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Abstract

Two new compounds of the Bi/Ca/Co/O and Bi(Pb)/Ca/Co/O systems have been prepared. Their structure is built up from the intergrowth of four rock-salt-type layers and one $[CoO_2]$ hexagonal layer. Both cobaltites exhibit large thermopower values ($S_{300\ K} \sim 140\ \mu V\ K^{-1}$), low resistivity values ($\rho_{300\ K} = 40$–60 mΩ cm) and small thermal conductivities ($\kappa_{300\ K} \sim 1\ W\ K^{-1}\ m^{-1}$). Furthermore, these compounds exhibit a negative magnetoresistance, (MR $= \frac{\rho_H - \rho_{H=0}}{\rho_{H=0}}$), reaching, at 2.5 K, -85% in 7 T for the Bi/Ca/Co/O misfit cobaltite. A large negative magnetothermopower is also found for these cobaltites in the same temperature range. A qualitative explanation of the observed behaviour is proposed.

1. Introduction

Because of their composite structure and their large thermopower values, the misfit bismuth based cobaltites have been recently the focus of attention [1–3]. These materials have an unusual combination of properties: despite their metallic character with relatively low resistivity, they have rather large Seebeck coefficient $\sim$+100 $\mu V\ K^{-1}$, which makes them very promising materials for practical applications.

In contrast to the previously studied Bi/Sr/Co/O system in which a structural analogy with the $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconducting cuprate ('Bi-2212' structure) was reported on the basis of the closeness of the cell parameters [4–6], the layer structure of the misfit cobaltite [1, 2, 7] is in fact similar to that of chalcogenides [8]. Especially, the single $[CoO_2]$ layer of the CdI_2

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type is stacked with four [(Bi/Sr)O] layers of the rock-salt (RS) type [2]. The difference in the cell parameters in one direction of these different structural blocks is at the origin of the misfit character of the Bi/Sr/Co/O cobaltite. The exact formula of this oxide is written as $[Bi_{0.86}SrO_2]_2[CoO_2]_{1.82}$ [2]. Within the CdI_2-type layer, the edge-sharing CoO_6 octahedra form a Co–O triangular lattice of low-spin trivalent and tetravalent cobalt. Such $[CoO_2]$ layers are also found in the $NaCo_2O_4$ metallic oxide [9] and they are believed to be responsible for its large thermopower value at room temperature [10]. By substituting Pb^{2+} for Bi^{3+} in the $[Bi_{0.86}SrO_2]_2[CoO_2]_{1.82}$ misfit oxide, a decrease in the resistivity was observed whereas the room temperature thermopower kept values close to 100–140 μV K^{-1} [6, 7, 11]. Moreover, a change in the magnetic properties is also induced by the Pb for Bi substitution, since weak ferromagnetism is found for Pb/Bi $\approx$ 0.3 but is not found in the lead free compound [11]. Interestingly, a large negative magnetoresistance (MR) is observed in the vicinity of the magnetic transition temperature. In the first studies by Tarascon *et al* of the Bi/Sr/Co/O system [4], isovalent substitutions of Ba (Ca) for Sr in the RS-type layers were shown to affect the transport properties. However, since the structures were believed to be of the Bi-2212 type, uncertainties about the physical properties remained.

In this work, we have studied the transport, thermopower and magnetic properties of the Bi/Ca/Co/O and Bi(Pb)/Ca/Co/O misfit cobaltites. From electron microscopy and x-ray diffraction, the misfit character of the structures is demonstrated. The corresponding chemical formulae can be written $[Bi_{1.7}Co_{0.3}Ca_2O_4]^{RS}$ $[CoO_2]_{1.67}$ and $[Bi_{1.3}Pb_{0.6}Co_{0.2}Ca_{1.9}O_4]^{RS}[CoO_2]_{1.72}$ where the first and second parts in the square brackets correspond to the RS-type layers and CdI_2-type CoO_2 layer, respectively. From these formulae, it appears that the formal cobalt valency in such structural architectures could be affected by the aliovalent Pb^{2+} (or Pb^{4+}) for Bi^{3+} substitution.

In the present study, we show that both calcium based Bi and Bi(Pb) misfit cobaltites exhibit, at room temperature, large positive thermopower value, $S_{300\ K} \approx +130$–140 μV K^{-1}, and small thermal conductivity value, $\kappa \sim 1$ W K^{-1} m^{-1}. Interestingly, a large negative MR $\left[MR = \frac{\rho(H)-\rho(0)}{\rho(0)}\right]$ reaching $\sim-85\%$ is found at low T in these cobaltites. The negative magnetothermopower which is observed in these compounds is attributed to weak magnetic order evidenced by magnetic measurements. The spin contribution to the excess entropy of the charge carriers revealed by the TEP measurements thus plays an important role. We propose a qualitative explanation of the observed properties using the phenomenological model with a sharp peak in the density of states. The proposed picture is similar to the one deduced for $NaCo_2O_4$ on the basis of the band structure calculations [12].

2. Experimental details

The synthesis of the different samples was carried out in several steps. First, the Bi/Ca/Co system was investigated for the nominal compositions $Bi_{1\pm x}CaCoO_{\propto}$ varying x from 0 to 0.5 by $\Delta x = 0.1$ steps. This first series of samples was prepared by mixing the stoichiometric amounts of Bi_2O_3, CaO and Co_3O_4, pressed in the form of bars and fired at 850 °C for 12 h in air. The powder x-ray diffraction patterns and energy dispersion spectroscopy (EDS) techniques were used for characterizing these materials. The best sample, nearly single phase, is obtained for the nominal composition $Bi_{0.9}CaCoO_\alpha$. In a second step, we investigated the system $Bi_{0.9-y}Pb_yCaCoO_\alpha$, following the same process with $\Delta y = 0.1$. The starting oxides were Bi_2O_3, PbO_2, CaO and Co_3O_4. The best sample has been obtained for $y = 0.4$; its homogeneity was checked by electron diffraction and EDS analyses.

Samples for transmission electron microscopy were prepared by crushing the bars in *n*-butanol and the small crystallites in suspension were deposited on to a holey carbon grid

supported by a nickel grid. The electron diffraction (ED) study was carried out at room temperature with JEOL 200 CX and 2010 electron microscopes, equipped with KEVEX analysers.

The magnetic properties have been studied with an ac–dc SQUID magnetometer (0–5 T; 1.8–400 K) by recording magnetization, as a function of temperature and magnetic field. The four-probe method was used to measure the resistance R of ceramic bars ($2 \times 2 \times 10$ mm). Electrical contacts of indium were ultrasonically deposited on the bars. A physical property measurement system (PPMS) from Quantum Design allows R measurements to be performed from 1.8 to 400 K in magnetic field ranging from 0 to 9 T. The same PPMS set-up was also used to measure the thermopower (Seebeck effect, S) and thermal conductivity (κ) but with a different sample holder (steady state method) which has been previously described [13]. For the magnetothermopower measurements, the effect of a magnetic field application of 8 T on the thermocouples is to shift the T by about -0.6 at 5 K. However, since our measurements are performed by using two differential thermocouples, this effect is cancelled.

3. Results

3.1. Structural characterizations

The ED study of cobaltites reveals the existence of two sets of reflections characteristic of a composite structure built of two subsystems S_1 and S_2, with an incommensurate periodicity along the $\vec{b}$ axis direction. These observations are very similar to those previously reported for the Bi/Sr/Co/O misfit cobaltite [2]. The structure of the latter is built up from the intergrowth of four RS-type layers and one [CoO$_2$] hexagonal layer along $\vec{c}$ [2]. It turns out that S_1 corresponds to the RS subsystem and S_2 to the hexagonal one. The EDS analyses, carried out on numerous crystallites, lead to the following average cationic ratio: Bi/Ca/Co = 0.85/1/1 and Bi/Pb/Ca/Co = 0.68/0.31/1/1 calculated for one Co atom. The previous studies showed that the two subsystems exhibit common a, c and β parameters, but different b cell parameters ($b_1 \neq b_2$). Coupling the EDS and ED the following chemical formulae can be proposed: $[\mathrm{Bi}_{1.7}\mathrm{Co}_{0.3}\mathrm{Ca}_2\mathrm{O}_4]^{\mathrm{RS}}[\mathrm{CoO}_2]_{1.67}$ and $[\mathrm{Bi}_{1.3}\mathrm{Pb}_{0.6}\mathrm{Co}_{0.2}\mathrm{Ca}_{1.9}\mathrm{O}_4]^{\mathrm{RS}}[\mathrm{CoO}_2]_{1.72}$ for the Bi/Ca/Co/O and Bi/Pb/Ca/Co misfit cobaltites, respectively. It is found that the b_1/b_2 ratio, characterizing the incommensurate nature of the structure, increases with the Pb content. This trend, previously also observed in the case of the Bi(Pb)/Sr/Co/O misfit cobaltites [1], is consistent with the substitution of Pb^{2+} for Bi^{3+}. The ionic radius of the former is larger than that of the latter so that the S_1 cell parameters increase whereas the lack of flexibility of the [CoO$_2$] layer [1] will thus make the ratio b_1/b_2 increase. Note that the cell parameter evolution would be the opposite with Pb^{4+}.

Finally, it should also be mentioned that in the absence of single crystals for these Ca based misfit cobaltites, crystallizing in very complex structures, an accurate structure refinement cannot be undertaken. In particular, if one refers to the oxygen non-stoichiometry existing in the Bi cuprates, the oxygen content in the RS slab most probably differs from the perfect 'O$_4$' stoichiometry. This makes very delicate any estimation of the oxidation state of the cobalt lying in the hexagonal layer from the chemical formula.

3.2. Magnetic behaviour

First, the inspection of the T dependent magnetic susceptibility ($\chi(T)$) curves registered in 0.3 T (field cooling 'FC' and zero-field cooling 'ZFC' modes) shows that both Ca based Bi cobaltites exhibit very similar magnetic properties (figure 1). From the corresponding

inverse susceptibility curves ($\chi^{-1}(T)$), in the T region where the Curie–Weiss law is obeyed, i.e. $T > 100$ K, the μ_{eff} value per cobalt can be extracted, leading to the values $\mu_{eff}/\text{Co} \sim 1.5\ \mu_B$ for both Bi/Ca/Co/O and Bi(Pb)/Ca/Co/O cobaltites. If one considers that these values are only created by the mixture of low-spin Co^{3+} ($S = 0$)/Co^{4+} ($S = 1/2$) at the level of the CoO_2 layers, one obtains a Co valency value, $v_{Co} \approx 3.70$, which is very large if one compares it to the $v_{Co} \approx 3.33$ value reported for instance in the Bi/Sr/Co/O cobaltite [14]. However, there is a clear change of slope below about 100 K where a second linear $\chi^{-1}(T)$ part can also be considered (dashed lines in figures 1(a) and (b)) from which smaller μ_{eff} values can also be extracted. This change in the μ_{eff} value as T increases may indicate the existence of a spin-state transition for the Co^{3+} species, from the low- ($S = 0$) to the intermediate-spin ($S = 1$) state, as reported for $LaCoO_3$, for which the LS to IS transition also occurs at $T \approx 100$ K [15]. Furthermore, in the $[Ca_2CoO_3][CoO_2]_{1.61}$ misfit cobaltite, a clear magnetic change was observed at 420 K on the $\chi^{-1}(T)$ curve [16]. The latter was interpreted as the spin transition from the low to the intermediate spin of the Co^{3+} and Co^{4+} species. Nonetheless, in the case of Bi/Ca/Co/O and Bi(Pb)/Ca/Co/O systems, one cannot exclude the Curie contribution of moments from local structural defects. From the $\chi^{-1} \to 0$ extrapolations of the high-T part of the curves, negative paramagnetic temperatures θ_P are found, with values of -45 and -68 K for the Bi/Ca/Co/O and Bi(Pb)/Ca/Co/O cobaltites, respectively. This shows that antiferromagnetic fluctuations dominate in the high-T part of the paramagnetic regime. However, the $\chi(T)$ (or $\chi^{-1}(T)$) curves do not exhibit a clear transition which could be attributed to the setting of a long-range antiferromagnetic state. The superimposition of the $\chi(T)$ curves collected upon warming in 0.3 T after ZFC and FC is also suggestive of a lack of a ferromagnetic component.

The present magnetic study shows that, in contrast to the weak ferromagnetism induced by the Pb for Bi substitution in the Bi/Sr/Co/O cobaltite, no significant change is induced by the Pb substitution on the magnetic properties of the corresponding Ca based compounds.

In this respect, the present $\chi(T)$ curves point towards the absence of long-range magnetic ordering as also reported for the Bi/Ba/Co/O cobaltite. However, the latter shows a shallow χ maximum at $\approx$35 K [17] attributed to the opening of a pseudo-gap which is not seen in both compounds under study. The study of the different Bi based systems thus shows that magnetic properties can be modified by the different substitutions in the RS layer and this should directly affect the low-temperature transport properties.

3.3. Resistivity

One similarity between the physical properties of these Bi cobaltites compared to their Sr based analogues lies in the T dependence of their electrical resistivity (ρ). As shown in figure 2, starting from the room temperature ρ value of the Ca based misfits, 60 and 40 mΩ cm^{-1} for Bi/Ca/Co/O and Bi(Pb)/Ca/Co/O, respectively, as T decreases, their $\rho(T)$ curves exhibit either a progressive change from $d\rho/dT > 0$ to $d\rho/dT < 0$ at $T \sim 100$ K for Bi/Ca/Co/O or a unique regime, $d\rho/dT < 0$ for the Bi(Pb)/Ca/Co/O cobaltite. Despite this different T dependence of ρ in the high temperature part, the low T ρ values are very close, reaching 80 and 30 Ω cm at 5 K for the Bi/Ca/Co/O and Bi(Pb)/Ca/Co/O respectively. In contrast, in the Bi/Sr/Co/O cobaltites, the low T upturn of ρ drops by two orders of magnitude as Pb is substituted for Bi [6, 14]. In the misfit layered cobaltite Bi(Pb)/Sr/Co/O, the CoO_2 layers of the CdI_2 structural type are responsible for the transport properties since the separating RS-type layers are less conductive [14]. Changes at low T in the shapes of the $\rho(T)$ curves as Pb is substituted for Bi in Bi(Pb)/Sr/Co/O was attributed to an increase of the holes density resulting from the Pb^{2+} for Bi^{3+} substitution [14, 18]. But the lack of such a change in the case of the
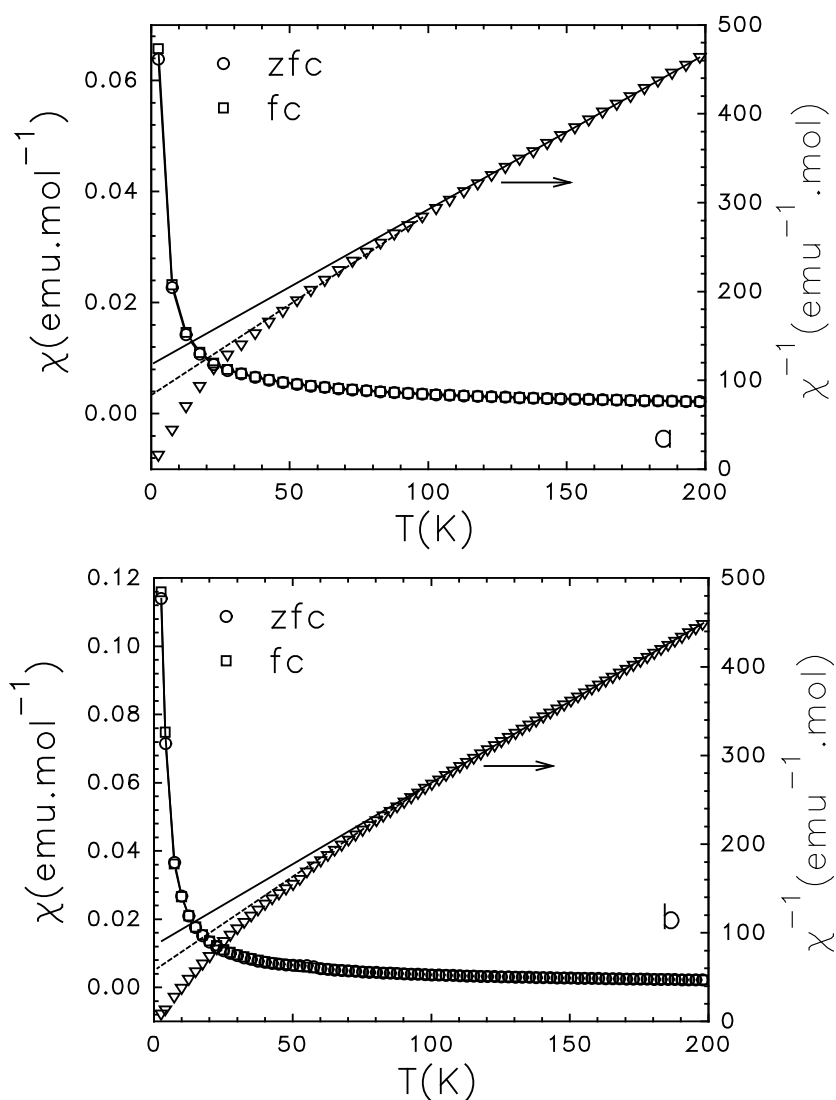
Figure 1. T dependence of the magnetic susceptibility (χ) collected in the FC and ZFC modes. $\mu_0 H_{dc} = 0.3$ T. (a) Bi/Ca/Co/O and (b) Bi(Pb)/Ca/Co/O.

Bi/Ca/Co/O misfit cobaltites suggest that the Pb for Bi substitution does not supply holes to the CoO_2 conductive layers. This assumption cannot be verified in our samples in the absence of a complete structural determination.

3.4. Magnetoresistance

The comparison of the $\rho(T)$ curves registered upon cooling in the absence and in the presence of a 7 T magnetic field demonstrates the existence of a negative MR in both cobaltites which is illustrated by the T dependence of the ρ_0/ρ_7 T ratio curves shown in the inset of figure 2. The existence of a negative MR has been confirmed by recording isothermal $\rho(H)$ curves. The magnitude of this MR can be directly read on the % MR $= f(H)$ curves shown in
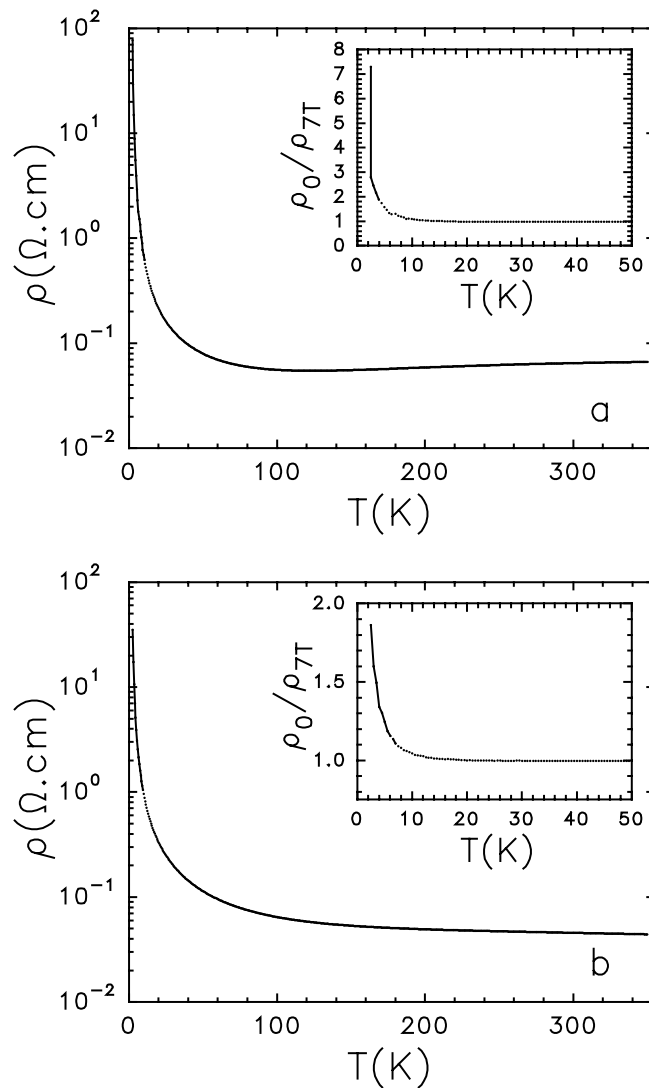
Figure 2. Temperature (T) dependence of the electrical resistivity (ρ) of the Bi/Ca/Co/O (a) and Bi(Pb)/CaCo/O (b) misfit layer cobaltites. Insets: corresponding T dependence of the $\rho_0/\rho_{7\,T}$ resistivity ratio from ρ measurements made upon cooling in 0 and then in 7 T; for the sake of clarity only the low-T part is shown.

figures 3(a) and (b) for the Bi and Bi(Pb)–Ca based misfit cobaltites. At 2.5 K, the MR values are maximum, reaching −87 and −46% in 7 T for Bi/Ca/Co/O and Bi(Pb)/Ca/Co/O, respectively. The saturation of MR is reached in Bi/Ca/Co/O but it can still increase in the case of Bi(Pb)/Ca/Co/O cobaltite. To our knowledge, this MR magnitude, reaching −87%, is the largest value reported for a misfit cobaltite. On the one hand, the Bi/Ba/Co/O [17] and the Tl based misfit Tl/Sr/Co/O [19] exhibit a positive MR even for T as low as 2.5 K, which is consistent with the absence of an ordered magnetic state down to the lowest temperature in these metallic misfit compounds. This indicates that the spin scattering effect is severely reduced in the latter. On the other hand, the obtained negative MR for the 2D Bi/Ca/Co/O misfit
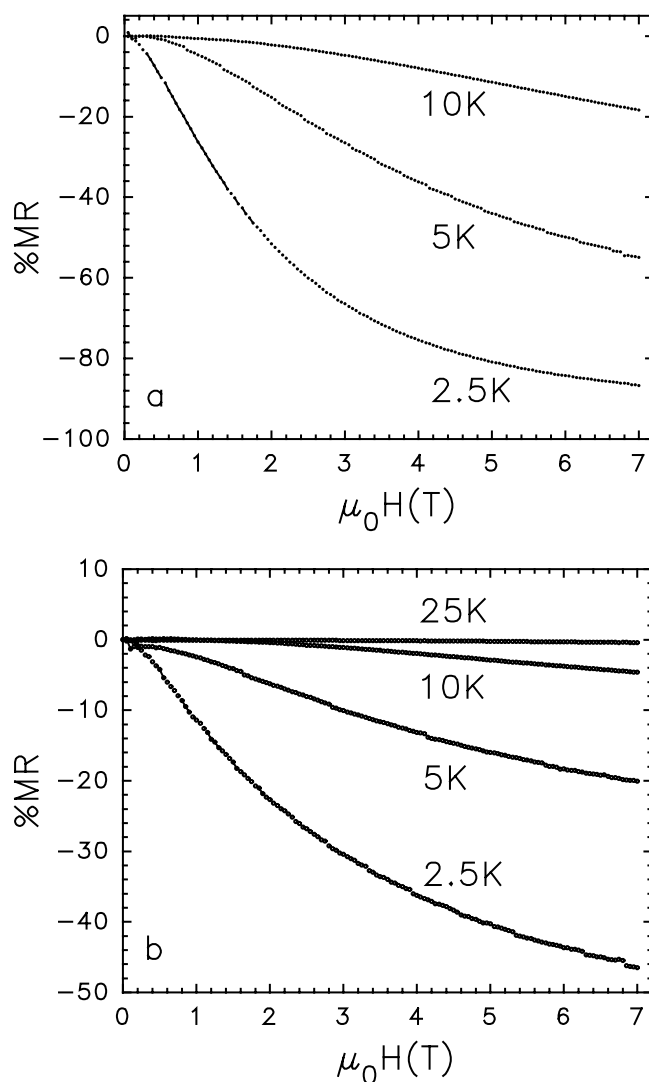
Figure 3. Magnetic field (H) dependence of % MR; Bi/Ca/Co/O (a) and Bi(Pb)/Ca/Co/O (b). The T values are labelled on the graph.

phases exceeds the best values reported in thin films of Bi(Pb)/Sr/Co/O misfit, reaching, at 2 K, -58% in 8 T [20], against -87% in 7 T at 2.5 K for our Bi/Ca/Co/O ceramic sample. These values are also better than the values reported for the $La_{1-x}Sr_xCoO_3$ perovskite, -40% at 20 K in 7 T for $x = 0.07$ [21], and for manganese doped cobalt perovskite, $La_{0.8}Sr_{0.2}Co_{0.9}Mn_{0.1}O_3$, MR reaching -60% in 7 T at 5 K in the latter [22]. It should also be pointed out that the values observed in the Bi/Ca/Co/O layered cobaltite are also better than those reported for the 1D $Ca_3Co_2O_6$ cobaltite which exhibits a MR value of -60% in 7 T at 2 K [23]. Compared to 3D and 1D cobaltites, the value observed in the 2D Bi/Ca/Co/O misfit cobaltite is thus remarkable. The origin of the MR in the misfit cobaltite can be addressed by plotting % MR as a function of M^2 plots (figure 4). The existence of a linear regime on these curves shows that there exists a coupling between itinerant carriers and the local spins. A similar behaviour was also found in the $La_{1-x}Sr_xCoO_3$ cobalt perovskite [24].

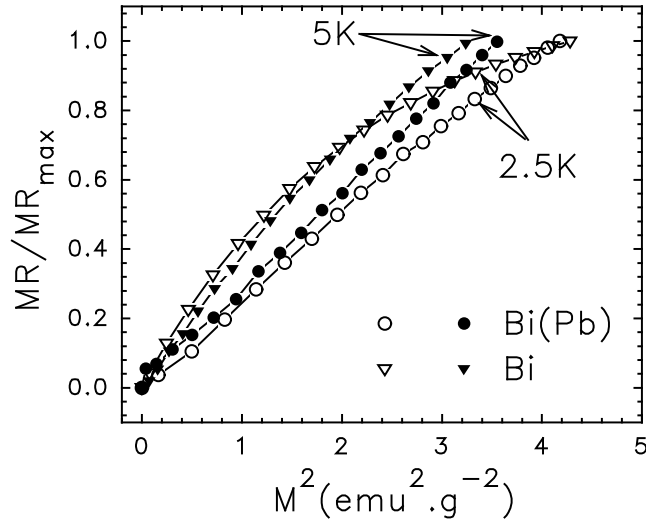**Figure 4.** MR/MR$_{max}$ as a function of M^2, where M is the magnetization registered in the same field and at the same T as the MR Bi/Ca/Co/O (triangles, 'Bi') and Bi(Pb)/Ca/Co/O (circles, 'Bi(Pb)'). The solid and open symbols are for $T = 5$ and 2.5 K, respectively.

3.5. Thermopower and thermal conductivity

One remarkable property of cobaltites containing CoO_2 layers made of edge-sharing CoO_6 octahedra is their large positive room-temperature thermopower values (ranging typically from $S = +90$ μV K^{-1} for NaCo$_2$O$_4$ [10] up to $S = +140$ μV K^{-1} for (Bi/Pb)Sr$_3$Co$_2$O$_9$ [3]) and low thermal conductivity (for instance, in NaCo$_2$O$_4$ $\kappa \approx 1.5$ W K^{-1} m^{-1} at 300 K [25]). Similar large S values, $S_{300 K} \approx +140$ and $+128$ μV K^{-1}, are found for the Bi/Ca/Co/O and Bi(Pb)/Ca/Co/O misfit cobaltites, respectively (figure 5). This confirms that their electronic properties are more comparable to those of the Bi(Pb)/Sr/Co/O cobaltites than to those of the recently discovered Bi/Ba/Co/O cobaltite, which exhibits a positive MR, with lower S values, $S_{300 K} \sim +95$ μV K^{-1} [17]. As proposed in previous reports, the presence or absence of a long-range magnetic ordering in these complex cobaltites could affect the transport behaviour through the spin polarization mechanism.

In addition to their low resistivity and large TEP values, the misfit cobaltites exhibit low thermal conductivities (κ). Assuming the Wiedemann–Franz law holds in these materials, the electronic contribution to the thermal conductivity κ_{el} can be estimated from the resistivity. κ_{el} is increasing from 10^{-7} W m^{-1} K^{-1} at 5 K to 7×10^{-3} W m^{-1} K^{-1} at 300 K. These very small values show that κ is mainly determined by the phonon contribution as in NaCo$_2$O$_4$ [26]. The low thermal conductivity makes these misfits potential candidates for high-temperature application as thermoelectric materials. This emerges from the figure of merit (Z) definition, $Z = \frac{S^2}{\rho\kappa}$, where the κ values must be as small as possible. As shown in figure 6, the measured value at 300 K for the Bi/Ca/Co/O cobaltite, $\kappa \approx 1$ W K^{-1}m^{-1}, is very weak for a metallic oxide. Such a value is very similar to those reported in Bi(Pb)/Sr/Co/O cobaltites, which shows that the Ca for Sr substitution at the level of the RS-type layers has only a very moderate impact on the thermal conductivity. Combining the results for S, ρ and κ, we obtain $ZT \sim 0.015$ at 300 K, a value comparable to the one obtained in NaCo$_2$O$_4$ (0.03 at 300 K [26]) or in the Bi/Sr/Co/O family (0.025 at 300 K for Bi$_{2.2}$Sr$_2$Co$_2$O$_8$ [27]). At room temperature, Z is smaller than that of classical thermoelectric materials such as Bi$_2$Te$_3$ for which $ZT \approx 1$ at 300 K [28].
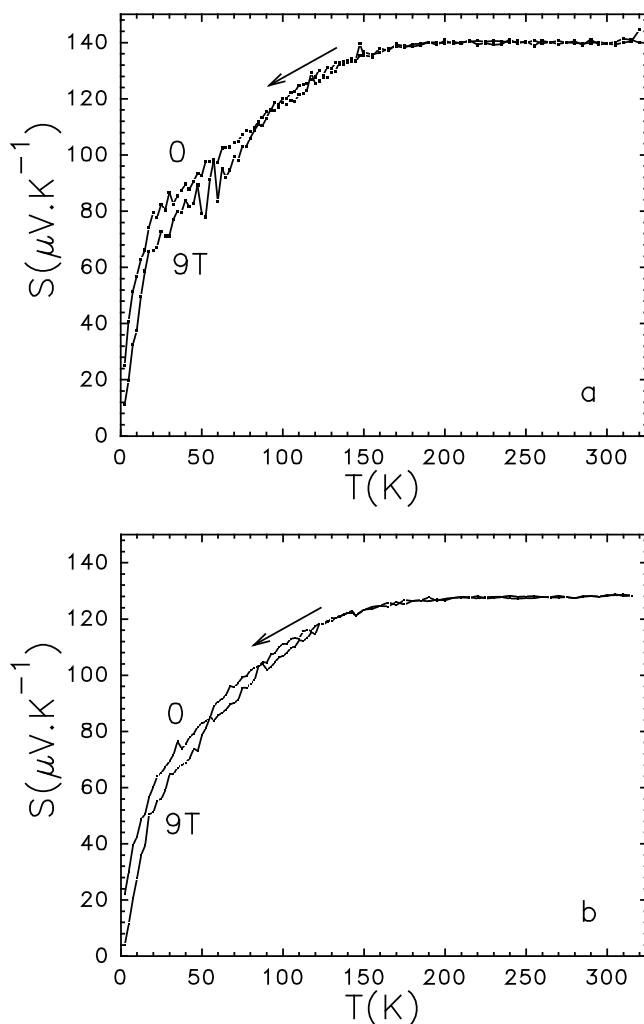
Figure 5. T dependence of the thermopower (Seebeck, S) of both Bi/Ca/Co/O (a) and Bi(Pb)/Ca/Co/O (b) misfit cobaltites. The curves have been collected upon cooling (arrow) in the absence of magnetic field (0) and in the presence of 9 T.

Nevertheless the use of these materials is restricted to $T < 600$ K as their melting points are small, while oxides can be used up to 1000 K with a Z increasing as T increases [5].

3.6. Magnetothermopower

As pointed out by Itoh and Terasaki [6], the S values of the Bi(Pb)/Sr/Co/O misfit cobaltites remain high even for the lowest T. For instance, $S = +30$ μV K^{-1} at 4.2 K in the Bi$_{1.89}$Pb$_{0.44}$Sr$_{2.6}$Co$_2$O$_y$ cobaltite. Very similar values are also found in our Ca based Bi cobaltites with $S_{5\,K} \approx 30$ μV K^{-1} or the Bi(Pb)/Ca/Co/O cobaltite. Such high values show that the entropy per carrier is enhanced at low T and this effect has been attributed to the occurrence of a pseudo-gap opening in the case of the Bi(Pb)/Sr/Co/O cobaltites. In our samples, this hypothesis is not easily verified since no signature of this opening can be found on the $\chi(T)$ curves.
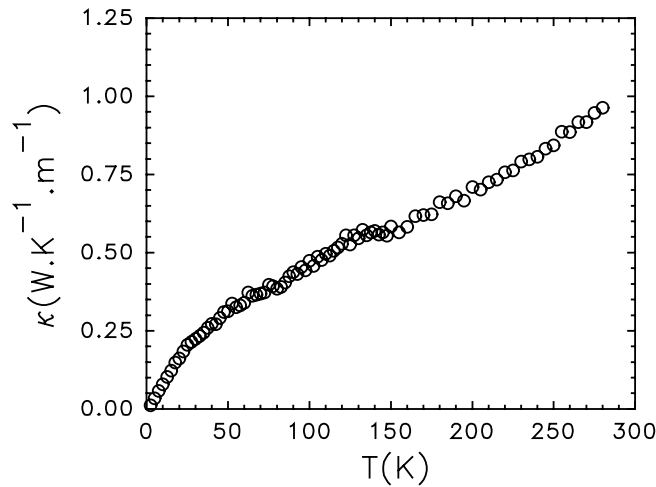
Figure 6. *T* dependence of the thermal conductivity (κ) of the Bi/Ca/Co/O cobaltite.
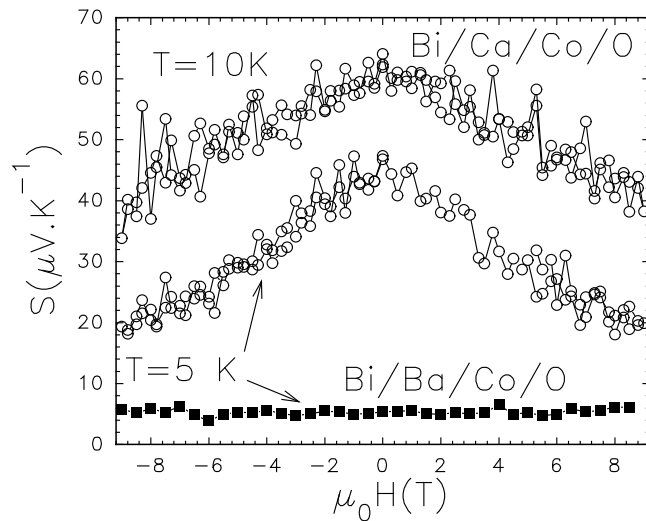

Figure 7. *H* dependence of the thermopower of the Bi/Ca/Co/O cobaltite and of the Bi/Ba/Co/O cobaltite from [17]. *T* values are labelled on the graphs.

Nonetheless, the magnetic field application during the *S* measurements shows that a clear negative magnetothermopower exists in the Bi/Ca/Co/O and Bi(Pb)/Ca/Co/O cobaltites (figure 5). If one compares $S_{H=0}(T)$ and $S_{H=9\,T}(T)$ (figures 5(a) and (b)), a clear *S* decrease under magnetic field, starting below ≈ 100 K, is observed for both cobaltites. The excess entropy per carrier [6] can thus be severely reduced if one refers to the induced $S_{5\,K}$ decrease in the Bi/Ca/Co/O cobaltite, from $+30\ \mu$V K^{-1} for $H = 0$ to $+12\ \mu$V K^{-1} for $H = 9$ T. This yields a negative magnetothermopower $\mathrm{MT} = \frac{S_H - S_{H=0}}{S_{H=0}}$ of about -60% under 9 T as also shown on the isothermal curves of figure 7. If one refers to their large negative MR, which shows a better conduction under magnetic field, it is thus not very surprising that the TEP decreases as the sample becomes more metallic.

It seems to us that the localization observed at low T on the $\rho(T)$ curves, below 100 K in the Bi/Ca/Co/O cobaltite, is related to the appearance of negative magnetothermopower.

The spin scattering, probably responsible for a less conductive state at $H = 0$, would thus be the origin of the excess thermopower. This observation contrasts with the absence of magnetothermopower in the corresponding Bi/Ba/Co/O misfit cobaltites which is more metallic at low T and characterized by a positive MR [17]. The $S(H)$ curve at 5 K of the Bi/Ba/Co/O system is shown in figure 7 for the sake of comparison.

4. Discussion and conclusion

To explain the main properties of mixed-valent cobaltites, especially their large thermopower, one can use two approaches. In [29] the d electrons are treated as more or less localized, and the large entropy needed for large values of S is attributed to the presence of many almost degenerate configurations of the Co cations: different valence states, possible participation of low-, intermediate- and high-spin states, and spin-disorder entropy. These factors may indeed play a role; however, the very possibility of applying these notions for metallic systems with rather high conductivity seems questionable. Another possible approach is based on treating the electronic structure and properties of these systems in a more metallic picture [12].

The LS state configuration of Co^{3+}/Co^{4+} in mixed-valent cobaltites is unique to the CdI_2-type CoO_2 layer in which the CoO_6 edge-shared octahedra imply a $\sim 90°$ Co–O–Co exchange. For both Bi/Ca/Co/O and Bi(Pb)/Ca/Co/O cobaltites, these spin configurations are also deduced from the low-T part of their $\chi(T)$ curves. The similarity of their properties with that of the Bi(Pb)/Sr/Co/O misfit cobaltites (ρ upturn, negative MR, large thermopower with an excess at low T) indicates that the electronic band structure, deduced from XAS measurements for the latter [18] must be close to that of the former. According to [18], both trivalent and tetravalent cobalt cations adopt the low-spin state configuration in Bi(Pb)/Sr/Co/O misfit cobaltites. The t_{2g} orbitals are split into one a_{1g} orbital and two e'_g orbitals. Most of the holes are small polarons or 'heavy holes' lying in the a_{1g} subband whereas a minority of light holes are located in the doubly degenerated e'_g subband. The contribution of the latter at the Fermi level may be responsible for the relatively low absolute value of resistivity. On the other hand, the large density of states, $f(E)$ at the Fermi level E_F for the a_{1g} subband would be responsible for the large thermopower according to the relation $S \propto \frac{\mathrm{d}f}{\mathrm{d}E}\big|_{E=E_F}$. This relation is valid in a two-component system if the current is predominantly carried by light carriers, but the scattering occurs into heavy band [30–32]. This expression comes from the definition of $S \sim \mathrm{d}\ln\sigma/\mathrm{d}E$ with $\sigma = ne^2\tau/m$, as in this two-component model the relaxation rate τ of light carriers is inversely proportional to the large density of states $f(E)$ in the heavy band, i.e. $\tau \sim 1/f(E)$ (see equation (9.11.9) in [31]).

The existence of two different types of carrier in misfit Co compounds allows a direct analogy with the situation encountered in the mixed valency with a heavy fermion, which may be also treated as a two-component system [32]. This model predicts a negative MR and a large thermopower value if the Fermi level is located close to a maximum in the density of states. For these heavy-fermion samples, large magnetothermopower values have also been reported at low T, for example $\%MT = -200\%$ in 6 T for $CeRu_2Si_2$ [33].

From this model, the very similar TEP values found for both Ca-misfit cobaltites indicate that their electronic band structure is not significantly modified by the Pb substitution. In principle this substitution should have shifted the Co valency in the CoO_2 layer as it does for the Bi(Pb)/Sr/Co/O cobaltites [14]. But when Pb is substituted for Bi, the oxygen content of the RS layers may change, so that it is not straightforward to predict the cobalt oxidation state in the hexagonal layer.

A second result which can be deduced from the analogy with the two-component model is the magnetothermopower. Under the application of magnetic field, the peak in the density of states $f(E)$ will be split into $f_\uparrow(E)$ and $f_\downarrow(E)$ for the up and down spins, respectively. Consequently, $\frac{df}{dE}\big|_{E=E_F}$ is changed so that the thermopower value is modified [32].

In the present study of two Ca based Bi misfit cobaltites, $[Bi_{1.7}Co_{0.3}Ca_2O_4]^{RS}[CoO_2]_{1.67}$ and $[Bi_{1.3}Pb_{0.6}Co_{0.2}Ca_{1.9}O_4]^{RS}[CoO_2]_{1.72}$, we show that the Pb for Bi substitution is also accompanied by a decrease of the content of Co and Ca cations in the block of RS-type layers. As follows from the very similar properties of these compounds, it is found that this substitution does not affect significantly the hole carrier concentration in the CoO_2 conducting layer. Furthermore, a large negative MR is observed at low T in these oxides showing a spin polarization of the charge carrier. The splitting of the t_{2g} orbitals into two subbands, $a_{1g} + e'_g$, proposed for the Sr based Bi misfit cobaltites, is most probably also relevant in these Ca analogues. If it is, the two-component model would explain the large thermopower, negative MR and magnetothermopower.

Crystal growth is now required to measure the mobile hole concentration, by the Hall effect, of the Bi/Ca/Co/O and Bi(Pb)/Ca/Co/O misfit cobaltites. This would also make it possible to measure the anisotropy of transport properties, which may be affected by the Pb for Bi substitution.

Summarizing, we have shown that the Bi(Pb)/Ca/Co/O misfit compounds have rather interesting properties. They have large thermopower, which in combination with rather low resistivity and thermal conductivity makes these materials good candidates for practical applications in thermoelectric devices. The large negative MR and negative magnetothermopower show that the spin degrees of freedom play an important role in their transport properties, although there exists no long-range magnetic ordering. The phenomenological two-component model is proposed which can qualitatively explain the experimental observations. We have also shown that the substitution of Bi by Pb in Ca based misfit cobaltites apparently does not significantly affect the hole concentration in the CoO_2 conduction layers. The study of single crystals is needed to actually measure the mobile hole concentration in both Bi/Ca/Co/O and Bi(Pb)/Ca/Co/O systems.

Acknowledgments

References

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