Selective spin-state and metal–insulator transitions in GdBaCo$_2$O$_{5.5}$

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Abstract

By means of ultra-high resolution synchrotron diffraction and calorimetry measurements we have studied the metal–insulator transition in GdBaCo$_2$O$_{5.5}$. The appearance of the metallic state is attributed to a sudden excitation of some electrons in the octahedral ($t_{2g}$ state) into the Co $e_{g}$ band (final $t_{2g}e_{g}^{4}$ state). In contrast, the $t_{2g}e_{g}^{4}$ state in the pyramids does not change at the transition. Calorimetry measurements show that the insulator-to-metal transition is first order and the entropy change estimated from the latent heat corroborates the pictured scheme.

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Cobalt oxides with perovskite structure have demonstrated to be a very challenging family of compounds. In addition to the strong spin–charge–lattice correlations present in Cu and Mn oxides, the spin-state degree of freedom of Co ions introduces new effects in these narrow band oxides [1,2]. Co$^{3+}$ ions can present three different spin states: the low spin state (LS, $t_{2g}e_{g}^{4}$), the intermediate spin state (IS, $t_{2g}e_{g}^{2}$), and the high spin state (HS, $t_{2g}e_{g}^{4}$). HS (LS) is associated with values of crystal field (CF) smaller (larger) than the intra-atomic exchange energy. The IS state appears when similar values of these two energies are combined with the electron–phonon coupling and the Jahn–Teller distortion that lifts the degeneracy of $t_{2g}$ and $e_{g}$ orbitals. In many cobaltites the energy differences between spin states are small and can be easily overcome by thermal fluctuations and/or changed by the lattice thermal evolution [2] leading to spin-state transitions. The size of Co$^{3+}$ ions depends on its spin state, and anomalous cell volume changes have been found at the spin state transitions in LaCoO$_3$ [2]. More recently, a great interest on LnBaCo$_2$O$_{5+\delta}$ ($Ln$ ≡ rare earth) cobaltites has appeared [3–10]. This family of compounds presents spin-state transitions [6,9,10], charge ordering [7,8], and giant magnetoresistance [4,10]. The oxygen content $\delta$ (0≤$\delta$≤1) controls the nominal valence of Co ions that varies from 3.5+ (50% of Co$^{3+}$ and 50% of Co$^{4+}$) for $\delta = 1$ to 2.5+ (50% of Co$^{3+}$ and 50% of Co$^{2+}$) for $\delta = 0$ passing through 100% of Co$^{3+}$ for $\delta = 0.5$. These compounds present a high degree of order. Ba and Ln order forming (001) layers alternating in the $c$ direction. In addition, the oxygen vacancies (when $\delta < 1$) are placed in the layers of the rare earth ions. Thus, these compounds are formed by the stacking sequence $[\text{Co}_2\text{O}_2]\,[\text{BaO}]\,[\text{Co}_2\text{O}_2]\,[\text{LnO}_3]$ along the $c$ direction, leading to the coexistence of two types of Co-coordination environments: pyramidal Co$_5$ and octahedral Co$_6$. Moreover, oxygen vacancies, within the [LnO$_3$] layers, present a strong tendency to order. For $\delta = 0.5$ the oxygen atoms and vacancies are located in alternating rows [5,9]. This order prevents the randomness in the magnetic superexchange interactions that causes spin glass behavior in oxygen-deficient La$_{1-x}$Sr$_x$Co$_{3-c}$ compounds.

A metal–insulator (MI) transition is present in several LnBaCo$_2$O$_{5.5}$ compounds [5]. Susceptibility measurements reveal that coinciding with this transition there is a large change in the effective paramagnetic moment of the samples. This is understood as a sudden increase, on heating, in the spin state of Co ions [5,9,10]. From magnetic measurements on several samples with different lanthanides, all displaying the MI transition, Maignan et al. [5] suggested a coexistence of IS (pyramids) and LS (octahedra) for $T < T_{MI}$ and HS Co$^{3+}$ at high enough temperatures. Nevertheless,
spin state at both sides of the MI transition is still unclear. A study of the structural changes was carried out for TbBaCo$_2$O$_{5.5}$ by Moritomo et al. [9]. Based on these structural data, they proposed a spin-state transition from a full IS state scheme to the HS state (for $L_n = \text{Tb}$) in both pyramidal and octahedral sites [9]. For $T > T_{MI}$ a HS state [5,9] and a coexistence of HS/IS states have been proposed [10] by different groups. The main conclusion of Moritomo et al. is that the orbital degree of freedom of the IS state ($\Delta^2_{2g} \Lambda^1$) and the electron–phonon coupling results in a Jahn–Teller cooperative distortion and a $d^3_{3z^2-r^2}/d^3_{y^2-r^2}$-type orbital order (OO) below $T_{MI}$. As the origin of the transition they proposed a sudden distortion of the basal planes, on cooling, that accommodate the $d^3_{3z^2-r^2}$ (pyramid) and $d^3_{y^2-r^2}$ (octahedron) orbital occupancy [9]. However, the sample studied in Ref. [9] had impurities and the reported errors in the Co–O distances were anomalously large.

We have studied a polycrystalline sample of GdBaCo$_2$O$_{5.4}$. It was prepared by standard solid-state reaction in air as has been previously reported [10]. We have characterized the structural evolution across the MI transition using X-ray thermodiffractometry (Gd has a very high neutron absorption coefficient). Ultra-high resolution synchrotron X-ray powder diffraction (SXRPD) patterns were collected at BM16 diffractometer of ESRF (Grenoble) in the standard Debye–Scherrer configuration. Measurements have been done at $T = 300, 320, 340, 360, 380$ and 400 K. The powder patterns were analyzed by the Rietveld method using the GSAS suite of programs [11]. No impurities peaks have been detected and the diffraction peaks were remarkably sharp for a three metal-containing perovskite. This warrants the good quality of the studied sample. The oxygen stoichiometry was determined to be 5.53(1) from SXRPD data, a usual oxygen content found for air-synthesis [5,9]. Moreover, according to Ref. [5] the MI transition is absent in Gd samples with $\delta > 0.6$. Differential scanning calorimetry (DSC) measurements have been taken in a TA-Instruments commercial calorimeter (model 2920) using a temperature ramp of 5 K/min.

The structure of TbBaCo$_2$O$_{5.5}$ reported in Ref. [9], with $Pmmn$ space group with $a \approx a_{\text{c1}}, b \approx c \approx 2a_{\text{P}}$ ($a_{\text{P}}$ primitive perovskite lattice parameter), was used as starting model for the Rietveld refinements. The oxygen vacancies were checked in our GdBaCo$_2$O$_{5.3}$ sample and found to be located at the lanthanide layers in such a way that CoO$_6$ octahedra form $\{010\}$ layers alternated along the $b$-axis with $\{010\}$ layers of corner-sharing CoO$_5$ square pyramids, as in TbBaCo$_2$O$_{5.5}$. $R_p$ agreement factor ranges between 3.91% ($T = 300$ K) and 4.36% ($T = 400$ K). Refined atomic coordinates will be published elsewhere. On cooling through the transition, $b$ and $c$ lattice parameters exhibit a sudden shrink (0.28 and 0.27%, respectively) while $a$ lengthens at $T_{MI}$ (0.35%), see Fig. 1(a). This contrasts with the results reported for TbBaCo$_2$O$_{5.5}$ [9]. Figs. 1(b) and (c) show the Co–O bond distances, for CoO$_6$ octahedra and CoO$_5$ pyramid respectively, along the three crystallographic axes (Co–Oi stands for bond lengths along $i = a$, $b$ and $c$-axis). There are also important differences with the case of TbBaCo$_2$O$_{5.5}$ [9]. We have found that pyramids and octahedra are deformed in both the insulating and metallic states. The longest Co–O distance is Co–Oa for the former (CoO$_6$) and Co–Ob for the latter (CoO$_5$). Long and short bonds alternate along the $b$-axis at both sides of the transition. This is well different from the evolution reported in Ref. [9] for TbBaCo$_2$O$_{5.5}$, where that alternation was only clearly observed below $T_{MI}$ and it was stated that the basal plane deformation in pyramids and octahedra vanishes above $T_{MI}$. Conversely with Ref. [9], our data discard the stabilization of a $d^3_{3z^2-r^2}/d^3_{y^2-r^2}$-type OO below $T_{MI}$ as the physical mechanism for the MI transition in GdBaCo$_2$O$_{5.5}$: we show in Figs. 1(b) and (c) that the difference between long and short Co–O bonds in the basal plane (the $Q_2$-type antiferrodistorsive distortion) remains practically unchanged in the pyramid and increases strongly in the octahedron when heating above $T_{MI}$.

Fig. 1(d) shows the temperature dependence of the inverse susceptibility in the paramagnetic region up to 625 K. As discussed in Ref. [10] the values of the effective magnetic moment obtained below and above $T_{MI}$ suggest that the spin state of Co$^{3+}$ is a 1:1 mixture of LS/IS and a 1:1 mixture of HS/IS, respectively. Since IS Co$^{3+}$ is most probable in the pyramids [5,12], the results indicate that, below $T_{MI}$, the octahedron contains LS Co$^{3+}$ and the pyramid IS Co$^{3+}$.

![Fig. 1](image-url) Temperature dependence of (a) lattice constants; (b) Co–O bond distances for the CoO$_6$ octahedra (Co–Oi stands for the bond lengths along $i = a$, $b$ and $c$-axis); (c) Co–O bond distances for the CoO$_5$ pyramids; and (d) inverse of the susceptibility $\chi_C$ (the straight lines show the Curie fits above and below $T_{MI}$).
Fig. 2(a) and (b) show the (underlying) heat flow obtained by DSC during heating and cooling, respectively. The hysteresis in the cooling and heating processes evidences that the transition is first order. Fig. 2(c) shows the thermal evolution of dq/dT. The latent heat and entropy change, during the transition, estimated from this curve are Δh = 8.155 kJ/mol and Δs = 2.73R.

Let us now analyze in more detail the Co–O bond length variation. As shown in Figs. 1(b) and (c), the apical Co–Oc distances of the octahedron and pyramid changes little across the transition. Co–Oa and Co–Ob basal distances of the pyramid both lengthen on cooling, in a so similar way that the basal plane deformation remains practically unchanged at both sides of TMI. This is not compatible with the stabilization of d32...2-type OO in the insulating phase. In contrast the Co–Ob distance in the octahedra displays a pronounced shrinking on cooling, which is accompanied by a moderate increase of the Co–Oa distance. As a result, the basal distortion decreases notably on cooling through TMI, the opposite of that one would expect for the stabilization of d32...2-type OO below TMI. At this point it is important to recall that a transition to a higher spin state in Co3+ (as deduced from magnetic data) implies a bigger effective ionic radius which should lengthen the average <dCo–O> bond length. Fig. 3(a) shows the evolution of <dCo–O> distance. A very significant finding is the different evolution of this distance in the octahedron and the pyramid: <dCo–O> distance of the octahedron increases substantially at TMI on heating but that of pyramid decreases. This finding constitutes the first experimental result establishing that the spin-state transition in LnBaCo2O5 occurs solely in the octahedra. Thus, in the pyramids we observe, on heating, the metal–oxygen bond-length contraction normally found when the gap closes and enters the metallic phase. This spin-state change is also responsible for the anomalous volume expansion at TMI plotted in Fig. 3(b). Normally, the cell volume contracts in an electron delocalization process but expands in a transition to a higher spin state [2].

The entropy change found by means of DSC confirms this picture. The LS state of Co3+ is non-degenerated (g_L = 1), while the degeneracy of the HS state is g_H = 15 [13]. Thus, the expected entropy change due to the larger degeneracy of the HS is Δs = R ln g_H / g_L ≈ 2.71R in complete agreement with the value found (2.73R).

In summary, from the analysis of structural changes, magnetic behavior and entropy change during the MI transition for GdBaCo2O5.5 we can conclude that: (i) There is a sudden expansion of <dCo–O> distance of octahedra at TMI, concomitant with a first-order spin-state transition from LS (insulating) to HS (metallic) state in the Co3+ ions of the octahedra, (ii) Co atoms in the pyramids hold the same spin state (Co3+ IS) before and after the electronic delocalization. Hence, the pyramid simply shrinks as commonly observed in Mott oxides when they enter the metallic phase. (iii) The alternation of short and long Co–O bonds along the b-axis is present in the insulating and the metallic phases. The Q2-type distortion (antiferrodistorsive) of the basal planes does not increase in the insulating phase, ruling out a d32...2/d32...1-type OO as the origin of the transition. So, the driving force for the MI transition is a spin-state change in the Co3+ ions located at the octahedra, which suddenly switch from LS (t2g, e2g) to HS (t2g, e2g) state at TMI. Thereby, the metallic conductivity in this family of oxides (full Co3+) seems related with the injection of electrons in the conduction band that accompanies this transition.

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References


W. Zhou, Chem. Mater. 6 (1994) 441;