

Large Thermopower in Metallic Misfit Cobaltites

A. Maignan,* L. B. Wang, S. Hébert, D. Pelloquin, and B. Raveau

Laboratoire CRISMAT, UMR 6508 CNRS/ISMRA, 6 boulevard du Maréchal Juin,
14050 Caen Cedex 4, France

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The possibility to improve the thermoelectric properties of the misfit layer cobaltite $[\text{Tl}_{1-x}\text{Sr}_{2+x-y}\text{Co}_y\text{O}_3][\text{CoO}_2]_{b_1/b_2}$, either by increasing the Tl content or by substituting Bi or Tl, has been investigated. Using a direct synthesis method, it is shown that the Tl content in this oxide, written for sake of clarity $\text{Tl}_\alpha\text{SrCoO}_{3+\delta}$, can be increased significantly up to a maximum value $\alpha = 2/3$, by simultaneously increasing the oxygen pressure during the synthesis. The so-prepared $\text{Tl}_\alpha\text{SrCoO}_{3+\delta}$ oxides are characterized by a decrease of resistivity as α increases up to $2/3$, whereas the thermopower remains unchanged, suggesting a possible improvement of the figure of merit. The substitution of Bi for Tl leads to larger thermopower at room temperature but, in contrast, induces an upturn in the resistivity and negative magnetoresistance at low temperature.

I. Introduction

Thermoelectric properties in oxides have been the focus of numerous studies these past years after the discovery of a high thermopower ($\approx 100 \mu\text{V}\cdot\text{K}^{-1}$ at 300 K) and a low resistivity ($\approx 200 \mu\Omega\cdot\text{cm}$ at 300 K) in NaCo_2O_4 .¹ Thermoelectric materials are very important because the electrical energy conversion into heat and vice versa is economical and nonpolluting. In this respect, the research and optimization of the “misfit” cobaltites^{2–5} are a very interesting challenge. The structure of these oxides is also built of the same CoO_2 layers as in NaCo_2O_4 , that is, 2D triangular Co sheets of the CdI_2 type containing edge-shared CoO_6 octahedra.

In NaCo_2O_4 , the cobalt valency is close to +3.5 and both trivalent and tetravalent cobalt cations adopt a low-spin state configuration.^{1,6–7} Nevertheless, the t_{2g} orbitals are split into two bands, two a_{1g} and one e'_{1g} levels, which make the richness of their physical properties because “heavy” and “light” holes in the a_{1g} and e'_{1g} orbitals, respectively, contribute at the Fermi level.^{8–9} A similar electronic configuration is expected in the case of the “misfit” cobaltites in which the 2D structural

character is even more pronounced. In the latter, the CoO_2 conducting layers are interleaved with three or four rock-salt- (RS-) type layers but each sublattice, RS (S_1) and CoO_2 (S_2), is incommensurate with respect to the other. The two monoclinic sublattices possess similar a , c , and β parameters but different b cell parameters. Their composite structure explains thus why they are called misfit by analogy with the misfit layer structures of chalcogenides. In the case of the oxides, the structure of RS layers is similar to that of high T_c superconducting (HTCS) cuprates, involving three RS-type layers, $\text{SrO}-\text{TlO}-\text{SrO}\dots$, or four RS-type layers, $\text{SrO}-(\text{Bi}/\text{Pb})\text{O}-(\text{Bi}/\text{Pb})\text{O}-\text{SrO}$, in thallium- and bismuth-based misfit cobaltites, respectively.^{2,3} A third example of such a structure has been more recently obtained with the compound $[\text{CoCa}_2\text{O}_3][\text{CoO}_2]_{1.62}$ where $b_1/b_2 = 1.62$.^{4,5} The structure of this oxide (Figure 1), whose chemical formula is generally rewritten $\text{Ca}_3\text{Co}_4\text{O}_9$ or $\text{Co}_{1/3}\text{CaCoO}_{3+\delta}$, has cell parameters close to those of $\text{Tl}_{0.4}\text{SrCoO}_{3+\delta}$.² This can be easily understood if one considers that its structure is described as the intergrowth of triple RS-type layers $\text{CaO}-\text{CoO}-\text{CaO}$ with single CoO_2 layers. Interestingly, thermopower (TEP) values at room temperature (RT) of all these misfit oxides are all in the range $+90$ to $+130 \mu\text{V}\cdot\text{K}^{-1}$,^{4,5,10,11} that is, very close to that of NaCo_2O_4 . Thus, although the misfit cobaltites can exhibit very different magnetic and electrical transport properties, the TEP originates in the peculiarities of their similar CoO_2 layers. For instance, this is illustrated by the differences in the T -dependent resistivities of $\text{Tl}_{0.4}\text{SrCoO}_{3+\delta}$ and $\text{Ca}_3\text{Co}_4\text{O}_9$ (rewritten $\text{Co}_{1/3}\text{CaCoO}_{3+\delta}$ in the following) misfits cobaltites, the former and the latter exhibiting, below 100 K, metallic¹¹ and semiconducting-like^{4,5} behaviors, respectively.

Chemical substitutions at the level of either RS or CoO_2 layers are expected to affect the properties of these

* To whom correspondence should be addressed. E-mail: antoine.maignan@ismra.fr. Tel.: 33 2 31 45 26 34. Fax: 33 2 31 95 16 00.

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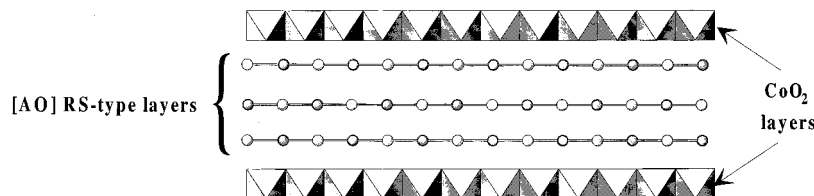


Figure 1. Schematic representation of a misfit structure where a block of three RS-type layers (sublattice S_1) is interleaved with one CoO_2 layer (sublattice S_2).

Table 1. Starting Composition, Cationic Composition from EDS Analysis, and Deduced Composite Formula^a

starting composition	cationic composition (EDS)	composite formula	$a_1 = a_2$ a (Å)	b_1 (Å)	$c_1 = c_2$ c (Å)	β (Å)	b_1/b_2
$\text{Tl}_{0.6}\text{SrCoO}_{3.5}$	$\text{Tl}_{0.38}\text{SrCo}_{1.06}$	$[\text{Tl}_{0.75}\text{Sr}_{1.97}\text{Co}_{0.28}][\text{CoO}_2]_{1.794}$	4.947	5.026	11.539	97.84	1.794
$\text{Tl}_{0.6}\text{SrCoO}_{4.28}$	$\text{Tl}_{0.54}\text{SrCo}_{1.01}$	$[\text{Tl}_{1.01}\text{Sr}_{1.88}\text{Co}_{0.11}][\text{CoO}_2]_{1.779}$	4.940	4.996	11.675	97.74	1.779
$\text{Tl}_{0.6}\text{SrCoO}_{4.86}$	$\text{Tl}_{0.66}\text{SrCo}_{1.08}$	$[\text{Tl}_{1.17}\text{Sr}_{1.75}\text{Co}_{0.10}][\text{CoO}_2]_{1.758}$	4.921	4.946	11.694	97.69	1.758

^a Cell parameters, β angle, and b_1/b_2 ratio from structural refinements. b_1 and b_2 belong to the RS (S_1) and CoO_2 (S_2) sublattices, respectively, reflecting the incommensurate nature of these oxides.

cobaltites by modifying the carrier content, the electrical coupling perpendicular to the CoO_2 planes, and the phonons' contribution to the thermal conductivity. Among all the misfit cobaltites, the Tl-based one, $\text{Tl}_{0.4}\text{SrCoO}_{3+\delta}$, is the only one showing metallic and paramagnetic behaviors down to 2 K.¹¹ In the following, we report on the possibility to increase the Tl content in this phase by controlling the internal oxygen pressure used during the synthesis in a closed ampule. Substitution of Bi for Tl has also been studied whereas the substitution of Pb leads always to a phase mixture. We show how two types of variations of the composition, that is, Tl content and Tl/Bi substitution, affect in very different ways the physical properties.

II. Effect of the Tl and Oxygen Contents on the Transport Properties

In previous studies, the $\text{Tl}_{0.4}\text{SrCoO}_{3+\delta}$ misfit cobaltite was prepared with a two-step preparation method.² At first, a SrCoO_3 precursor was prepared in air by mixing SrCO_3 and $\text{CoO}_{1.38}$. Then, the Tl_2O_3 oxide was added to the precursor according to the nominal $\text{Tl}_{0.6}\text{SrCoO}_x$ composition. After careful grinding, the powder was pressed into bars that were set in silica ampules which were sealed under vacuum. The reaction was carried out at 900 °C. X-ray energy-dispersive analysis (EDS) of the reacted bars leads to the following homogeneous cationic composition, “ $\text{Tl}_{0.4}\text{SrCo}$ ”. In this method, the extra amount of Tl_2O_3 [nominal $\text{Tl}_{0.6}$, final $\text{Tl}_{0.4}$] brings an internal oxygen pressure in the tube during the synthesis according to the reaction $\text{Tl}_2\text{O}_3 \leftrightarrow \text{Tl}_2\text{O} + \text{O}_2$. Although it was successful, this technique does not allow the oxygen pressure to be controlled independently of the Tl content. In the present study, we have thus developed a one-step route of preparation by using the SrO_2 peroxide as an additional source of oxygen in the tube. For instance, when the nominal Tl content is kept fixed to “ $\text{Tl}_{0.6}$ ”, the nominal oxygen content can be increased by using SrO_2 and varying the $\text{Co}/\text{CoO}_{1.38}$ ratio. The corresponding powders pressed in the form of bars are heated at 900 °C in sealed silica tubes. A first series of $\text{Tl}_{0.6}\text{SrCoO}_x$ samples has thus been prepared by varying the nominal oxygen content x from 3.5 to 4.28, the latter corresponding to the maximum oxygen content (without Co metal). For $\text{Tl}_{0.6}\text{SrCoO}_{3.5}$, the X-ray diffraction (XRD) pattern reveals extra peaks, indicating

the presence of impurities beside the powder misfit phase. From “ $\text{O}_{3.7}$ ” to “ $\text{O}_{4.1}$ ”, the XRD patterns of the reacted material show that the samples are pure. When electron diffraction and EDS cationic analyses are combined, it is found that a misfit phase, isostructural to $\text{Tl}_{0.4}\text{SrCoO}_{3+\delta}$, is formed with a Tl content that increases with the oxygen nominal content (x) from “ $\text{Tl}_{0.38}$ ” to “ $\text{Tl}_{0.54}$ ” for $x = 3.7$ and $x = 4.28$, respectively.

From powder X-ray diffraction data, the cell parameters of several samples (Table 1) have been refined starting from the structural model of $[\text{CoCa}_2\text{O}_3][\text{CoO}_2]_{1.62}$ ⁴ and by using a 4D formalism as described in ref 15. By combining the structural parameters deduced from these refinements with the cationic contents deduced from EDS analyses, an ideal formula of the composite structures is derived as shown in Table 1. The inspection of the cell parameters shows that as the Tl content increases, a , b_1 , b_1/b_2 , and β decrease whereas the c cell parameter increases. The decrease of the a_1 and b_1 cell parameters of the RS-type sublattice is consistent with the smaller ionic radius of Tl^{3+} than Sr^{2+} . The generic formula can thus be expressed $[\text{Tl}_{1-x}\text{Sr}_{2+x-y}\text{Co}_y\text{O}_3][\text{CoO}_2]_{b_1/b_2}$, where x , y , and b_1/b_2 vary concomitantly in the respective ranges $-0.16 \leq x \leq 0.25$, $0.12 \leq y \leq 0.28$, and $1.76 \leq b_1/b_2 \leq 1.79$. Moreover, it also appears that for $x < 0$ the excess Tl can be accommodated at the level of the SrO layers. It should be also emphasized that some Co cations can be incorporated in the RS slab as shown previously in $[\text{CoCa}_2\text{O}_3][\text{CoO}_2]_{1.62}$.⁴

Changes in the final Tl content affect directly the transport properties as illustrated in Figure 2 by the T -dependent resistivity (ρ) curves (four-probe method). At 300 K, ρ decreases as the final Tl content increases from 64 $\text{m}\Omega\cdot\text{cm}$ in the phase mixture obtained for $\text{O}_{3.5}$, down to 22 $\text{m}\Omega\cdot\text{cm}$ for $\text{O}_{4.28}$, which corresponds to $\text{Tl}_{0.54}$. Interestingly, the shape of the $\rho(T)$ curves is only slightly changed as the Tl content increases as shown by the normalized $\rho(T)/\rho_{300\text{K}}$ curves in the inset of Figure 2. All the obtained compounds remain metallic down to the lowest T with all $\rho_{300\text{K}}/\rho_{5\text{K}}$ ratios close to 10–20.

For thermopower materials, one has to calculate the figure of merit $Z = S^2\sigma/\kappa$ where S , σ , and κ stand for thermopower, electrical conductivity, and thermal conductivity. The ρ decrease as the Tl content increases corresponds thus to a possible Z improvement in the

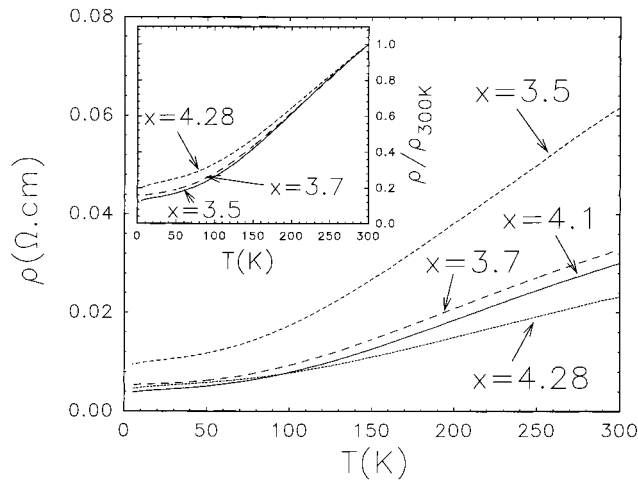


Figure 2. T -dependent resistivity of Tl-based misfit compounds obtained by increasing the nominal oxygen content x from 3.5 to 4.28 in $\text{Tl}_{0.6}\text{SrCoO}_x$. Increasing x induces an increase of the Tl content from “ $\text{Tl}_{0.38}$ to $\text{Tl}_{0.54}$ ” for “ $\text{O}_{3.7}$ ” and “ $\text{O}_{4.28}$ ”, respectively. Inset: T -dependent normalized $\rho/\rho_{300\text{K}}$ curves obtained for reacted compounds of $\text{Tl}_{0.6}\text{SrCoO}_x$ nominal compositions. Nominal oxygen content x is indicated on the graph.

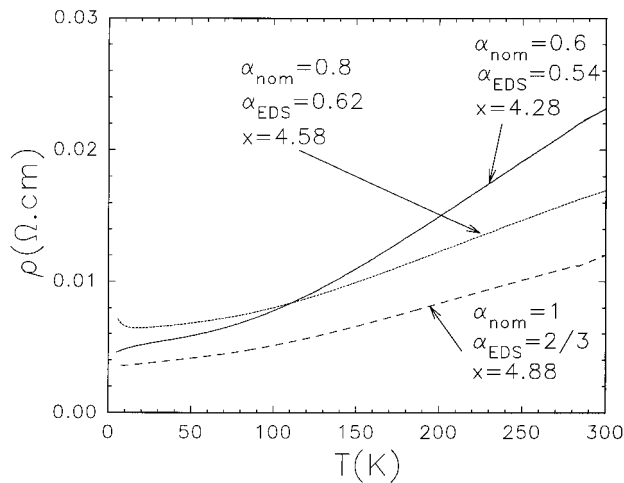


Figure 3. $\rho(T)$ curves of $\text{Tl}_{\alpha_{\text{EDS}}}\text{SrCoO}_{3+\delta}$ misfit oxides. α_{EDS} and α_{nom} are for the EDS and nominal Tl contents, respectively. x corresponds to the nominal oxygen content. x and α values are labeled on the graph.

case of TlSrCoO misfit cobaltite. In a second step, we have then tried to use the beneficial effect of the Tl content increase on ρ by increasing further the nominal Tl content via the use of the maximum nominal oxygen content (only SrO_2 and $\text{CoO}_{1.38}$ are used). Four nominal Tl contents α_{nom} ranging from “ $\text{Tl}_{0.6}$ to $\text{Tl}_{1.5}$ ” have been used with corresponding nominal oxygen contents in the range $\text{O}_{4.28}$ – $\text{O}_{5.63}$. As shown in Figure 3, ρ decreases from $\text{Tl}_{0.6}$ to $\text{Tl}_{1.0}$ through $\text{Tl}_{0.8}$. This trend can be compared to the cationic contents (from EDS) which show that the Tl content α_{EDS} does not regularly evolve with α_{nom} ; $\alpha_{\text{EDS}} = 0.54$ and $\alpha_{\text{EDS}} = 0.66$ for $\alpha_{\text{nom}} = 0.6$ to $\alpha_{\text{nom}} = 1$, respectively, and then α_{EDS} increases only to 0.68 for $\alpha_{\text{nom}} = 1.5$. This means that the latter composition contains more impurities as confirmed by XRD (the corresponding resistivity curve is not shown). Nonetheless, these results show that the maximum amount of Tl incorporated in the Tl misfit is close to $2/3$, yielding the chemical formula $\text{Tl}_{2/3}\text{SrCoO}_{3+\delta}$.

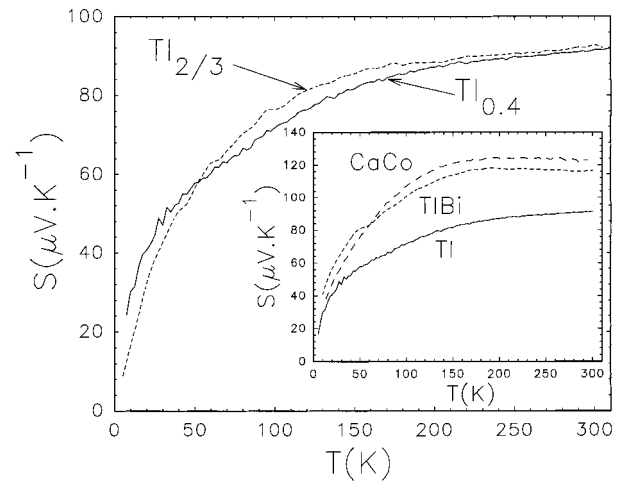


Figure 4. T -dependent thermopower (S) of $\text{Tl}_{0.4}\text{SrCoO}_{3+\delta}$ (“ $\text{Tl}_{0.4}$ ”) and $\text{Tl}_{2/3}\text{SrCo}_{3+\delta}$ (“ $\text{Tl}_{2/3}$ ”). These thallium contents in the final samples are obtained from EDS analyses. Inset: $S(T)$ curves of “Tl”- and “TlBi”-misfit cobaltites.

It should be emphasized that the ρ decrease obtained by increasing the Tl content is not simply an effect of the increase of the oxygen content since by annealing under high-oxygen pressure ($\text{PO}_2 = 150$ atm) samples of different Tl contents, no change in the $\rho(T)$ curves can be induced. From the viewpoint of the figure of merit, a higher amount of Tl is beneficial since ρ decreases, although the thermopower (steady-state method) is unchanged as shown from the $S(T)$ curves in Figure 4 for $\text{Tl}_{0.4}$ and $\text{Tl}_{2/3}$, which both exhibit S values of $+92 \mu\text{V}\cdot\text{K}^{-1}$ at 300 K.

III. Substitution of Bismuth for Thallium

Structural relationships between the RS-type layers of misfit cobaltites and of HTCS opens the route to the discovery of new Tl-based misfit cobaltites. Because bismuth and lead were substituted for Tl in the case of Tl-based cuprates such as the $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ “1212” superconductor, leading to the following formulas, $\text{Tl}_{2/3}\text{Bi}_{1/3}\text{Sr}_2\text{CaCu}_2\text{O}_7$ and $\text{Tl}_{1/2}\text{Pb}_{1/2}\text{Sr}_2\text{CaCu}_2\text{O}_7$,¹² several attempts of Bi or Pb substitutions for Tl have been made in the Tl-based misfit prepared with the one-step method described in the previous part. First of all, by variation of the nominal Pb content from $x = 0.1$ to $x = 0.3$ in $\text{Tl}_{0.6-x}\text{Pb}_x\text{SrCoO}_{4.28}$, the EDS analyses of the reacted materials always reveal the existence of a phase mixture made of Pb-rich and Pb-poor misfit cobaltites. If one refers to the recent discovery of the Pb/Sr/Co/O misfit,¹³ this result may be due to the higher thermodynamical stability of the end members compared to that of the mixed Tl/Pb misfit. Second, since in the case of bismuth there is no pure Bi-based misfit equivalently made of three RS-type layers interleaved with the CoO_2 layer, it is found that a single misfit phase of analyzed cationic composition “ $\text{Tl}_{0.28}\text{Bi}_{0.14}\text{SrCo}$ ” can be stabilized by starting from the nominal composition $(\text{Tl}_{2/3}\text{Bi}_{1/3})_{0.6}\text{SrCoO}_{4.28}$. It should be pointed out that by starting from the Tl/Bi = 1 ratio, a Tl/Bi = 2 final ratio

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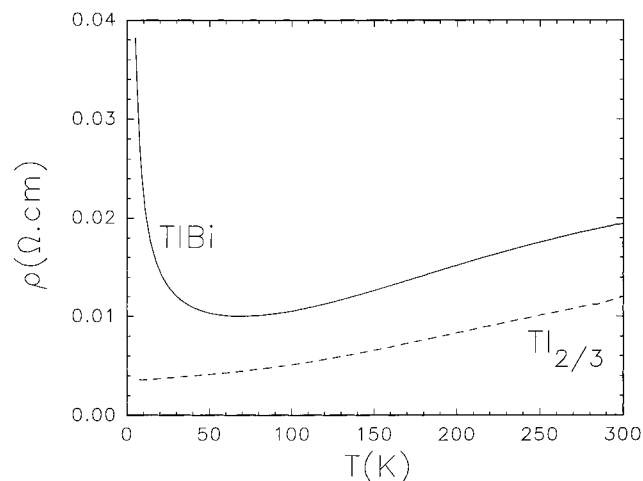


Figure 5. $\rho(T)$ curves of $\text{Tl}_{0.28}\text{Bi}_{0.14}\text{SrCoO}_{3+\delta}$ (“TlBi”) and $\text{Tl}_{2/3}\text{SrCoO}_{3+\delta}$ (“Tl”). Tl and Bi contents are the result of EDS analyses.

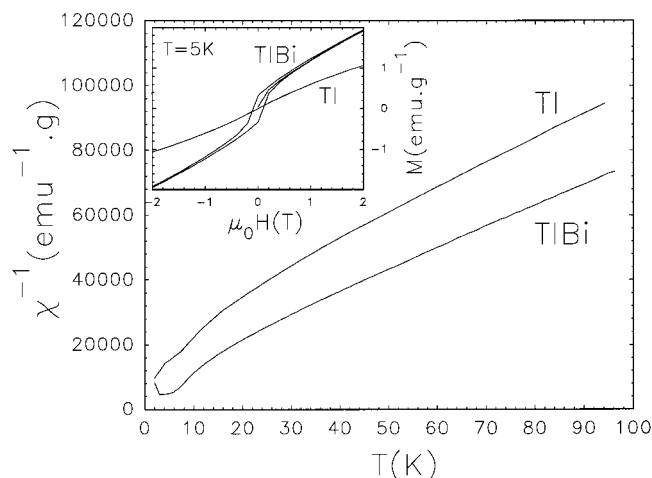


Figure 6. T -dependent inverse magnetic susceptibility (χ^{-1}) of “Tl” and “TlBi” misfits. χ^{-1} values are calculated from magnetization data measured with a SQUID magnetometer ($\mu_0 H = 0.3$ T). Inset: Magnetic field dependence of the magnetization at 5 K for both “Tl” ($\text{Tl}_{0.4}\text{SrCoO}_{3+\delta}$) and “TlBi” ($\text{Tl}_{0.28}\text{Bi}_{0.14}\text{SrCoO}_{3+\delta}$) misfit cobaltites.

is always measured by EDS, indicating the great stability of the phase corresponding to the ratio Tl/Bi = 2, as is the case for the $\text{Tl}_{2/3}\text{Bi}_{1/3}$ -1212 superconducting cuprate.¹²

Although the Bi for Tl partial substitution does not modify significantly the 300 K resistivity value, $\rho_{\text{Tl/Bi}} = 20$ m $\Omega\cdot\text{cm}$ vs $\rho_{\text{Tl}} = 12$ m $\Omega\cdot\text{cm}$ for the more conductive sample (see the corresponding $\rho(T)$ curves in Figure 5), the low- T part of the curve is dramatically changed by the Bi substitution which induces a metal–insulator crossover at 60 K. Accordingly, ρ reaches a minimum value of 10 m $\Omega\cdot\text{cm}$ at 60 K and then increases as T further decreases to reach $\rho = 38$ m $\Omega\cdot\text{cm}$ at 5 K. A similar $\rho(T)$ shape was also found in the case of the $\text{Co}_{1/3}\text{CaCoO}_{3+\delta}$ misfit⁴ in the form of polycrystals or single crystals (along the ab plane). This shape modification of the $\rho(T)$ curve compared with that of the Tl–Sr–Co–O misfits can be ascribed to the different magnetic behavior induced by Bi. As shown in the T -dependent inverse susceptibility $\chi^{-1}(T)$ curves of Figure 6, the TlBi misfit undergoes a magnetic transition below 10 K and χ^{-1} starts to deviate from the

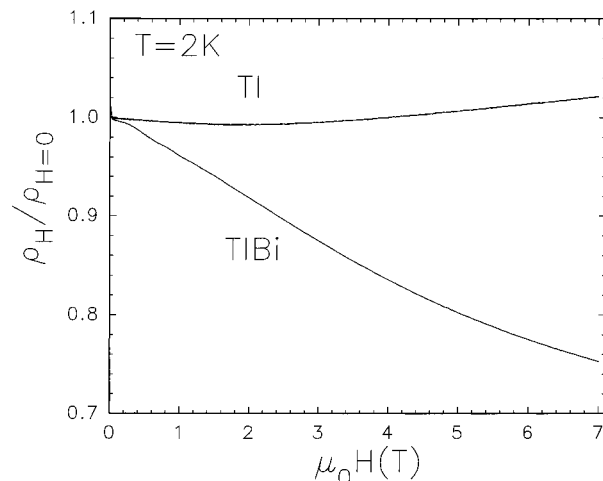


Figure 7. Comparison of the isothermal ($T = 2$ K) magneto-resistance of “Tl” and “TlBi”-misfits cobaltites.

linearity below ≈ 50 K, whereas the Tl–Sr–Co–O misfit remains paramagnetic down to 2 K.¹¹ This is also shown in the inset of Figure 6 where a clear hysteresis is found in the $M(H)$ loop of the Tl/Bi misfit. Accordingly, in the absence of applied magnetic field, disorder in the spins alignment makes the resistivity increase as the sample becomes magnetic and under field application the spin scattering reduction leads to a negative magneto-resistance.

The latter, defined as $\text{MR} = -100 \times [\rho_H/\rho_{H=0} - 1]$, reaches 25% in 7 T at 2 K for TlBi (Figure 7), whereas in the absence of magnetic ordering, the magneto-resistance is positive in the metallic Tl misfit MR, reaching 2% in 7 T.

In contrast to the results of the previous section, which show a RT thermopower independent of the Tl content, the thermopower values of the TlBi misfit are larger than those of the Tl misfit (see inset of Figure 4), $+120$ and $+90$ $\mu\text{V}\cdot\text{K}^{-1}$ for TlBi- and Tl-based misfits, respectively. In fact, the TlBi $S_{300\text{K}}$ value is similar to that of $\text{Co}_{1/3}\text{CaCoO}_{3+\delta}$, that is, $\text{Ca}_3\text{Co}_4\text{O}_9$.^{4,5}

IV. Concluding Remarks

We have tried to improve the physical properties required for thermoelectric materials by using two different “chemical” approaches in the Tl-based misfit, either increasing the Tl content or substituting Bi for Tl. The first one consists of increasing the Tl content in the RS-type layers, which are interleaved with the CoO_2 layers. This is realized by controlling the oxygen pressure used during the synthesis via the use of Tl_2O_3 , SrO_2 , $\text{CoO}_{1.38}$, and Co precursors. This one-step preparation has allowed the increase of the Tl content α in $\text{Tl}_\alpha\text{SrCoO}_{3+\delta}$ from $\alpha = 0.4$ up to $\alpha = 0.68$. Interestingly, the Tl content increase has a direct impact on the resistivity values at RT, $\rho_{300\text{K}}$ decreasing as α increases until $\alpha = 2/3$. Moreover, since the RT thermopower value is kept unchanged, one can expect an improvement for the figure of merit. This point will be definitely proved only when the thermal conductivity will be shown to be insensitive to the Tl content.

Among the misfit cobaltites, the Tl/Sr/Co/O one is unique since this is the only compound which exhibits metallicity and paramagnetism down to the lowest tem-

perature accompanied by a positive magnetoresistance. As discussed in the paper by Singh on the electronic structure of NaCo_2O_4 ,⁸ it is very difficult to predict the low- T magnetic state of the cobalt oxides made of CdI_2 -type CoO_2 layers since magnetically ordered or paramagnetic solutions cannot be distinguished. In this respect, the second chemical route consisting of the Bi for Tl substitution is interesting since, on one hand, it induces at low T , a metal–insulator transition and negative magnetoresistance, and on the other hand, an increase of the thermopower value at RT. It should be pointed out that, in these cobaltites, all the compounds exhibiting a RT thermopower value larger than that of a Tl-based misfit show a negative magnetoresistance linked to the nonmetallic resistivity at low T .

Finally, since all the thermopower values of misfit cobaltites are close to those of NaCo_2O_4 , one has to consider that the peculiar rhomboedral splitting of the t_{2g} orbitals of $\text{Co}^{3+}/\text{Co}^{4+}$ of the CoO_2 layer into a_{1g} and e'_g levels is responsible for these high values. In this framework, it was proposed that the narrow band made

of heavy holes in the a_{1g} orbitals mostly contributes at the Fermi level to yield large thermopower.^{8,14} It appears thus that this band is not very sensitive to the nature of the separating layers interleaved between the CoO_2 layer. In contrast, the different behaviors of resistivity and magnetism can be interpreted as the result of a modification in the filling or in the position of the e'_g band made of mobile holes. However, the composite nature of these misfit oxides makes very difficult the refinements of their structures. Subtle changes in the cell parameters can affect the a_{1g} and e'_g respective contributions at E_F . Single crystals are now required to quantify the mobile holes density by the Hall effect and to check simultaneously the structural changes induced by the change of Tl content or by Bi for Tl substitution.

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