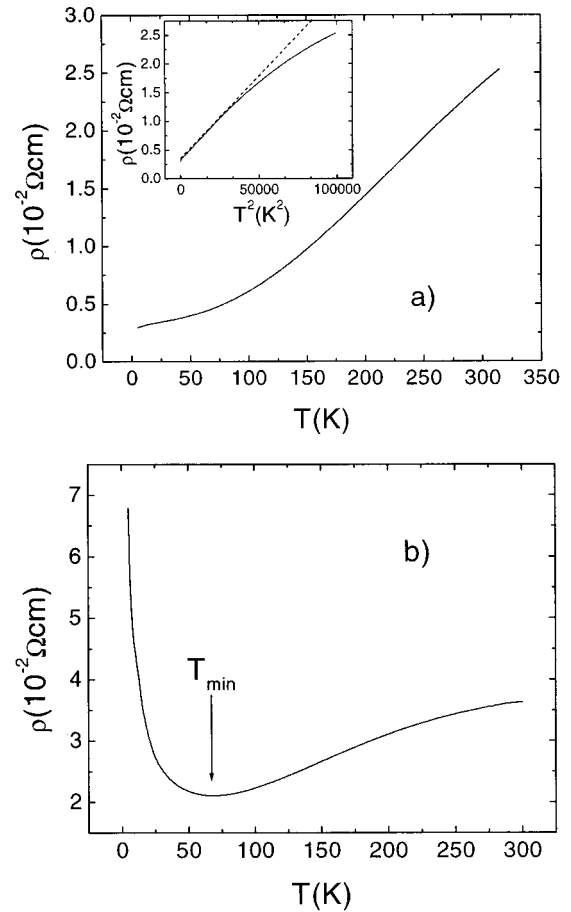


FIG. 1. T dependent resistivity of the TlSrCoO (a) and CaCoO from Ref. 8 (b) misfit cobaltites.

through a minimum at $T_{\min} \approx 75$ K below which they exhibit a reentrant behavior shown in Fig. 1(b) for Ca₃Co₄O₉. This temperature dependence contrasts with the positive slope $d\rho/dT > 0$ observed at all T for the Tl based misfit.

The resistivity is not the only physical properties of TlSrCoO which differs from that of the (Bi, Pb)SrCoO and CaCoO layered cobaltites. From T dependent magnetization (M) registered in 0.3 T, the inverse susceptibility $\chi^{-1}(T)$ has been obtained (Fig. 2) from which a clear paramagnetic re-

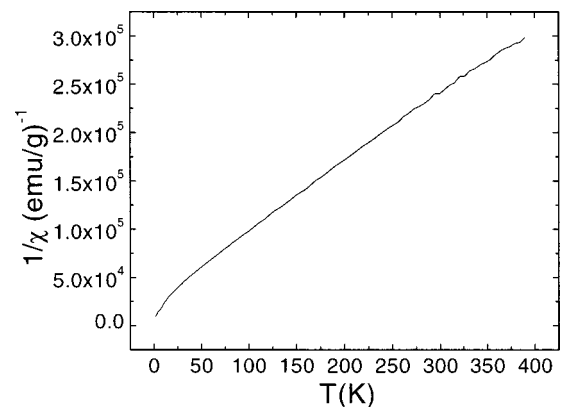


FIG. 2. T dependent inverse susceptibility (χ^{-1}) of TlSrCoO ($\mu_0 H = 0.3$ T).

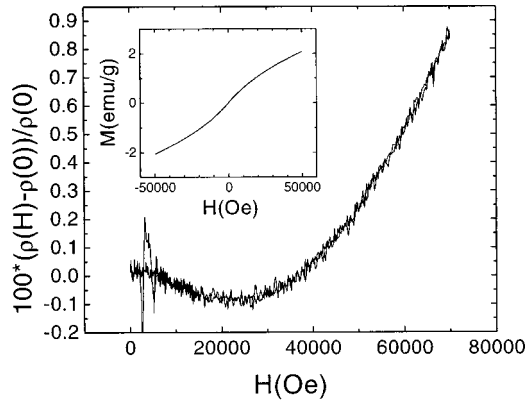


FIG. 3. Isothermal ($T=5$ K) magnetic field (H) dependence of resistivity (ρ) for the TI-based misfit cobaltite. Inset: corresponding isothermal $M(H)$ curve.

game extending down to 2 K is deduced. The absence of magnetic ordering at low T differs thus from the weak ferromagnetism of (Bi, Pb)SrCoO (Ref. 11) and the $\chi^{-1}(T)$ deviating from linearity for $\text{Ca}_3\text{Co}_4\text{O}_9$.⁹ From the slope of the $\chi^{-1}(T)$ curve (Fig. 2), the effective moment μ_{eff} is found to be $1.14\mu_B/\text{Co}$ for TlSrCoO assuming that all cobalt sites contribute equally to the Curie constant. This small μ_{eff} value can be explained by considering a mixture of low-spin Co^{3+} ($S=0$) and Co^{4+} ($S=1/2$; $\mu_{\text{eff}}=1.73\mu_B$) in the TlSrCoO misfit, yielding a ratio 57:43 for the $\text{Co}^{3+}:\text{Co}^{4+}$ species.

An interesting property of the misfit cobaltites is their large negative magnetoresistance which is connected with spin polarized transport at temperatures below or close to the magnetic ordering transitions. But, as aforementioned, the absence of magnetic ordering in TlSrCoO precludes a large negative magnetoresistance to be observed in the TI based misfit. This is confirmed by the $\rho(H)$ curves showing that the magnetoresistance under 7 T is small and positive reaching $\sim +1\%$ at 5 K (Fig. 3). This is in accordance with the corresponding paramagnetic behavior attested by the linearity of the $M(H)$ curve (inset of Fig. 3). The same $\rho(H)$ behavior is also observed at 2 K. A positive and small MR is typical of metals and it originates in the cyclotron magnetoresistance.

At first glance, compared to the misfits CaCoO and BiPbSrCo, the TlSrCoO cobaltite exhibits differences in the resistivity (absence of reentrant behavior at low T), magnetism (absence of magnetic ordering) and magnetoresistance (positive with a small magnitude). Nevertheless, despite this different behavior, the “TEP” is not strongly affected (Fig. 4). For instance, although the room temperature value at 300 K is smaller than that of $\text{Ca}_3\text{Co}_4\text{O}_9$ (also shown in Fig. 4), $S(300\text{ K})$ decreases only from $+125\ \mu\text{V K}^{-1}$ to $+90\ \mu\text{V K}^{-1}$ for $\text{Ca}_3\text{Co}_4\text{O}_9$ and TlSrCoO, respectively. This S value is still very large if one considers the metallicity of this compound.

To our knowledge, the TlSrCoO oxide is the first example among the misfit cobaltites to show a metallic behavior down to 2 K. The absence of localization in TlSrCoO even at 2 K, suggests that the carriers mean free path is longer than in

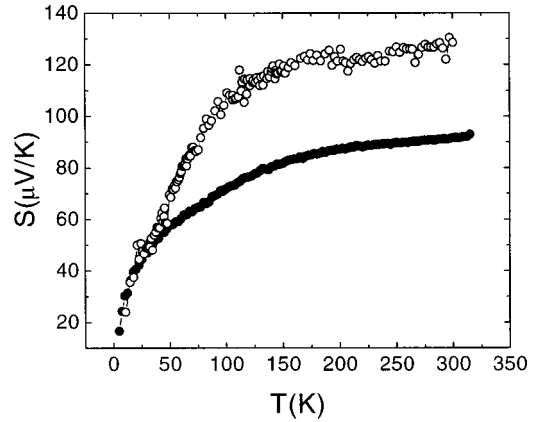


FIG. 4. T dependent thermopower (Seebeck, “ S ”) of two misfit cobaltites TlSrCoO (\bullet) and $\text{Ca}_3\text{Co}_4\text{O}_9$ (\circ).

other misfits, i.e., (Bi, Pb)SrCoO and CaCoO. Reduction in the spin scattering at low temperature under magnetic field application was thought to explain the large negative MR of (Bi/Pb)SrCoO misfit and CaCoO which both exhibit magnetically ordered states at low T . In this respect, observed metallic behavior together with the absence of a large negative MR even at 2 K in the TlSrCoO misfit is most probably linked to the absence of magnetic ordering phenomena.

The existence of metallicity in the TlSrCoO oxide down to very low temperatures and the absence of magnetic ordering makes this compound more similar to the other cobalt oxide containing CoO_2 layers of CdI_2 type Na_xCoO_2 ,¹⁶ the most studied composition being $x=0.5$.¹ However, at very low temperature, the resistivity behaves differently in these two compounds: the residual resistivity of NaCo_2O_4 is very small when $T \rightarrow 0$ K and corresponds to 5% of the room temperature resistivity, independently of the quality of grain boundaries¹⁷ whereas in TlSrCoO it goes down to only 15% of the resistivity at 295 K as $T \rightarrow 0$ (Fig. 1). Since ρ decreases as T decreases down to the lowest T , the electron-phonon scattering is weak at low T in the TlSrCoO which is characteristic of the strongly correlated system. For the latter, one expects $\rho \propto T^2$ temperature dependence, which is verified in the temperature range 20–150 K where ρ depends quadratically on the temperature as shown in the inset of Fig. 1. This behavior is characteristic of a Fermi liquid. For $T > 150$ K, ρ exhibits a quasilinear behavior as a function of T . Note that for NaCo_2O_4 the T^2 dependence of ρ is never observed which again emphasizes the existence of subtle differences in their transport properties. Also, negative magnetoresistance is reported for NaCo_2O_4 (Ref. 18) which is, however, more metallic than TlSrCoO.

These two different types of low temperature behaviors could be reconciled by considering the calculations of the electronic and magnetic properties of the oxide NaCo_2O_4 .⁶ But at first an hypothesis should be made. The CoO_2 layers are very similar in both NaCo_2O_4 and TlSrCoO and the separating layers, partially filled Na layer or rock-salt type (Tl/Sr)O layers, play only a role of donors to the CoO_2 metallic layers. According to the composite structure of the misfit, the interaction between the sublattices is probably weak as in NaCo_2O_4 between Na and CoO_2 layers. In first approxima-

tion, it seems thus reasonable to apply the calculations (local density and local spin density approximations) made by Singh for NaCo_2O_4 (Ref. 6) to the TlSrCoO misfit. From the obtained electronic and magnetic properties, it appears that at low temperature weak instabilities of itinerant magnetic character could be formed, but that the paramagnetic solution could also be stabilized even at 0 K via quantum fluctuations. The negative MR of NaCo_2O_4 would thus reflect a magnetically ordered state whereas the positive MR, the $\rho\alpha T^2$ behavior below $T < 100$ K, and the paramagnetic state in TlSrCoO is more compatible with a renormalized Fermi liquid stabilized by quantum fluctuations. A metallic behavior of ρ at low T for these cobaltites, would not necessarily imply a positive MR, whereas a reentrant ρ at low T would go with a magnetic ordering and a negative magnetoresistance.

Finally, this study of the TlSrCoO misfit demonstrates that a RT high positive thermopower value is always observed in layered cobalt oxides in which CoO_2 layer is made of edge-shared CoO_6 octahedra. First, this is in strong contrast with the small negative thermopower value of the 1201-type $\text{TlSr}_2\text{CoO}_{5-\delta}$ cobaltite ($S = -10 \mu\text{V K}^{-1}$ in the metallic state) containing a CoO_2 layer derived from the perovskite (corner-shared octahedra like in cuprates) with a $\text{Co}^{3+}/\text{Co}^{4+}$ mixed valency.¹⁹ This difference can be ascribed to the LS configurations of both $\text{Co}^{3+}/\text{Co}^{4+}$ which are stabilized in the CdI_2 type CoO_2 layer. Such a configuration is also found in the TlSrCoO misfit if one refers to the small μ_{eff} value extracted from the Curie-Weiss fitting of T dependent inverse susceptibility. As proposed in Ref. 6 and experimentally observed by photoemission work,²⁰ the t_{2g} orbitals of the LS $\text{Co}^{3+}/\text{Co}^{4+}$ are further splitted by the rhombohedral distortion of the octahedron in one a_{1g} orbital and two e'_g orbitals. Accordingly, even if the modified Heikes formula,

$$S = -\frac{k_B}{e} \ln\left(\frac{g_3}{g_4} \frac{x}{1-x}\right), \quad (1)$$

where the Co^{3+} and Co^{4+} number of configurations which depends on the spin configuration (low-, intermediate-, and high-spin states) and x is the concentration of Co^{4+} ,⁴ leads to a reasonable cobalt valency for TlSrCoO misfit, $x = 0.68$, i.e., $\nu_{\text{Co}} = 3.68$, by taking $g_3 = 1$ and $g_4 = 6$ for LS $\text{Co}^{3+}/\text{Co}^{4+}$ in Eq. (1) and the experimental value $S^{300\text{K}} = +90 \mu\text{V K}^{-1}$, this model which does not take into account the peculiar splitting of the t_{2g} levels in the CoO_2 layer is probably not realistic enough.

The thermopower calculated from the LDA band structure of NaCo_2O_4 (Ref. 6) which takes into account the effect of rhombohedral crystal field is thus more correct and it gives $S^{300\text{K}} = +110 \mu\text{V K}^{-1}$, i.e., a value very close to the experimental one $S = +100 \mu\text{V K}^{-1}$ observed for NaCo_2O_4 . In this scenario, the smaller TEP value measured in TlSrCoO , $+90 \mu\text{V K}^{-1}$, would reflect a decrease either in the DOS at the Fermi level [$N(E_F)$] or in the band velocity. It should be emphasized that in this framework, the TEP depends linearly on T but this is not what is experimentally observed (Fig. 4). Nevertheless, the narrow a_{1g} band containing strongly electron-phonon coupled holes would be responsible for the large TEP values of the cobalt oxides containing CdI_2 type layers such as NaCo_2O_4 and misfit layered cobaltites. The “light” itinerant holes in the e'_g are responsible for the more or less pronounced metallicity. Respective changes in the bandwidths and in the hole filling as T is varying could probably explain the low temperature differences from phase to phase and particularly the reentrant resistivity and the large negative magnetoresistance only observed in (Bi/Pb)- SrCoO and CaCoO misfit cobaltite.

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