Thermoelectric Power of HoBaCo$_2$O$_{5.5}$: Possible Evidence of the Spin Blockade in Cobaltites

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Thermoelectric power measurements have been performed for an ordered oxygen-deficient perovskite, HoBaCo$_2$O$_{5.5}$, in which the alternative layers of CoO$_6$ octahedra and of [CoO$_5$]$_2$ bipyramids are occupied by Co^{3+} species. The T-dependent Seebeck coefficient S shows a clear change of the conduction regime at the metal-insulator (MI) transition ($T_{MI} \sim 285$ K). The sign change of S from $S < 0$ to $S > 0$ can be explained assuming that a spin state transition occurs at T_{MI}. In the metallic state, Co^{2+} e_g electrons are moving in a broad band on the background of high or intermediate spin Co^{3+} species. In contrast, the insulating behavior may result from the Co^{3+} spin state transition to a low-spin Co^{3+} occurring in the octahedra. In this phase the transport would occur by hopping of the low-spin Co^{4+} t_{2g} holes, whereas the high-spin Co^{2+} electrons become immobilized due to a spin blockade.

The coupling of charge and spin degrees of freedom is an intrinsic feature of systems with strongly correlated electrons. Thus, it is well known that the antiferromagnetic ordering suppresses electrons hopping, both in a nondegenerate single-band case [1] and in a situation with charge carriers moving in a different band [2]. The stable background antiferromagnetic ordering leads to an electron confinement [3]. Alternatively, the tendency to electron delocalization may suppress antiferromagnetism and give ferromagnetic ordering (or double-exchange ferromagnetism).

In real materials there may also exist situations in which not only the spin ordering but also the very spin state of ions may change. This is, for instance, often the situation with compounds containing Fe^{2+} and Co^{3+}. In this case there may occur even more intricate phenomenon—the appearance of a spin blockade for the motion of charge carriers of one type as for electrons, whereas the motion of holes would still occur freely albeit in a much narrower band [4]. In this Letter we introduce the concept of spin blockade and present experimental data confirming the existence of the effect in cobaltites containing Co^{3+}.

Rich properties of cobaltites containing trivalent cobalt are linked to the comparable energies of their crystal field and intra-atomic coupling. As a consequence, the structural and electron transport properties of Co(III)/Co(IV) perovskites are strongly coupled to the cobalt spin state as shown for the various properties of the perovskites La$_{1-x}$Sr$_x$CoO$_3$ [5–11]. In this respect, the oxygen-deficient perovskites LnBaCo$_2$O$_{5+\delta}$ or (Ln$_{1/2}$Ba$_{1/2}$)CoO$_{3-\delta/2}$ with $\delta = 0.5$, which exhibit a simultaneous ordering of the Ln^{3+} and Ba^{2+} cations on one side and of the oxygen vacancies on the other, are of great interest, due to their metal-insulator transition (MIT)

(Fig. 1) which appears to be strongly correlated with the spin state transition [12–17]. In these ordered oxygen-deficient perovskites, the Co^{3+} species are sitting in rows of CoO$_5$ pyramids alternating in an ordered way with rows of CoO$_6$ octahedra (inset of Fig. 1). Although there is still some controversy about the spin state of Co^{3+} [18], the most common view is that at sufficiently low temperature, Co^{3+} adopts the intermediate-spin [(IS) $t_{2g}^5 e_g^1$] configuration in the pyramids and the low-spin [(LS) t_{2g}^6] configuration in the octahedra, whereas they are both in the high-spin (HS) or IS state above the MIT. This picture is also consistent with the structural and magnetic data obtained by neutron diffraction or synchrotron x-ray
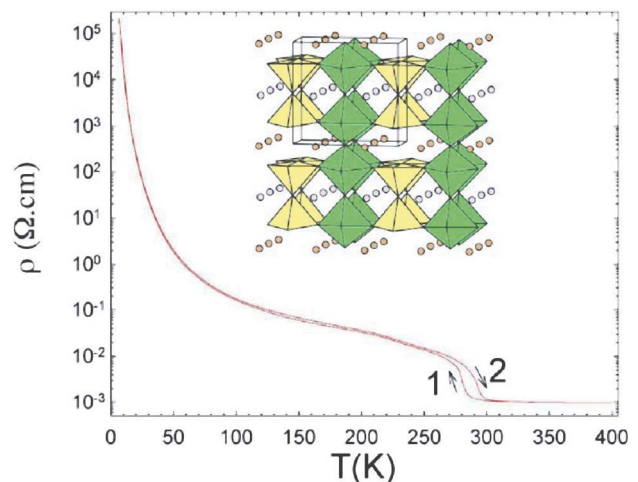

FIG. 1 (color online). Temperature dependence of the resistivity (ρ) for HoBaCo$_2$O$_{5.5}$. The "1" and "2" arrows are for the cooling and warming curves, respectively. Inset: drawing of the structure showing the planes of CoO$_6$ octahedra and double rows of CoO$_5$ pyramids.

powder diffraction [14,16,19], and with recent NMR results [20]. In the present Letter, based on the study of the thermoelectric properties of the oxygen-deficient perovskite $HoBaCo_2O_{5.5}$, we propose a model for this MIT, which, in particular, suggests that in case of the LS Co^{3+} there should appear a "spin blockade" for the electron transport.

In order to check the strong coupling between charges and spins in this phase, the ac-magnetic susceptibility (χ) was measured as a function of T (Fig. 2). The data were collected upon cooling from 350 down to 5 K. On this curve (solid line), at about 280 K, the χ jumps abruptly, to reach a maximum at 270 K, and then decreases again very abruptly. The inspection of the $\chi^{-1}(T)$ curve (dashed line in Fig. 2) also clearly shows the abruptness of the transition and gives a second smaller bump developing below ~ 250 K, hardly detectable on the $\chi(T)$ curve. The comparison of the $\rho(T)$ and $\chi^{-1}(T)$ curves, collected upon cooling, confirms that the MIT is concomitant with the χ^{-1} drop. The data of Figs. 1 and 2 are consistent with the usual interpretation that there appear LS Co^{3+} ions in a low temperature phase.

The thermoelectric power (TEP) measurements were performed with a physical properties measurements system from Quantum Design, in the range 5–320 K with magnetic fields up to 7 T. The $S(T)$ curve in zero magnetic field (Fig. 3) shows that above the T_{MI} transition temperature (280 K in the cooling mode), S is negative with a small absolute value ($S \sim -2\ \mu V\ K$). At T_{MI}, S changes sign between 285 and 290 K, jumping by more than $10\ \mu V\ K^{-1}$ in less than 5 K. Then the S value keeps on increasing as T decreases, reaches a maximum value $S = +170\ \mu V\ K$ at 75 K, and, finally, S decreases down to $+90\ \mu V\ K$ at 15 K. Note that for $T < 15$ K, the impedance of the sample becomes too large and exceeds the upper limit of our TEP measurement setup. Then, the
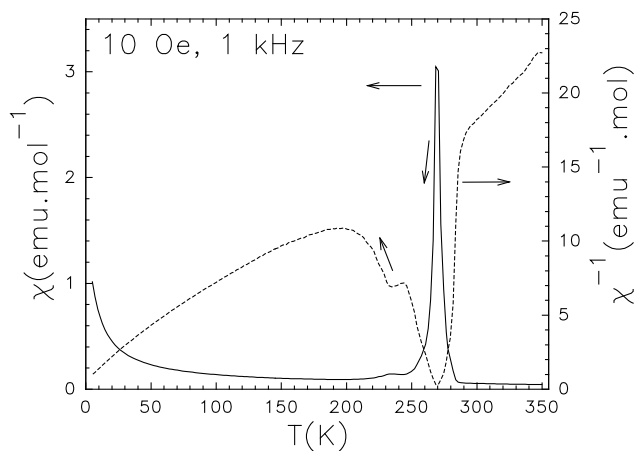
warming branch evidences the existence of a hysteresis which is persisting up to ~ 220 K. Remarkably, by applying a 7 T magnetic field at 320 K, the $S(T)_{H=0\,T}$ and $S(T)_{H=7\,T}$ curves collected upon cooling from 320 K remain superimposed down to 210 K, and below 210 K they start to separate with $S_{7T} < S_{0T}$ (inset of Fig. 3). This negative magnetothermoelectric power persists down to the lowest T values. Additionally, the comparison of the cooling and warming curves is consistent with the first order nature of the transition at T_{MI} as revealed by the hysteresis in the $S(T)$ curves.

From these results the metallic behavior of $HoBaCo_2O_{5.5}$ above $T_{MI} = 290$ K can be interpreted as the delocalization of an electron (HS Co^{2+} species, $t_{2g}^5 e_g^2$) moving in an ordered array built up from HS and IS Co^{3+} chains. Then, according to the usual interpretation [12,13,16], below T_{MI}, the octahedral HS Co^{3+} species are converted into LS Co^{3+} species, and the majority of carriers become localized holes (LS Co^{4+} species $t_{2g}^5 e_g^0$) as shown by the large positive S value that increases as T decreases below T_{MI} (Fig. 3). This scenario of the hole transfer from Co^{4+} to Co^{3+} is in perfect agreement with the thermally activated behavior of the conductivity below 210 K (not shown).

To explain the observed behavior of the thermopower, in particular, to understand why the electron conductivity at $T > T_{MI}$ is substituted by the hole one for $T < T_{MI}$, we propose the following model: in the insulating state of nominally stoichiometric material, containing in the ground state Co^{3+} ions in one or another spin state, charge transport occurs as in conventional semiconductors due to thermal excitation of electrons in the initially empty conduction band and holes in the valence band. In a localized picture these electron excitations would correspond to Co^{2+} states and holes to Co^{4+}. The resulting

FIG. 2. Left axis: ac-$\chi(T)$ curve of $HoBaCo_2O_{5.5}$ (real part χ') cooling curve (solid line); right axis: $\chi'^{-1}(T)$ curve obtained from the cooling $\chi'(T)$ curve. $H_{ac} = 10$ Oe and $f = 10^3$ Hz.
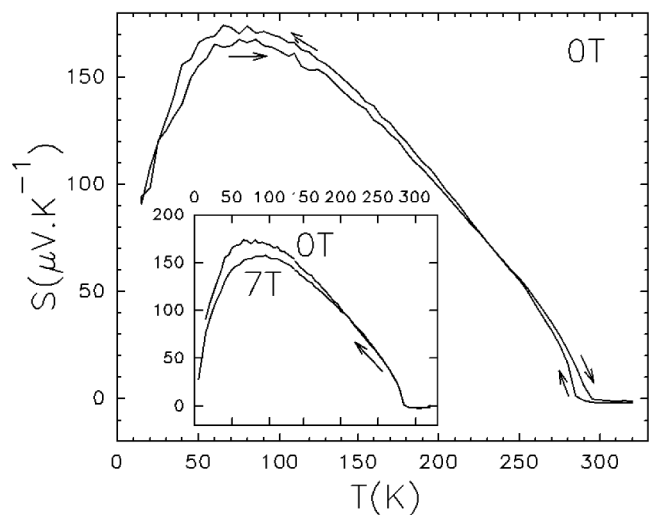

FIG. 3. Temperature dependent Seebeck coefficient S measured upon cooling and warming. Inset: comparison of $S(T)$ curves collected upon cooling in 0 T and then 7 T.

transport properties are determined by the respective mobility of these extra electrons (Co^{2+}) and holes (Co^{4+}). The main idea is that these mobilities depend strongly on the spin state of the background Co^{3+}. Indeed, when one considers the motion of an extra electron on a background of a lattice of HS or IS Co^{3+} ions [Fig. 4(a)], we see that one can easily move an extra electron from the middle Co^{2+} ion both to the HS and IS Co^{3+} (to the left and to the right), i.e., one can interchange corresponding ionic states by moving one electron. This would, of course, depend as usual on a relative spin orientation of these ions.

The situation is, however, quite different if the background Co^{3+} are in a LS state [Fig. 4(b)]. An extra electron creates Co^{2+} which is always a HS ion. If we now move one of the electrons of Co^{2+} to the neighboring

a) Co^{3+}, HS Co^{2+}, HS Co^{3+}, IS

b) Co^{3+}, LS Co^{2+}, HS
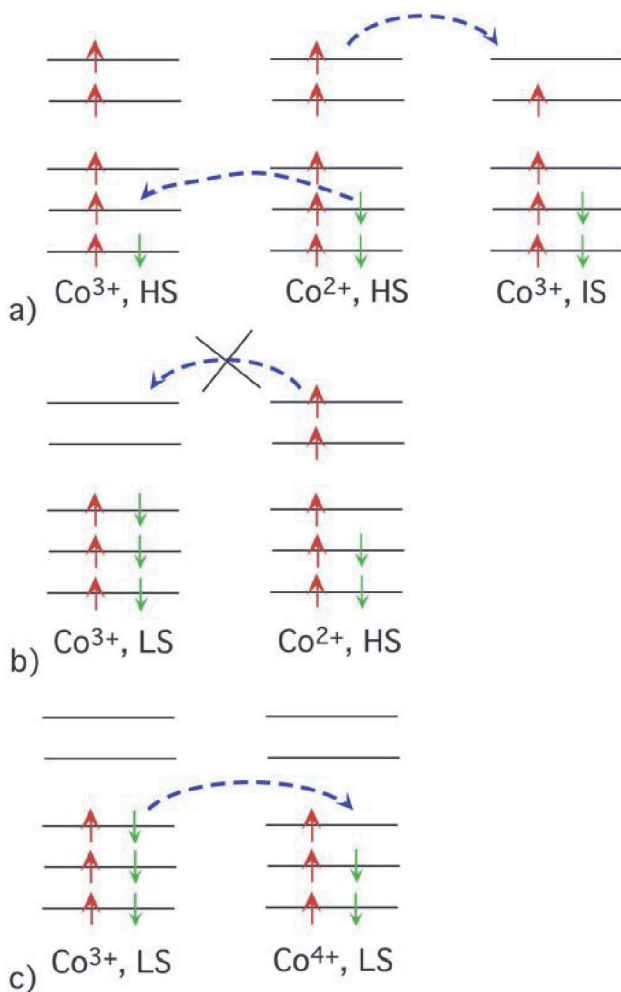
c) Co^{3+}, LS Co^{4+}, LS

FIG. 4 (color online).   The scheme showing the processes of electron (a),(b) and hole (c) hopping on the background of the HS and IS Co^{3+} (a) and LS Co^{3+} (b),(c). (b) illustrates the phenomenon of a spin blockade. (a) applies to the high-temperature metallic phase of $HoBaCo_2O_{5.5}$, whereas (c) corresponds to the processes available at the low temperature insulating phase.

Co^{3+} ion, we end up in both ions in a wrong spin state: Co^{2+} created at the left side will be in a LS state instead of HS required for Co^{2+}, and Co^{3+} left behind will be in the IS state instead of the required LS state. In others words, one cannot interchange LS Co^{3+} and HS Co^{2+} by only moving one electron—one should simultaneously also flip some others spins or change corresponding multiplets. This is also clear from the fact that one cannot interchange states with spins $S = 0$ (LS Co^{3+}) and $S = 3/2$ (HS Co^{2+}) by moving only one electron which carries spin $1/2$: this process will be strongly suppressed. One can call it a spin blockade.

On the other hand, one can easily see that in a similar situation the extra hole (Co^{4+} ion, which is always in a LS state with $S = 1/2$ can move on the background of LS Co^{3+} [Fig. 4(c)]. However, this motion would occur only by hopping of a t_{2g} electron, and this hopping remains small in comparison to the Co^{2+} electron predominantly moving in a broad e_g band. Thus one should expect that in the high temperature phase of $RBaCo_2O_{5.5}$, consisting predominantly of HS and IS Co^{3+}, there will be a rather high conductivity carried out by electrons in a relatively broad e_g band, whereas in the low temperature state, the presence of LS Co^{3+} sheets (octahedral layers) would suppress the transport of electrons, and only much weaker hole hopping would remain. This is consistent with our experimental observations (Fig. 3) that the thermopower is small and negative at $T > T_{MI}$, typical for metal with electrons as the main carriers, whereas it becomes positive and much larger at $T < T_{MI}$. The increase of S with decreasing T may be connected with the localization of heavy t_{2g} holes due, for instance, to disorder.

Furthermore, the magnetothermopower gives additional information concerning the field-induced magnetic state of $HoBaCo_2O_{5.5}$. The inspection of the $S(T)$ curves collected upon cooling in 0 and 7 T (inset of Fig. 3) reveals that the TEP becomes sensitive to the magnetic field below 210 K. This indicates a clear change in the spin-charge interactions as also discussed in Ref. [21]. Most probably, the magnetic moments of the cobalt cations start to develop antiferromagnetic correlations [14] (although the corresponding ordered magnetic structure is hardly detectable by neutron powder diffraction [19]). This is seen by the behavior of the magnetic susceptibility, Fig. 2, and is also consistent with the dependence of the thermopower on magnetic field shown in Fig. 3: when upon application of magnetic field some of the magnetic moments of IS Co^{3+} become parallel, the electron hopping in the pyramid layers will be enhanced which would reduce (positive) thermopower in the temperature region $T < 210$ K. This is fully consistent with the negative magnetoresistance found in the same T region [13].

The present study of the magneto-TEP of $HoBaCo_2O_{5.5}$ demonstrates the existence of a clear sign change for the charge carriers at the metal-insulator transition observed at 280 and 290 K upon cooling and warming,

respectively. The metallic regime originates from electrons delocalized in a broad band. This scenario is fully compatible with the formation of an e_g conduction band of the HS Co^{3+} orbitals. As argued above, the natural explanation of the change in the transport properties at T_{MI} is the assumption of a complete or partial conversion of the HS Co^{3+} located in the octahedra to the LS state. This conversion "immobilizes" the electron charge carriers due to the phenomenon of spin blockade, and the latter is replaced by an activated regime for holes (LS Co^{4+}) moving in the much narrower t_{2g} band. A similar phenomenon of spin blockade was also observed in mesoscopic transport through quantum dots [22].

The conclusion that an electron (HS Co^{2+}) could hardly move on the background of the LS Co^{3+} due to spin blockade may have a general character and may apply also to other systems with the LS Co^{3+}, such as $LaCoO_3$ at low temperatures.

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[1] L. N. Bulaevskii and D. I. Khomskii, Sov. Phys. JETP **25**, 1067 (1967).

[2] P. -G. de Gennes, Phys. Rev. **118**, 141 (1960).

[3] L. N. Bulaevskii, E. L. Nagaev and D. I. Khomskii, Sov. Phys. JETP **27**, 836 (1968).

[4] G. A. Sawatzky, in *Lecture Notes of the ICTP Spring College in Condensed Matter on "Superconductivity," ICTP, Trieste, Italy, 1992*, edited by Paul N. Butcher and Lu Yu (World Scientific, Singapore, 1995).

[5] G. H. Jonker and J. H. Van Santen, Physica (Utrecht) **19**, 120 (1953).

[6] M. A. Senaris-Rodriguez and J. B. Goodenough, J. Solid State Chem. **118**, 323 (1995).

[7] R. Mahendiran and A. K. Raychaudhuri, Phys. Rev. B **54**, 16 044 (1996).

[8] M. A. Korotin, S. Yu Ezhov, I. V. Solovyev, V. I. Asimov, D. I. Khomskii and G. A. Sawatsky, Phys. Rev. B **54**, 5309 (1996).

[9] K. Asai, P. Gehring, H. Chou, and G. Shirane, Phys. Rev. B **40**, 10 982 (1989).

[10] R. R. Heikes, R. C. Miller, and R. Mazelsky, Physica (Utrecht) **30**, 1600 (1964).

[11] S. Stolen, F. Gronvold, H. Brinks, T. Atake, and H. Mori, Phys. Rev. B **55**, 14 103 (1997).

[12] C. Martin, A. Maignan, D. Pelloquin, N. Nguyen and B. Raveau, Appl. Phys. Lett. **71**, 1421 (1997).

[13] A. Maignan, C. Martin, D. Pelloquin, N. Nguyen and B. Raveau, J. Solid State Chem. **142**, 247 (1999).

[14] F. Fauth, E. Suard, V. Caignaert and I. Mirebeau, Phys. Rev. B **66**, 184421 (2002).

[15] H. Kusuya *et al.*, J. Phys. Soc. Jpn. **70**, 3577 (2001).

[16] C. Frontera, J. L. García-Munoz, A. Llobet, and M-A. G. Aranda, Phys. Rev. B **65**, 180405(R) (2002).

[17] M. Respaud, C. Frontera, J. L. Garcia-Muñoz, M-A. G. Aranda, B. Raquet, J. M. Broto, H. Rakoto, M. Goiran, A. Llobet, C. Ritter, and J. Rodriguez Carvajal, Phys. Rev. B **64**, 214401 (2001).

[18] Z. W. Hu *et al.* (to be published).

[19] J. C. Burley, J. F. Mitchell, S. Short, D. Miller, and Y. Tang, J. Solid State Chem. **170**, 339 (2003).

[20] M. Itoh, Y. Nawata, T. Kiyama, D. Akahoshi, N. Fujiwara, and Y. Ueda, Physica (Amsterdam) **329B–333B**, 751 (2003).

[21] Y. Wang, N. S. Rogado, R. J. Cava, and N. P. Ong, Nature (London) **423**, 425 (2003).

[22] D. Weinmann, W. Häusler, and B. Kramer, Phys. Rev. Lett. **74**, 984 (1995).