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Structural, spin state, and magnetic transitions in $GdBaCo_2O_{5+\delta}$ ($\delta \approx 0.5$)

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Abstract

Structural, spin state, magnetic and field-induced transitions have been studied in $GdBaCo_2O_{5.5}$ over a wide range of temperatures. We have found that, concomitant with a metal–insulator transition at 370 K, remarkable structural changes take place. These changes evidence the onset of orbital order at this temperature. Magnetization measurements, and the observation of a field-induced transition, below 250 K, by applying high magnetic fields, confirm that, below this temperature, an antiferromagnetic arrangement of the magnetic moments is present.

Keywords: Magnetically ordered materials; Chemical synthesis; X-ray diffraction; Phase transitions; Synchrotron radiation

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1. Introduction

Cobaltites are a very rich and interesting family of metal-transition oxides with perovskite structure. Besides the extensive work done on La cobaltites, both undoped ($LaCoO_3$, La_2CoO_4) or doped with Sr ($La_{1-x}Sr_xCoO_3$, $LaSrCo_2O_6$), there has been recent interest in rare-earth-based cobaltites that are half doped with Ba [1–9]. In the general formula $LnBaCo_2O_{5+\delta}$ ($0 \leq \delta \leq 1$), the oxygen content, δ, controls the valence state of cobalt ions. In samples with the full oxygen content, $\delta = 1$ and Co ions are in a mixed valence state: Co^{3+} and Co^{4+} are present in a 1:1 ratio. When the oxygen content is the minimum, $\delta = 0$, and the mixed valence state is between Co^{3+} and Co^{2+}, both of which are present in the same proportion. In the intermediate case, $\delta = 0.5$, the unique presence of Co^{3+} must be expected.

It has been found that, in powder samples prepared by solid state reaction in air, the oxygen content, δ, depends on the mean size of the rare earth Ln. In general, the larger the lanthanide size, the larger the oxygen content is. However, δ can somehow be tailored by means of different heat treatments after sinterization [5]. The oxygen content, δ, controls not only the magnetic and transport properties but also determines the existence of some transitions [1,5]. For instance, samples with $\delta \approx 0.5$ present a metal–insulator transition at a temperature controlled by the lanthanide, Ln; for instance, $T_{MI} \approx 280$ K for Ln ≡ Ho, $T_{MI} \approx 370$ K for Ln ≡ Gd. This transition is inhibited by either augmenting or decreasing δ.

Charge ordering (CO) of $Co^{2+} - Co^{3+}$ ions ($\delta \approx 0$) has been reported in $YBaCo_2O_5$ [7] and $HoBaCo_2O_5$ [8]. In addition, these samples present other remarkable coincidences. (i) From neutron powder diffraction (NPD) data, well above T_{CO}, there is a Néel transition to a G-type antiferromagnetic (AFM) order of the moment of Co ions ($T_N \sim 330$ K and $T_{CO} \sim 220$ K, for Ln ≡ Y [7]; $T_N \sim 340$ K and $T_{CO} \sim 210$ K for Ln ≡ Ho [8]). (ii) At the Néel transition, there is a change in the space group (SG) from tetragonal $P4/mmm$ ($T > T_N$) to orthorhombic $Pmmm$ ($T_{CO} < T < T_N$). Moreover, at the CO transition, the crystallographic unit cell doubles along the *b* direction and the SG changes to $Pmmb$ ($T < T_{CO}$). (iii) The Ln (Y or Ho) and Ba display an ordering in alternating layers, and the oxygen vacancies (□) are placed in the rare earth layer, forming Ln□ planes. (iv) The value of the magnetic moment found at low temperature clearly indicates that the

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Co ions are in a high spin (HS) state. In spite of these coincidences, there is a certain controversy concerning the behavior of the spin state of the Co ions. Vogt et al. [7] (Ln ≡ Y) concluded, from the ordered moment found at $T = 300$ K (just 30 K below T_N), that, above T_{CO}, Co^{2+} and Co^{3+} ions are in a low spin (LS) and intermediate spin (IS) state, respectively, and that the sample presents a spin-state transition in which the spin changes from low to high spin upon cooling. Beside this, Suard et al. [8], who monitored the ordered magnetic moment from T_N down to T_{CO}, do not find such a spin state transition.

In a $\delta = 0.5$ sample, $TbBaCo_2O_{5.5}$ (with an oxygen content very similar to the sample studied in this work), Moritomo et al. [9] have reported that, coinciding with the aforementioned metal–insulator transition ($T_{MI} \approx 340$ K), a sudden change of the lattice parameters and Co − O bond distances takes place. These changes indicate the presence of orbital order (OO) in the insulating phase but not in the metallic one. Moreover, from the behavior of the $\chi^{-1}(T)$ ($\chi \equiv$ magnetic susceptibility) curve, a spin state transition from HS ($T > T_{MI}$) to IS ($T > T_{MI}$) state was proposed. From neutron diffraction measurements, the magnetic moment of the Co ions at low temperature was roughly estimated to be 0.4(2) μ_B [9], which is much lower than the saturation value in a IS state (2 μ_B). In agreement with the $\delta = 0$ samples, Tb and Ba ions were found to be ordered in (0 0 1) layers and the oxygen vacancies are located (and ordered) in the Tb layers forming $TbO_{0.5}\square_{0.5}$ planes.

In this paper, we present synchrotron X-ray powder diffraction (SXRPD) and magnetotransport data on $GdBaCo_2O_{5+\delta}$ ($\delta \approx 0.5$). The macroscopic behavior of similar samples has been found to be analogous to that found for a Ln ≡ Tb sample[1] [5,9]. Our data confirm that the metal–insulator transition coincides with structural changes that do not imply a symmetry change, and that no structural changes can be appreciated at T_N. Magnetic and magnetotransport data coincide with the observation of a small ordered moment in the Ln ≡ Tb sample. In addition, the transport measurements under applied high magnetic field show some novel interesting results.

2. Experimental details

Polycrystalline samples of $GdBaCo_2O_{5.5}$ were prepared by solid state reaction in air. High purity powders of Gd_2O_3, $BaCO_3$ and Co_3O_4 were mixed at stoichiometric weights. After a de-carbonation process at 900°C, the powder was pressed into a pellet and annealed over 24 h at 1125°C in air. After a re-grinding of the resulting pellet, the compression and annealing (at 1125°C in air) processes were repeated three times. The quality of the sample was tested by laboratory X-ray diffraction and it was found to be well crystallized in a single phase. SXRPD data were collected at BM16 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble) using $\lambda = 0.442377$ Å in Debye-Scherrer (transmission) configuration at temperatures ranging from 10 to 400 K. The sample was mounted in a borosilicate glass capillary ($\phi = 0.5$ mm) and rotated during data collection. The resulting patterns have been refined using the programs GSAS [10] and FULLPROF [11]. Low magnetic field studies have been done using a SQUID. High magnetic field magnetization measurements were performed at the facilities of the SNCMP in Toulouse (France), at temperatures between 4.2 and 300 K. Using the discharge of a bank capacitor in a coil, pulsed fields of up to 35 T were obtained with a duration time of more that 1 s. The conventional four-probe method in DC configuration was used to measure the resistivity and its magnetic-field dependence for reasonable sample resistance ($R \lesssim 10^7\ \Omega$). In the insulating regime, magnetotransport measurements were performed by magneto-conductivity using a low noise pre-amplifier.

3. Results and discussion

Fig. 1 shows the temperature dependence of the DC magnetization, and its inverse at 1 T of applied field. This magnetization is affected by the high moment of Gd ions, and a direct estimation of the paramagnetic moment coming from Co ions is difficult to extract. Nevertheless, a change in the paramagnetic contribution, similar to that found in $TbBaCo_2O_{5.5}$ [9], can be clearly appreciated at $T_{MI} \simeq 370$ K. From the fitting of the Curie law, μ_{eff} changes from 22.2(6) μ_B/(f.u.) for $T > T_{MI}$ to 13.6(9) μ_B/(f.u.) for $T < T_{MI}$. However, in contrast to the case of Ln ≡ Tb, above T_{MI} $\theta_C \approx -120$ K, indicating AFM correlations, and below T_{MI}, $\theta_C \approx 200$ K. The reduction of the paramagnetic moment has been interpreted as a spin state transition from a HS state to an IS or LS state [9], but the change of the sign of θ_C needs further investigation. Fig. 1

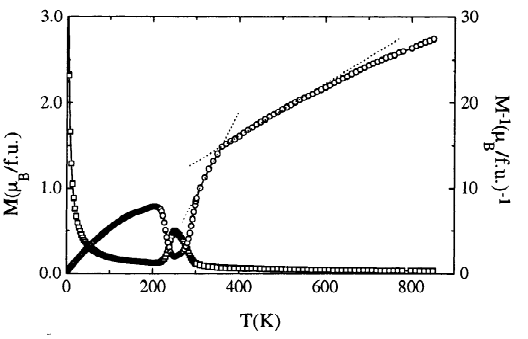

Fig. 1. DC magnetization measured at $\mu_0 H = 1$ T and its inverse vs. temperature. Dotted lines are guides to the eyes.

[1] In Ref. [2], the air sinterized sample of $GdBaCo_2O_{5+\delta}$ studied, which the authors assumed to have $\delta = 1$(without performing an oxygen content analysis), can be assumed, from results of Ref. [5], to have a value of $\delta \approx 0.5$.

also shows a considerable enhancement, when cooling, of the magnetic moment at ~295 K that suddenly stops at $T_N \approx 250$ K.

SXRPD data have been successfully refined at RT (R_B = 4.5%, with Q ranging from 0.5 to 10.5 Å^{-1}) using the $P\,mm2$ orthorhombic SG with cell parameters $b \sim a_p$ and $a \sim c \sim 2a_p$ (a_p is the unite cell of the primitive perovskite). The same SG successfully reproduces the SXRPD patterns at all of the temperatures studied ($10\,K \leq T \leq 400$ K). The refinement of the oxygen content at RT rendered δ = 0.5(1), near the value reported in Ref. [5] for an air-sintetized (Ln ≡ Gd) sample. We have found a disposition in (0 0 1) layers of the Gd and Ba ions and a concentration of the oxygen vacancies in the Gd planes. The evolution of the cell parameters obtained from SXRPD data is shown in Fig. 2. At T_{MI}, an anisotropic change of the cell parameters and a sudden decrease of the unit cell volume can be clearly seen. Examination of the anisotropic changes suggests a certain charge localization in rods perpendicular to the *ac* plane, probably due to the occurrence of OO at T_{MI}. We noticed that, surprisingly, the unit cell volume in the insulating phase was smaller than in the metallic phase. The sudden decrease of the unit cell volume could arise from two different facts: (i) the onset of OO (as has been reported to happen in manganites [12]); and (ii) a spin state transition of the Co ions, as far as their size depends on their spin state [13]. In contrast, no structural changes are observed at $T_N \approx 250$ K, which coincides with the sudden decrease in the magnetization, so a spin state transition at this temperature can be discarded. Presumably, as happens in $TbBaCo_2O_{5.5}$ [9], this decrease in the $M(T)$ curve corresponds to the onset of AFM order.

Fig. 3 shows the dependence of the magnetization on the applied field up to 32 T at T = 4.2 K. The initial increase in the magnetization (up to a field of about 17 T) corresponds to the alignment of Gd's moments, but a jump in the $M(H)$ dependence is clearly visible at 17 T. During this field-induced transition, the total moment increases by about 0.4 μ_B per Co ion, which is the same value as that reported by Moritomo et al. [9] for the ordered moment per Co ion of $TbBaCo_2O_{5.5}$ at 50 K. Moreover, we have observed that

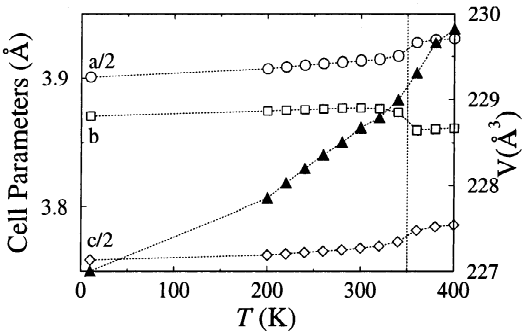

Fig. 2. Temperature dependence of the lattice parameters (open symbols) and unit cell volume (solid symbols) obtained from SXRPD patterns. The lines are guides to the eyes.

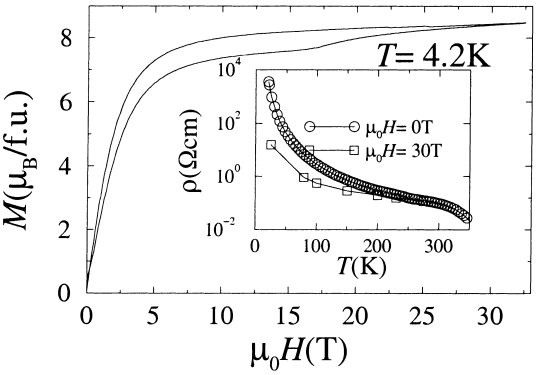

Fig. 3. Magnetization per formula unit vs. applied field up to $\mu_0 H = 32$ T at 4.2 K. The field-induced transition is observed to disappear at T_N. The inset shows the $\rho(T)$ curve for 20 K ≤ T ≤ 350 K without an applied field and under an applied field of 30 T.

this field-induced transition disappears at T_N = 250 K. It is worth noting that the nature of this field-induced transition is different from that found in Mn perovskites [14] with CO. In the present case, it does not correspond to the melting of a CO phase: in a manner consistent with the expected valence of Co, superlattice peaks associated with charge modulation have not been observed in the SXRPD patterns over the entire temperature range. Moreover, we have found that the high field state does not correspond to a metallic state. The inset of Fig. 3 shows the $\rho(T)$ curves without applied field and under a field of 30 T. In contrast with the FM metallic phase of CO manganites, $GdBaCo_2O_{5.5}$ remains insulating even under 30 T. These findings indicate that the transition found under a field is just the disruption of the AFM order established in this compound below $T_N \approx 250$ K, but it does not imply disruption of the orbital order achieved at $T_{OO} = T_{MI} \approx$ 370 K and involves no changes in the spin state of Co. Higher fields are necessary to induce such transitions.

4. Conclusions

We have found that the $P\,mm2$ space group nicely reproduces our diffraction data. This contrasts with the $P\,mmm$ space group previously reported for $TbBaCo_2O_{5.5}$ [9]. In addition, we have not detected a symmetry change in the whole 10–400 K temperature range. Coinciding with the metal–insulator transition found in $GdBaCo_2O_{5.5}$ at $T_{MI} \approx 370$ K, a sudden anisotropic change of the lattice parameters occurs. This change has been interpreted as the signature of an electronic redistribution (OO). Contrarily, no sudden structural changes are appreciated at $T_N \simeq 250$ K when the ferromagnetic moment disappears. Below this temperature, high field magnetization causes a field-induced transition to occur. The features presented by this transition confirm the ordered magnetic moment found in Ref. [9] for $TbBaCo_2O_{5.5}$ and that a spin state transition at this temperature can be ruled out. In contrast to the usual

behavior in manganites, the field-induced state is insulating.

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