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## Does the orbital degeneracy play any role in the high thermopower of lamellar cobaltites?

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This article investigates the role of the  $\text{CoO}_6$  octahedron distortion on the electronic properties and more particularly on the high value of the Seebeck coefficient in the  $\text{BiCaCoO}$  lamellar cobaltites. Our measurements provide clues indicating that the  $t_{2g}$  orbital degeneracy lifting has to be considered to account for the observed high temperature limit of the thermopower. They also provide experimental arguments for locating the  $a_{1g}$  and  $e'_g$  orbitals levels on the energy scale, through the compression of the octahedron. These results are in agreement with recent *ab initio* calculation including the electronic correlations and concluding for the inversion of these levels as compared to the expectation from the crystal field theory. © 2007 American Institute of Physics. [DOI: 10.1063/1.2717602]

### I. INTRODUCTION

It is well known that a trigonal distortion ( $D_{3d}$ ) of a regular octahedron splits further the  $t_{2g}$  orbitals into one  $a_{1g}$  singlet and one  $e'_g$  doublet.<sup>1</sup> A simple crystal field theory predicts that when the octahedron is compressed along the ternary axis ( $x+y+z$  direction in the octahedron;  $c$  axis direction in the structure), the singlet is stabilized with respect to the doublet (Fig. 1).

However, several theoretical reports mention the role of the electronic correlations in the positioning of the  $a_{1g}$  and  $e'_g$  orbitals in sodium cobaltites  $\text{Na}_x\text{CoO}_2$ . They point out that this simple ionic scheme does not correctly describe the ground state and that correlations can dramatically modify it, leading to an inversion of the orbitals position, the singlet lying then above the doublet by a few tenths of electron-volts.<sup>2,3</sup>

In this article, we present electronic measurement results on pristine single crystals. We propose that the enhanced thermopower of some nonmetallic cobaltites (for which the extended Heikes formula can strictly be applied) can be analyzed in terms of spin/orbital degeneracy if one consider both the splitting of the  $t_{2g}$  orbitals and their respective positions.

### II. EXPERIMENT

Single crystals (SC) were grown by the flux method. Precursor powders of  $\text{Bi}_2\text{O}_3$ ,  $\text{CaCO}_3$ , and  $\text{Co}_3\text{O}_4$  were mixed with a cationic composition of  $\text{Bi}:\text{Ca}:\text{Co}=2:2:2$  and cal-

cined at 850 °C for 50 h. The process was repeated several times until a single phase was obtained. The powder was then mixed with  $\text{Bi}_2\text{O}_3$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{KCl}$  powders (weight ratio of 3:70:10:17) and heated in an alumina crucible at 900 °C for 20 h. The temperature was decreased down to 700 °C at a rate of 2 °C/h and next furnace cooled. The plate-like single crystals have a typical hexagonal shape with an area of 5–10 mm<sup>2</sup> and a thickness of 10–20 μm. A single crystal specimen is shown in Fig. 2.

The cationic composition of the single crystals was probed using wavelength dispersive spectroscopy (WDS) (CaMeCa). Iodometric titration was used to determine the average oxidation state of cobalt.<sup>4</sup> The temperature dependence of  $\rho$  was measured by a standard four-probe method using a Quantum Design Physical Properties Measurement System (PPMS) system (5–300 K). Thermopower measurements were performed with an experimental setup described elsewhere.<sup>5</sup> The magnetic measurements were carried out over a 2–325 K range using a Quantum Design MPMS facility equipped with a superconducting quantum interference device (SQUID) magnetometer. Several single crystals were stacked together (typically 20 SC). The raw signal was treated to remove the blank contribution from the sample holder. The  $M(H)$  curve at 4 K is characteristic for paramagnets ( $M \propto H$ ). A magnetic field of 4 T was applied parallel to the  $(ab)$  planes for the  $M(T)$  measurements in order to optimize the signal.

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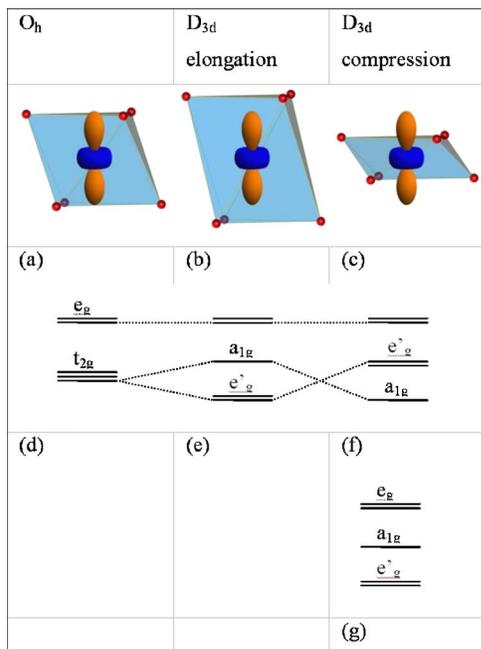


FIG. 1. (Color online) (a), (b), (c) Schematic representation of the distorted octahedron in  $O_h$  and  $D_{3d}$  elongation and compression symmetry; the  $d_{z^2}^2(a_{1g})$  orbital is also sketched; (d), (e), (f) crystal field results for the orbital splitting and positioning; (g) *ab initio* calculation result showing the singlet/doublet inversion through the compression. The degeneracy of the  $t_{2g}$  orbitals is lifted by a few tenths of electron-volts (see Ref. 2).

### III. RESULTS AND DISCUSSION

The average composition obtained from the WDS measurements on several crystals is  $\text{Bi}_{1.62(1)}\text{Ca}_{2.00(2)}\text{Co}_{1.62(2)}\text{O}_x$ . The x-ray diffraction (XRD) structure refinement,<sup>6</sup> for the same batch of single crystals, leads to the composition  $\text{Bi}_{1.64}\text{Ca}_{1.94}\text{Co}_{1.62}\text{O}_x$ . These two analyses match reasonably and mainly show that both layers are deficient in cations. In the following, we will assume the composition of our crystals to be  $\text{Bi}_{1.62(1)}\text{Ca}_{2.00(2)}\text{Co}_{1.62(2)}\text{O}_{7.38-\delta}$  where  $\delta$  is the overall oxygen deficiency in both sublattices.

Assuming fully occupied anionic sublattices ( $\delta=0$ ) and a 3+ valence for the bismuth in the rock salt layer, the average valence for the cobalt should be 3.64. Such a high value in

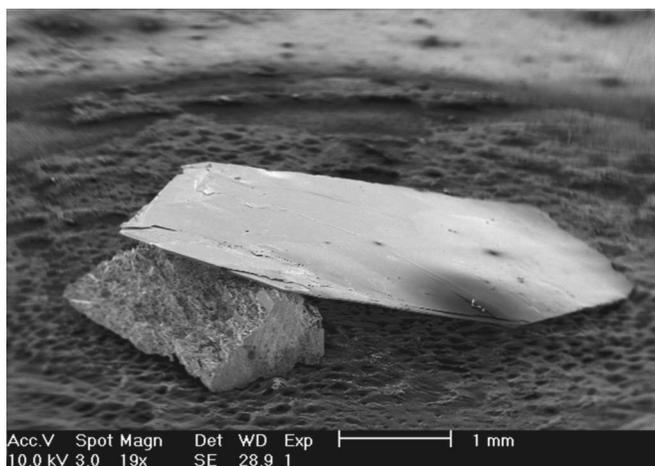


FIG. 2. Scanning electron microscopy image of a plate-like single crystal with a typical hexagonal shape.

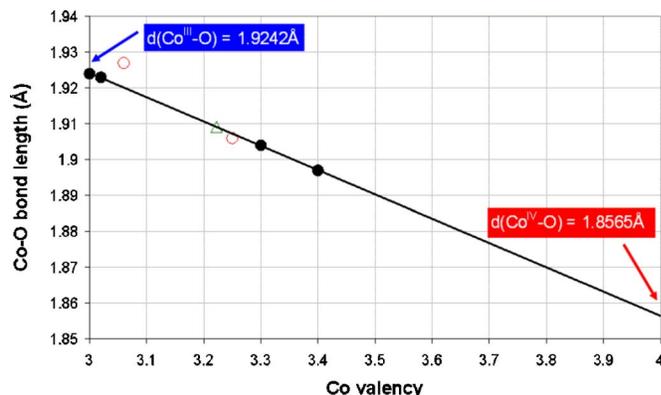


FIG. 3. (Color online) Evolution of the Co-O bond length vs the cobalt averaged valency in  $\text{Li}_x\text{CoO}_2$  (see Refs. 9 and 10). (Black filled circles) data from the solid solution; (red opened circles) excluded data from mixed phase materials; (green triangle) present work measurement.

this kind of cobaltite structures has never been observed yet and it sounds reasonable to consider also an oxygen deficiency. It has already been shown<sup>7</sup> that  $\text{Na}_x\text{CoO}_2$  can accommodate quite high oxygen deficiency down to  $\text{Na}_x\text{CoO}_{1.84}$ . Moreover, it is known<sup>8</sup> that the binding between the two BiO plans in the rock salt layer is very weak and could thus also accommodate defaults like bismuth and oxygen vacancies. The significant concentration in bismuth vacancies observed in our material, 1.62 vs 2 for the totally occupied double BiO layer, also supports this assumption.

The average oxidation state of the cobalt, which depends on the oxygen deficiency  $\delta$ , was first determined by means of iodometric titration.<sup>4</sup> The experiment was repeated several times and results in a 3.24(5) average valence for the cobalt, assuming the bismuth in a 3+ state. This value is by far lower than the one predicted from the stoichiometry and leads to  $\delta=0.33$ .

This result is confirmed using the structural analysis reported by Grebille *et al.*<sup>6</sup> From their description of the structure, the calculated average Co-O distance is 1.909 Å. Based on the work of Levasseur *et al.*,<sup>9,10</sup> a clear linear dependence of Co-O bond length as a function of the Co valence can be observed for electron localized systems (Fig. 3). The value obtained for the pristine is also plotted in Fig. 3; it corresponds to an average Co-valence of 3.22, in very good agreement with the value obtained from the iodometric titration. [One may further notice that, considering the ionic radius of  $\text{Co}^{3+}$  in low spin state given by Shannon<sup>15</sup> (0.545 Å), and keeping the oxygen ionic radius constant, we find for a six-fold coordinated LS  $\text{Co}^{4+}$  an ionic radius of 0.477 Å.]

The magnetic measurements are presented in Fig. 4. No anomaly or long range order can be observed on this curve; zero field cooling (ZFC) and field cooling (FC) measurements are superimposed. The total susceptibility was fitted using the expression  $\chi(T)=\chi_{\text{dia}}+\chi_{\text{vv}}+\chi_{\text{cw}}(T)$ ,  $\chi_{\text{dia}}$  being the core electron's diamagnetism,  $\chi_{\text{vv}}$  is the VanVleck temperature independent paramagnetic contribution, and  $\chi_{\text{cw}}$  describing the standard Curie-Weiss (CW) dependence. The diamagnetic contribution is calculated from the free ion constants. The temperature independent paramagnetic term  $\chi_{\text{vv}}$  used to fit the data is equal to  $261 \times 10^{-6}$  emu/mol/Co in

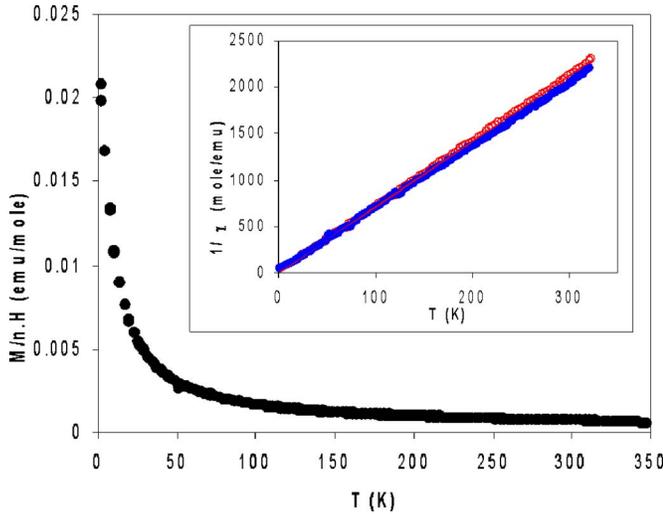


FIG. 4. (Color online)  $M(T)$  curve (ZFC and FC) with a 4 T applied field. Inset: inverse susceptibility on heating (ZFC; red open circles) and cooling (FC; blue closed circles).

agreement with the values expected from the localization of the electron on  $\text{Co}^{3+}$ .<sup>1,11,12</sup> The CW law contribution to the magnetism leads to  $C=0.09$  and  $\theta=-2$  K. Assuming LS states for both  $\text{Co}^{3+}$  ( $S=0$ ) and  $\text{Co}^{4+}$  ( $S=1/2$ ), the proportion of  $\text{Co}^{4+}$  estimated from the Curie constant is 0.24, in good agreement with the results obtained from iodometric titration and XRD refinement. Because of the small value of  $\theta$ , no anti-ferromagnetic long range ordering could be evidenced down to 2 K.

Contrariwise to the magnetic measurements, the transport ones give rise to several regimes versus temperature. Figure 5 shows data for the in-plane resistivity. The conductivity is clearly activated except at high temperature ( $>280$  K) where it decreases as the temperature increases.

The low temperature data can be well fitted using an Arrhenius law from 37 to 156 K. The activation energy is rather small at 7.06(2) meV. In an intermediate regime, up to 230 K, the resistivity tends to saturate. At higher temperature, a new activated regime appears with an activation energy of 13.6(2) meV. On the other hand, from a plot of  $\ln(\sigma T)$  vs  $1/T$  (Fig. 6) at  $T > 156$  K, both the intermediate

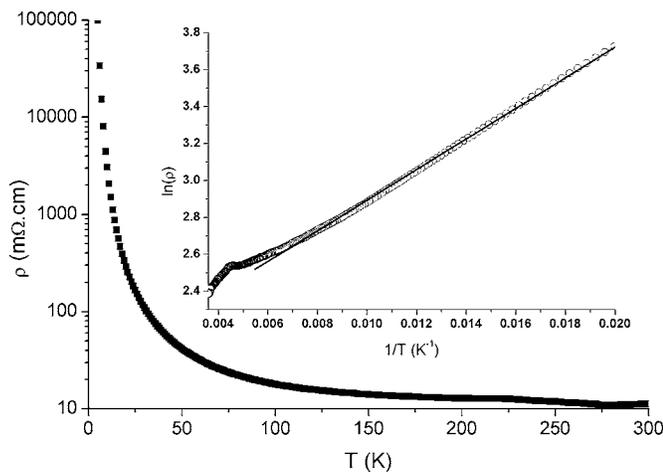


FIG. 5. In-plane resistivity vs temperature. Inset: same data,  $\log(\rho)$  vs  $1/T$ .

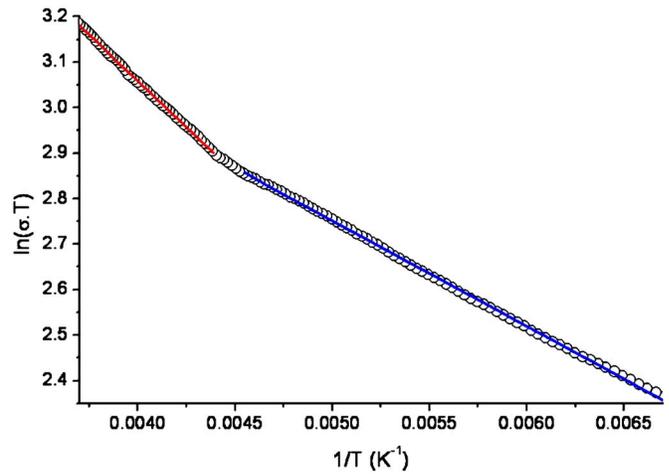


FIG. 6. (Color online)  $\ln(\sigma T)$  vs  $1/T$ .

and the high temperature regimes could be described as hopping ones with activation energies of, respectively, 20.3(1) and 35.2(2) meV.

The Seebeck coefficient measurements in a range from 5 to 300 K are shown in Fig. 7. It is positive and increases with temperature in the whole temperature range. The positive sign indicates a hole type carrier typical for these lamellar cobaltites. The increase in the thermopower with the temperature indicates the absence of activation for the carrier density and excludes a band-semiconductive behavior.

The low temperature data exhibit a  $\ln(T)$  dependence with two different regimes [Eqs. (1) and (2)]

$$S_{LT} = 0.21(1)(k_B/e)\ln(T), \quad T < 50 \text{ K}, \quad (1)$$

$$S_{IT} = 0.70(1)(k_B/e)\ln(T) - 162(3), \quad 50 \text{ K} \leq T \leq 160 \text{ K}. \quad (2)$$

At high temperature, the thermopower seems to tend toward a constant value for  $T \rightarrow \infty$ . In order to better estimate its asymptotic value, the following fit was used:

$$S_{HT} = (-k_B/e)(T_0/T) + 157.5(5) \text{ with } T_0 = 26(1) \text{ K}. \quad (3)$$

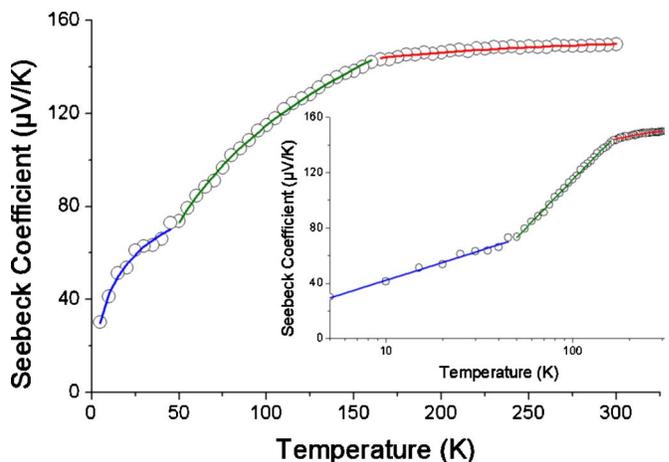


FIG. 7. (Color online) Open circles: experimental data showing the evolution of the Seebeck coefficient with temperature. The inset shows the same data with a logarithmic scale for the temperature.

TABLE I. Summary of the value obtained for  $x$  in  $\text{Bi}_{1.62}\text{Ca}_{2.00}[\text{Co}_{1-x}^{\text{III}}\text{Co}_x^{\text{IV}}]_{1.62}\text{O}_{7.38-\delta}$  using different methods.

Measurement	$x$
Iodometric titration	0.24(5)
XRD (Co-O bond length)	0.22
Magnetization (Curie constant)	0.24
Thermopower	0.24(1)

This high temperature behavior suggests that the thermopower can be modeled using the Heikes modified formula [Eq. (4)] as already proposed in previous studies of lamellar cobaltites<sup>13,14</sup>

$$S_{T \rightarrow \infty} = k/e \cdot \ln\left(\frac{g^{\text{IV}}}{g^{\text{III}}} \frac{1-x}{x}\right) = k/e \cdot \ln(\beta r) \quad (4)$$

with  $g = g_{\text{spin}}g_{\text{orbital}}$ , the degeneracies for each cobalt state (III and IV),  $x$  is the concentration of  $\text{Co}^{\text{IV}}$  and  $(1-x)$  is the concentration of  $\text{Co}^{\text{III}}$ .

Using this approach, considering both  $\text{Co}^{\text{III}}$  and  $\text{Co}^{\text{IV}}$  in LS state, and the  $t_{2g}$  degeneracy, i.e., considering no deformation of the octahedron, one obtains  $\beta=6$  ( $g_{\text{spin}}^{\text{III}}=1$ ;  $g_{\text{orbital}}^{\text{III}}=1$  and  $g_{\text{spin}}^{\text{IV}}=2$ ;  $g_{\text{orbital}}^{\text{IV}}=3$ ) leading to  $x=0.49(2)$  with the constant  $S_{T \rightarrow \infty}=157.5 \mu\text{V/K}$  from Eq. (3). However, if the lifting in the  $t_{2g}$  degeneracy is taken into account, two cases can be considered depending on the position of the  $e'_g$  doublet. If it lies above the  $a_{1g}$  singlet, as predicted from the crystal field theory, then  $\beta=4$  ( $g_{\text{spin}}^{\text{III}}=1$ ;  $g_{\text{orbital}}^{\text{III}}=1$  and  $g_{\text{spin}}^{\text{IV}}=2$ ;  $g_{\text{orbital}}^{\text{IV}}=2$ ) leading to  $x=0.39(2)$ . On the opposite, if it lies lower than the  $a_{1g}$  singlet, as calculated by taking into account the electronic correlations,<sup>2</sup> one obtains  $\beta=2$  ( $g_{\text{spin}}^{\text{III}}=1$ ;  $g_{\text{orbital}}^{\text{III}}=1$  and  $g_{\text{spin}}^{\text{IV}}=2$ ;  $g_{\text{orbital}}^{\text{IV}}=1$ ) leading to  $x=0.24(1)$ . This last value is in very good agreement with the ones obtained using other techniques as shown in Table I. These results confirm (i) the LS state for the two cobalt ions (III and IV), (ii) the orbital degeneracy lifting, and (iii) the  $a_{1g}$  singlet higher energy versus the  $e'_g$  doublet. This last conclusion is in opposition with the expectation from the simple crystal field theory but agrees with the *ab initio* calculations including the effect of the correlations.<sup>2</sup> We also evidence that the anionic sublattice is oxygen deficient ( $\delta=0.33$ , i.e., an average deficiency  $\approx 4.5\%$ ).

Further investigations are now clearly needed in order to elucidate the complex temperature dependence of both the thermopower and the conductivity at low temperature.

#### IV. CONCLUSION

This article investigates the role of the  $\text{CoO}_6$  octahedron distortion on the electronic properties. From the literature, three possibilities should be considered: (1) a complete de-

generacy of the  $t_{2g}$  orbitals, (2) a crystal field approach predicting a partial lifting of degeneracy with a low energy singlet  $a_{1g}$  and a higher energy doublet  $e'_g$ , and (3) the inversion of position in energy for these last mentioned orbitals, as suggested from recent *ab initio* calculations.

Single crystals of pristine have been synthesized and their composition established ( $\text{Bi}_{1.62(1)}\text{Ca}_{2.00(2)}\text{Co}_{1.62(2)}\text{O}_{7.38-\delta}$ ). Several methods have been used to accurately determine the average oxidation state of the cobalt: iodometric titration, use of the crystallographic data and magnetization data. All these measurements agree with an average oxidation state  $\approx 3.24$ , i.e., a concentration in  $\text{Co}^{4+}$  of 0.24. This low value implies an oxygen deficiency  $\delta = 0.33$ .

The conductivity and the thermopower have been measured and reveal a complex behavior at low temperature. The high temperature regime can be modeled using the modified Heikes formula and the Co valence previously determined. It can be concluded that both  $\text{Co}^{\text{III}}$  and  $\text{Co}^{\text{IV}}$  ions are in low spin state and that the degeneracy of the  $t_{2g}$  orbitals is lifted with an  $a_{1g}$  singlet lying above the  $e'_g$  doublet.

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