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2009 J. Phys.: Condens. Matter 21 235404

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Metallicity and positive magnetoresistance induced by Pb substitution in a misfit cobaltate crystal

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Received 23 December 2008, in final form 18 March 2009

Published 18 May 2009

Online at stacks.iop.org/JPhysCM/21/235404

Abstract

We have synthesized single crystals of the misfit-layered cobalt oxide, $[\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_{1.86}$, with quadruple NaCl-type layers, using a flux method, and measured their transport properties. From structural refinements, it is found that the modulation in the BiO layer observed in $[\text{Bi}_{1.74}\text{Sr}_2\text{O}_{4-\delta}]^{\text{RS}}[\text{CoO}_2]_{1.82}$ is suppressed by Pb substitution. The in-plane resistivity, thermopower, and Hall coefficient are $4.3 \text{ m}\Omega \text{ cm}$, $101 \mu\text{V K}^{-1}$, and $1 \times 10^{-2} \text{ cm}^3 \text{ C}^{-1}$ at 300 K, respectively; these are consistent with those of the misfit-layered cobalt oxides. All of these values are smaller than those of $[\text{Bi}_{1.74}\text{Sr}_2\text{O}_4][\text{CoO}_2]_{1.82}$, indicating that the carrier concentration is larger than that of the undoped crystal. Moreover, the low T upturn of resistivity observed for most of the cobalt misfit oxides is replaced by a metallic behavior, following a T^2 dependence, indicating strong correlations in the Pb-doped crystal. Also, the magnetoresistance, usually negative for misfit oxides, is replaced by a small positive magnetoresistance. Doping with Pb is thus an efficient way to suppress the low T localized behavior usually observed for misfits.

1. Introduction

Misfit-layered cobalt oxides $[\text{Bi}_2\text{A}_2\text{O}_4]^{\text{RS}}[\text{CoO}_2]_p$ ($\text{A} = \text{Ca}$, Sr , and Ba) show interesting properties such as large negative magnetoresistance and magnetothermopower for $\text{A} = \text{Ca}$ [1], a metal–insulator transition at low temperatures [2], and high thermoelectric performance. In particular, the whisker crystal of Bi–Sr–Co–O shows a dimensionless figure of merit $ZT > 1$ ($ZT = (S^2/\rho\kappa)T$, where S , ρ , κ , and T represent thermopower, resistivity, thermal conductivity, and temperature, respectively) at 973 K [3], which shows that the Bi-based misfit oxides can be good candidates for thermoelectric applications. In $[\text{Bi}_2\text{A}_2\text{O}_4]^{\text{RS}}[\text{CoO}_2]_p$, the $[\text{CoO}_2]$ layer with a hexagonal lattice isostructural to CdI_2 is separated by four rocksalt-type block layers (RS-type layers) with a tetragonal lattice [4]. These two kinds of structures are alternately stacked along the c axis (see figure 1), with the misfit feature characterized by the p ratio ($p = b_1/b_2$, where

b_1 and b_2 represent b parameters of the monoclinic RS-type and CoO_2 sublattices, respectively²).

Comparing to Na_xCoO_2 ($x \sim 0.7$), the misfits present similar characteristics for $T > 100 \text{ K}$, with large thermopower and metallic resistivities. However, at lower T , a striking difference is observed in the resistivity curves, with a strong increase of ρ , and the appearance of large negative magnetoresistance, in most misfit oxides [5, 6]. Due to the low T upturn of both resistivity and S/T , the formation of a pseudogap has been proposed, and this pseudogap would be at the origin of the large negative magnetoresistance observed at low T [2]. More recently, the upturn and related negative magnetoresistance have been attributed to a localized spin dependent scattering mechanism [7]: in this scenario, itinerant carriers are diffused by paramagnetic $S = 1/2$ spins.

It has been shown that this low T behavior can be different, replaced by a metallic behavior at low T . Two metallic compounds down to 2 K with a T^2 behavior have been reported

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² p is also defined by b_2/b_1 . In that case, we use the composition formula $[\text{Bi}_2\text{A}_2\text{O}_{4-\delta}]_p\text{CoO}_2$.

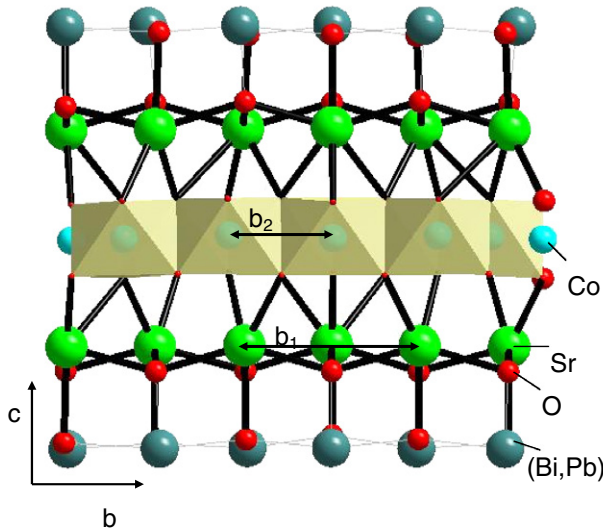


Figure 1. Crystal structure of $[\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_{1.86}$.
(This figure is in colour only in the electronic version)

so far: polycrystals of $[\text{Ti}_{0.81}\text{Co}_{0.2}\text{Sr}_{1.99}\text{O}_3]^{\text{RS}}[\text{CoO}_2]_{1.79}$ [8] and $[\text{Sr}_2\text{O}_{2-\delta}][\text{CoO}_2]_{1.89}$ [9]. Single crystals of the $[\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_p$ family have been previously investigated in detail for $x \leq 0.44$ [6] and it was found that Pb doping induces a reduction of resistivity, even if the low T upturn of resistivity still exists for $x = 0.44$. Measurements of the resistivity within the ab plane showed that a metallic behavior is observed in the a direction for $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Co}_2\text{O}_y$ with $x = 0.4$ [10], but that a small upturn is still observed in the b direction. The Pb substitution therefore seems to be an efficient way to induce a more metallic behavior in this family of oxides.

In the misfit cobalt oxides, the Co formal oxidation state in the CoO_2 layers ν_{Co} is expressed as $\nu_{\text{Co}} = 4 - \alpha/p$, deriving from its compositional formula, where α and p represent the charge of the block layer and the misfit ratio, respectively [11]. The Pb ions are efficient dopants for decreasing the α value through a substitution of Pb^{2+} for Bi^{3+} . If p is almost constant, the small α value should correspond to a higher Co oxidation state according to $\nu_{\text{Co}} = 4 - \alpha/p$. It should be kept in mind that Pb has also a strong impact on the structural properties as it completely suppresses the BiO modulation [10], as previously observed in the case of high T_c superconductors [12]. In the present paper, the investigation of Pb substitution with a large Pb content has been carried out on the BiSrCoO family. A new single-crystal phase, $[\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_{1.86}$, has been synthesized in this family, with a large Pb^{2+} content $x = 0.5$. This Pb substitution completely suppresses the upturn of the in-plane resistivity observed at low T , recovers a T^2 behavior characteristic of a Fermi liquid, and moreover induces positive magnetoresistance at low T .

2. Experimental procedure

Single crystals of $[\text{Bi}_{1.74}\text{Sr}_2\text{O}_{4-\delta}]^{\text{RS}}[\text{CoO}_2]_{1.82}$ have been synthesized as previously described [4]. Single crystals

of $[\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_{1.86}$ were grown by the flux method using $\text{K}_2\text{CO}_3\text{--KCl}$ as fluxes. In the first step, polycrystalline samples were prepared by a solid-state reaction method. Stoichiometric amounts of the precursors Bi_2O_3 , Pb_3O_4 , SrCO_3 , and Co_3O_4 were mixed in the molar ratio 0.75:0.17:2:0.62, and the mixtures were heated at 1073 K. Then the prepared powder sample and a $\text{K}_2\text{CO}_3\text{--KCl}$ mixture were mixed in a ratio 1:30 and 2.5 g of this mixture was put in an alumina crucible. The $\text{K}_2\text{CO}_3\text{--KCl}$ ratio of the flux was 4:1. The loaded crucible was kept at 1093 K for 12 h, and cooled at 4 K h^{-1} to 973 K, then at 10 K h^{-1} to 873 K, and finally to room temperature at 100 K h^{-1} . Small single-crystal samples were extracted from the batch by dissolving the flux in water. These black crystals are in platelet shape with typical dimensions of 1 mm \times 1 mm \times 0.02 mm.

Single-crystal x-ray diffraction studies were performed at room temperature using Mo $\text{K}\alpha$ radiation with a Nonius Kappa CCD diffractometer. The cationic composition was determined using energy dispersive x-ray spectroscopy coupled to scanning electron microscopy using a Zeiss Supra 55 scanning electron microscope.

The in-plane resistivity was measured by a four-probe method from 2.5 to 400 K using a physical properties measurement system (PPMS, Quantum Design). Four contact terminals were made from Ag paste (Dupont 6838) and gold wire with a diameter of 20 μm on a surface of the crystal. The magnetoresistance was measured at 2.5 K under 0–7 T using the PPMS. The in-plane thermopower was measured using a steady-state technique with a small temperature difference of about 1 K detected using a chromel–constantan thermocouple from 5 to 320 K using the PPMS. The in-plane Hall coefficient measurement was performed using the PPMS by applying –5 to 5 T. Due to the inhomogeneous thickness of the samples, the resistivity and Hall coefficient have error bars of $\pm 10\%$.

3. Results and discussion

The structure of the pure Bi phase $[\text{Bi}_{1.74}\text{Sr}_2\text{O}_{4-\delta}]^{\text{RS}}[\text{CoO}_2]_{1.82}$, hereafter labeled ‘BSCO’, has already been reported [4]. It is characterized by two aperiodicities, a first one related to the irrational misfit ratio of the unit-cell parameter mismatch between the two sublattices and a second one related to a dispersive longitudinal modulation in the BiO layers. Compared to those of other BSCO crystals reported in the literature, this misfit ratio is smaller (1.82 [4] as compared to 1.93 [6, 10]), and this difference could be due to a difference in oxygen stoichiometry induced by the sealed tube technique [4], or by a slight shift of cation contents at the level of the RS sublattice. A similar impact of the oxygen content on b_1/b_2 has been evidenced in $[\text{Ca}_2\text{CoO}_3][\text{CoO}_2]_{1.62}$ [13], with the smaller b_1/b_2 observed for the more reduced compound.

The misfit character of the Pb-substituted phases is still observed with a very close misfit ratio ($p = 1.86$), but the intrinsic modulation of the BiO layer systematically disappears. A similar trend of the modulation of this type of (Bi, Pb)O layers was already observed in high T_c Bi-based superconducting copper oxides: with Pb substitution, a locking of the modulation vector on a simple commensurate value or

Table 1. Formula and crystallographic parameters of the BSCO and BPSCO crystals.

Formula	a (Å)	b_1 (Å)	b_2 (Å)	$p = b_1/b_2$	c (Å)	β (deg)
$[\text{Bi}_{1.74}\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_{1.82}$	4.91	5.11	2.81	1.82	14.93	93.45
$[\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_{1.86}$	4.90	5.25	2.83	1.86	15.14	96.37

even the disappearance of the modulation was observed [12]. The combination of energy dispersive x-ray spectroscopy coupled to electron scanning microscopy and x-ray diffraction revealed the cationic formula ‘ $\text{Bi}_{1.57}\text{Pb}_{0.6}\text{Sr}_2\text{Co}_{1.86}$ ’ with an apparent excess of Bi and Pb probably related to surface contamination of the samples. A rescaling of this composition, taking into account the misfit ratio, and the maximum number of four cations in the RS layers, leads to $[\text{Bi}_{1.45}\text{Pb}_{0.55}\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_{1.86}$ which is rounded to $[\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_{1.86}$. The unit-cell parameters of the two crystals investigated here are given in table 1. Hereafter we denote $[\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_{1.86}$ as BPSCO.

Figure 2(a) shows the in-plane resistivity of $[\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_{1.86}$ and $[\text{Bi}_{1.74}\text{Sr}_2\text{O}_{4-\delta}]^{\text{RS}}[\text{CoO}_2]_{1.82}$. The resistivity for BPSCO is 4.3 mΩ cm at 300 K, smaller than the 8.2 mΩ cm for BSCO. The temperature dependence of BPSCO is very interesting. BPSCO exhibits metallic conduction down to 2.5 K, while BSCO exhibits insulating behavior below 75 K. Below 170 K, the resistivity of BPSCO is fitted by $\rho = AT^2 + B$, where A is $4.8 \times 10^{-8} \Omega \text{ cm K}^{-2}$ as shown in figure 2(b). Similar T^2 behaviors are observed below 1 K in $\text{Na}_{0.7}\text{CoO}_2$ [14], below 30 K in $\text{Na}_{0.31}\text{CoO}_2$ [15], and below 180 K in $[\text{Tl}_{0.81}\text{Co}_{0.2}\text{Sr}_{1.99}\text{O}_3][\text{CoO}_2]_{1.79}$ [8]. A metallic behavior has already been observed in BPSCO with $x = 0.4$ [10] in the a direction, but with an upturn still existing in the b direction. Here, the upturn must have been suppressed in the two directions; otherwise it would still be observed as $\rho(T)$ depends on both the a and the b components.

Figure 3 shows the magnetoresistance MR ($\text{MR} \equiv [R(H) - R(0)]/R(0) \times 100$) at 2.5 K for BPSCO and BSCO single crystals. BPSCO exhibits a large positive magnetoresistance +14% at 2.5 K, while Yamamoto *et al* observed a large negative MR in the Pb-doped BSCO crystal [6]. The difference may be related to the behavior of the resistivity at low temperatures. Generally, the layered cobalt oxides which exhibit an upturn in resistivity at low temperatures exhibit a large negative MR [5, 6] and ones which do not exhibit an upturn exhibit a positive MR [8], whose origin is still under investigation, as discussed later. The small positive MR proportional to $(\mu_0 H)^2$ for conventional metal can be explained by the Lorentz force, but the positive MR observed here is rather large (+14%) and does not obey the characteristic $(\mu_0 H)^2$ law.

Figure 4 shows in-plane thermopower as a function of temperature for BPSCO and BSCO single crystals. The thermopower is $101 \mu\text{V K}^{-1}$ at 300 K, smaller than the S of $123 \mu\text{V K}^{-1}$ at 300 K for BSCO. The value for BPSCO is comparable to S for metallic misfit oxides such as $[\text{Sr}_2\text{O}_2]_{0.53}\text{CoO}_2$ ($75 \mu\text{V K}^{-1}$) [9] or $[\text{Tl}_{0.81}\text{Co}_{0.2}\text{Sr}_{1.99}\text{O}_3]^{\text{RS}}[\text{CoO}_2]_{1.79}$ ($90 \mu\text{V K}^{-1}$) [8]. Also, for polycrystals of BiBaCoO which exhibit metallic behavior, except for a small upturn at low T , and positive magnetore-

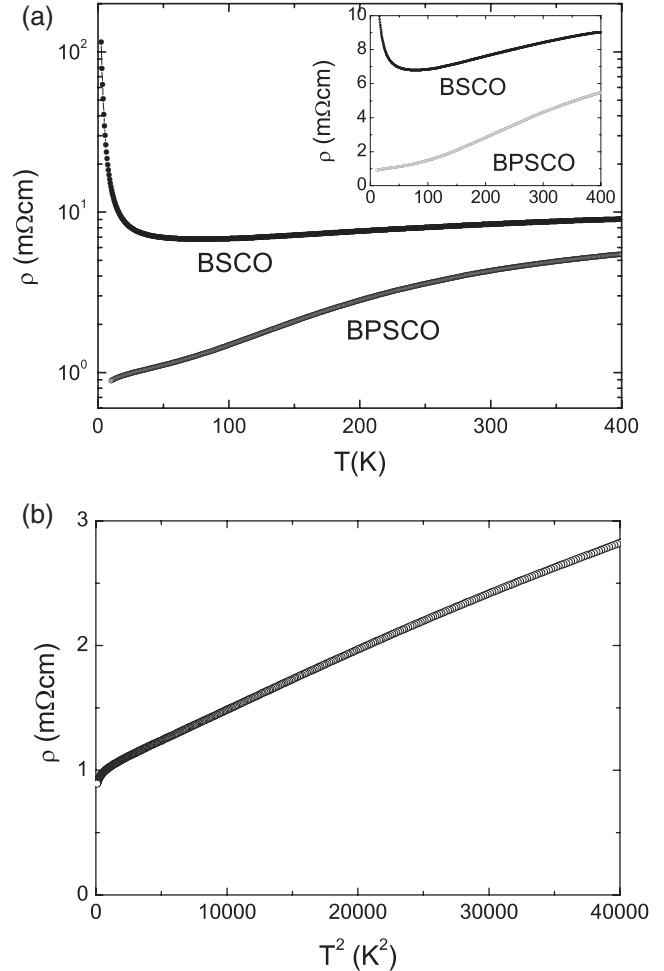


Figure 2. (a) In-plane resistivity on a logarithmic scale or linear scale (inset) for BSCO and BPSCO, and (b) as a function of T^2 for BPSCO.

sistance, the thermopower is equal to $95 \mu\text{V K}^{-1}$ [16]. The present S values for the BPSCO crystal are much smaller than the one reported for the $x = 0.4$ BPSCO crystals in [10], in which S at 300 K was found to be $150 \mu\text{V K}^{-1}$ in the metallic crystallographic a direction, but our values are closer to those of [2]. Such a difference of S for similar Pb contents emphasizes the importance of systematically coupling the structural analysis with the transport property measurements. The c axis of the sample investigated here is indeed closer to the one of [2] rather than the one of [10].

Temperature dependence of the thermopower is characteristic of all misfits: below 150 K a rather steep slope (dS/dT) is observed, while an almost constant value is observed at around room temperature. The inset shows the power factor $\text{PF} = S^2/\rho$, which characterizes the material for potential thermoelectric applications. At 300 K, the PF reaches

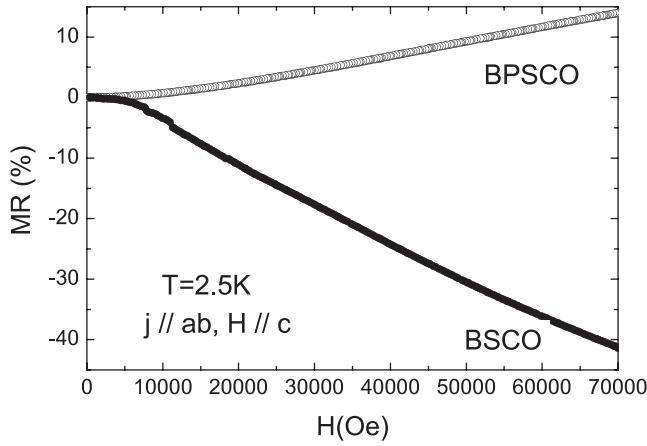


Figure 3. In-plane magnetoresistance for BSCO and BPSCO single crystals.

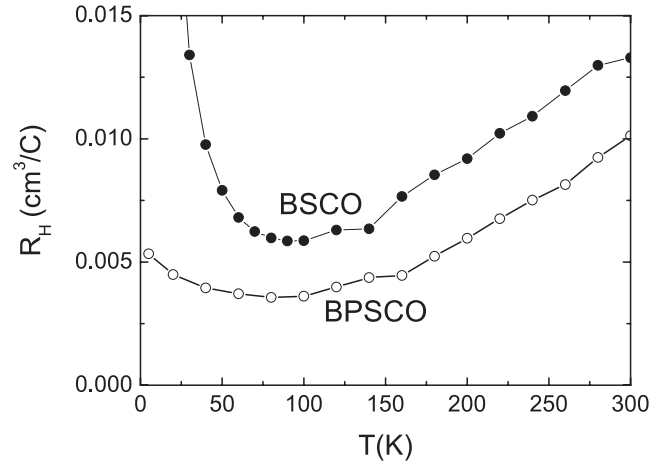


Figure 5. In-plane Hall coefficient for BSCO and BPSCO single crystals.

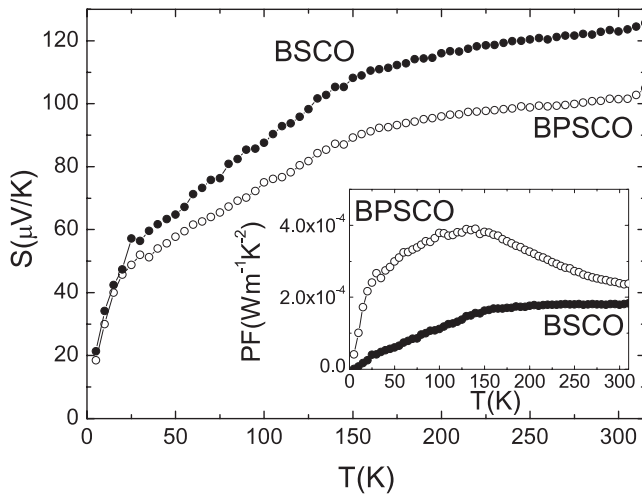


Figure 4. In-plane thermopower for BSCO and BPSCO single crystals. The inset shows the power factor for the crystals.

$2.4 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$, slightly larger than that of BSCO ($1.8 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$). Moreover, due to the metallic behavior of BPSCO, the PF is strongly increased in the low T range compared to that of BSCO, reaching $4 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ at 100 K.

Figure 5 shows the in-plane Hall coefficient R_H of BPSCO as a function of temperature. At 300 K, the value is $1 \times 10^{-2} \text{ cm}^3 \text{ C}^{-1}$ for BPSCO and the temperature dependence is linear-like down to 100 K. The linear-like temperature dependences are typical of layered cobalt oxides with triangular CoO_2 lattices [6, 10, 17]. Below 100 K, a small upturn is observed, while a large upturn for BSCO below about 100 K is observed. The value is two orders of magnitude smaller than that of BSCO at 5 K. The interpretation of the Hall effect data for these strongly correlated systems is not trivial [18], but according to the simplest equation $R_H = 1/ne$, we can estimate the carrier concentration to be $1.73 \times 10^{21} \text{ cm}^{-3}$ for BPSCO and $1.06 \times 10^{21} \text{ cm}^{-3}$ for BSCO at 100 K. The carrier concentration corresponds to $\text{Co}^{+3.178}$ for BPSCO, and $\text{Co}^{+3.109}$ for BSCO.

The evolution of R_H confirms that the doping plays a crucial role, both for metallicity and thermopower. The increase of the carrier concentration mainly comes from the modified α value via Pb^{2+} substitution for Bi^{3+} through $\nu_{\text{Co}} = 4 - \alpha/p$. Note that the carrier concentration can also be slightly changed by the small shift of the misfit ratio, i.e. from 1.82 for BSCO to 1.86 for BPSCO. Compared to the previous reports [6], the Pb^{2+} concentration is larger, and the low T upturn of $\rho(T)$ which was progressively suppressed by Pb^{2+} in [6] has now completely disappeared. This shows that metallicity can be obtained in this family of layered cobaltates, even when the misfit ratio is far from rational, as previously shown for $[\text{Ti}_{0.81}\text{Co}_{0.2}\text{Sr}_{1.99}\text{O}_3]^{\text{RS}}[\text{CoO}_2]_{1.79}$ [7]. It should be noted that the modulation in the BiO layer has been completely suppressed with this doping, and this could also play a role in the appearance of metallicity.

The only value reported for the A coefficient of $\rho(T) \sim AT^2$ has been obtained in the intermediate T range for $\text{Ca}_3\text{Co}_4\text{O}_9$ single crystals and is equal to $A = 3.63 \times 10^{-8} \Omega \text{ cm K}^{-2}$ [19]. The value obtained here is close, equal to $4.8 \times 10^{-8} \Omega \text{ cm K}^{-2}$. This A value of $4.8 \times 10^{-8} \Omega \text{ cm K}^{-2}$ should correspond to $69.3 \text{ mJ mol}^{-1} \text{ K}^{-2}$ according to the Kadowaki–Woods relation $A/\gamma^2 = 1 \times 10^{-5}$ (γ : electronic specific heat coefficient). Thus, the A value implies rather strong electron–electron correlation.

The increase of the carrier concentration induces a reduction of the Seebeck coefficient, for $T > 25 \text{ K}$. A quantitative analysis of the Seebeck coefficient is still lacking, but for high T , it was proposed that S follows the extended Heikes formula:

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

with x the Co^{4+} concentration, and g_3 and g_4 the spin and orbital degeneracies of Co^{3+} and Co^{4+} in low spin states ($g_3/g_4 = 1/6$) [20]. This formula shows that S should decrease when the Co^{4+} concentration increases, as observed here. It has been recently shown that this value of g_3/g_4 should be replaced by $g_3/g_4 = 1/2$ [21, 22]. Using $g_3/g_4 = 1/6$ would lead to Co valencies close to 3.59 for BSCO and 3.65

for BPSCO, much larger than the values extracted from the Hall effect. With $g_3/g_4 = 1/2$, Co valencies are smaller, close to 3.32 for BSCO and 3.38 for BPSCO. These values are closer to the Co oxidation state obtained by the scaling of S at 300 K, both in misfits and in Na_xCoO_2 [23]. From this scaling (figure 4 in [23]), the Co valency should be close to 3.3 for $S \sim 100 \mu\text{V K}^{-1}$. There is still a discrepancy between the different values extracted from the Seebeck coefficient or from the Hall effect due to the complicated interpretation of these data, but the important result is that the two different evaluations of the Co oxidation state, from the Heikes formula and from the Hall effect, qualitatively confirm that the introduction of Pb^{2+} in the BSCO family induces an increase of the Co oxidation state, resulting in a purely metallic behavior for $[\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_{1.86}$.

Considering the pseudogap interpretation [2], the suppression of negative magnetoresistance means that this pseudogap can be suppressed by doping. More recently, a phase diagram of the misfit cobaltates and Na_xCoO_2 has been established from the thermopower measurements [23]. Our results show that Pb^{2+} substitution has induced a strong shift of doping, towards smaller 'x' (i.e. large ' Co^{4+} ' concentration). The susceptibility of BPSCO should thus be smaller than that of BSCO, outside the peak region of susceptibility. The BPSCO crystals thus possess the same transport properties as $[\text{Tl}_{0.81}\text{Co}_{0.2}\text{Sr}_{1.99}\text{O}_3]^{\text{RS}}[\text{CoO}_2]_{1.79}$ [8] or $[\text{Bi}_2\text{Ba}_{1.8}\text{Co}_{0.2}\text{O}_4][\text{CoO}_2]_2$ [16] which also exhibit T^2 behavior and positive MR at low T , and would also exhibit a very small magnetic susceptibility [23]. This could be why the large negative magnetoresistance associated with a diffusion of carriers by localized paramagnetic spins [7] is suppressed.

Furthermore, it is important to notice that the modulation in the BiO layer has been suppressed by Pb substitution. For a given doping level, it was shown [23] that the resistivities of Na_xCoO_2 with $x \sim 0.7\text{--}0.85$ are metallic at 5 K, but, in contrast, very high for misfits such as BSCO ($\sim 10\text{--}10^4 \Omega \text{ cm}$). This suggests that beyond doping, the structural modulation probably favors a strong localization at low T in misfits, for this range of x .

4. Conclusion

Single crystals of the misfit cobaltate $[\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_{1.86}$ have been synthesized and the resistivity, magnetoresistance, thermopower, and Hall coefficient have been measured. By increasing the Pb^{2+} content compared to those of previous reports, the transition observed in resistivity between a metallic state and a $d\rho/dT < 0$ regime at low T is suppressed. A T^2 dependence of $\rho(T)$, characteristic of a Fermi liquid, is recovered for $T < 170$ K by Pb^{2+} doping. Moreover, in the case of $[\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{O}_{4-\delta}][\text{CoO}_2]_{1.86}$, the typical negative magnetoresistance observed in this family of layered oxides is replaced by a positive magnetoresistance. Hall effect measurements show that the charge carrier concentration has been increased by Pb^{2+} doping, in good agreement with the decrease of the Seebeck coefficient. For the thermoelectric power factor, this Pb^{2+} substitution has a beneficial impact, showing that the S decrease is more than compensated by the

decrease of the electrical resistivity. These results show that the doping can have a drastic influence on the low T properties of misfits. Moreover, the modulation observed in the BiO layer in BSCO has been completely suppressed by Pb^{2+} , and this suppression could favor metallicity.

Acknowledgments

We would like to thank O Perez for his help with the crystallographic analysis, and J Bobroff and V Brouet for fruitful discussion. We also thank CNRS for a postdoctoral fellowship, and ANR OCTE for financial support.

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