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Spin-locking effect in the nanoscale ordered perovskite cobaltite $LaBaCo_2O_6$

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A nanoscale ordered perovskite cobaltite, which consists of 90° ordered domains of the layered "112" $LaBaCo_2O_6$, has been evidenced by high resolution-transmission electron microscopy. This form, such as the disordered $La_{0.5}Ba_{0.5}CoO_3$ and ordered $LaBaCo_2O_6$, exhibits a ferromagnetic transition at $T_C \approx 179$ K. However, it differs from the two previous forms by its strong magnetic anisotropy and, correlatively, by its high value of coercivity (4.2 kOe) at low temperature. We suggest that this behavior originates from the locking of magnetic spins in the 90° oriented nanodomain. Moreover, one observes a semimetal to semimetal transition at T_C with a maximum magnetoresistance of $\sim$6.5% at this temperature.

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Perovskite cobaltites with the general formula $Ln_{1-x}A_xCoO_{3-\delta}$ (Ln=trivalent rare earth cation and A =divalent alkaline earth cation) have been explored by many authors due to their fascinating magnetic and electron transport properties, involving complex transitions.[1–9] The latter originate from the various oxidation states of cobalt which, in general, exhibit mixed valent states ($Co^{2+}/Co^{3+}/Co^{4+}$) and from the various spin state configurations of Co^{3+} and Co^{4+} which are susceptible to change with temperature as shown for Co^{3+} from low spin (LS) $t_{2g}^6e_g^0$ to intermediate spin (IS) $t_{2g}^5e_g^1$ or high spin (HS) $t_{2g}^4e_g^2$ states.[10–12] In those materials, the spin state configuration is mainly dictated by two competing contributions: the crystal field splitting on one hand and the exchange energy for occupied orbitals and 3*d* electrons on the other hand.[12,13] As a consequence, the nature of the A-site cations, especially their size, and their distribution, ordered or disordered, may influence drastically the spin state configuration of Co ions.[5,6] In this respect, the two isochemical perovskites, $La_{0.5}Ba_{0.5}CoO_3$ and $LaBaCo_2O_6$, A-site disordered and ordered, respectively,[13,14] are of great interest. Both were found to be ferromagnetic with close Curie temperatures ranging from 175 to 190 K. However, there remains a controversy about the transport properties of the disordered perovskite $La_{0.5}Ba_{0.5}CoO_3$. Nakajima *et al.*[14] observed for this phase a metallic behavior down to 140 K, followed by an abrupt increase of resistivity below this temperature. Whereas Fauth *et al.*[13] observed a semimetallic behavior down to 110 K, but with a sudden decrease of resistivity at T_C. As a consequence, the first authors observed magnetoresistance (MR) below 140 K, whereas the second authors reported a maximum of MR around T_C.

We have revisited the perovskite with the composition "$La_{0.5}Ba_{0.5}CoO_3$" using a different method of synthesis. We report herein on a third form of this stoichiometric perovskite that we call nanoscale ordered $LaBaCo_2O_6$, which consists of 90° oriented domains of the ordered 1:1 $LaBaCo_2O_6$ perovskite. We show that this ferromagnetic perovskite exhibits a T_C close to the other two phases, but it differs from the latter by a strong magnetic anisotropy and a much higher coercive field of 4.2 kOe. Such a difference is interpreted by a spin-locking effect due to its particular nanostructure. Moreover, we observe a transition from a semimetallic paramagnetic (PM) to ferromagnetic (FM) semimetallic state near T_C with an upturn in the resistivity below 35 K. At low temperature, the MR value in an applied field of 70 kOe is only $\sim$4%, whereas the highest MR value is observed around 179 K ($\sim$6.5%).

The nanostructurally ordered polycrystalline $LaBaCo_2O_6$ compound was synthesized by sol-gel method from metal nitrates using citric acid as a complexant. The resulting gel was then decomposed at elevated temperatures, pressed into pellets, and finally sintered in Ar atmosphere at 1423 K for 48 h controlling carefully the oxygen pressure (10 ppm O_2). For preparation of the cubic disordered $La_{0.5}Ba_{0.5}CoO_3$, the method described in Ref. 14 was applied. To obtain the fully stoichiometric materials, both of the prepared compounds were oxygenated under elevated O_2 pressure (130 bar) at 623 K. Oxygen content was verified by wet-chemical redox analysis to be 2.99 and 6.01 for disordered and nanostructurally ordered compounds, respectively.

The X-ray powder diffraction patterns were registered with a Philips Xpert Pro diffractometer, employing Cu $K\alpha$ radiation. Both compounds can be refined using the Pm-$3m$ space group[13] with a cell parameters of $a_p = 0.3886(1)$ nm for disordered $La_{0.5}Ba_{0.5}CoO_3$ and $a_p = 0.3885(1)$ nm for the nano-ordered $LaBaCo_2O_6$, respectively. However, a clear *hkl* dependent peak broadening can be detected in the case of the nanostructured $LaBaCo_2O_6$. The transmission electron microscopy and high resolution electron microscopy (HREM) images were carried out with a JEOL 2010F electron microscope. HREM observations at room temperature revealed that this sample is actually made of 90° oriented domains of ordered $LaBaCo_2O_6$ fitted into each other at a nanoscale level (Fig. 1). As observed by selected area electron diffraction on all $\langle 100 \rangle_p$ zone axis patterns, the Fourier transform (FT) of the area (inset of Fig. 1) indicates clearly the existence of two sets of supercell reflections 90° oriented and compatible with the $a_p \times a_p \times 2a_p$ supercell characteristic of the 112-type ordered structure.[8]

Temperature dependent zero field cooled (ZFC) and field cooled (FC) magnetization measurements were carried out with a superconducting quantum interference device magnetometer (MPMS Quantum Design) in an applied field of 100 Oe, as shown in Fig. 2. The curves exhibit a completely different magnetic behavior in the same applied field conditions. A sharp increase of the magnetization occurs in the FC

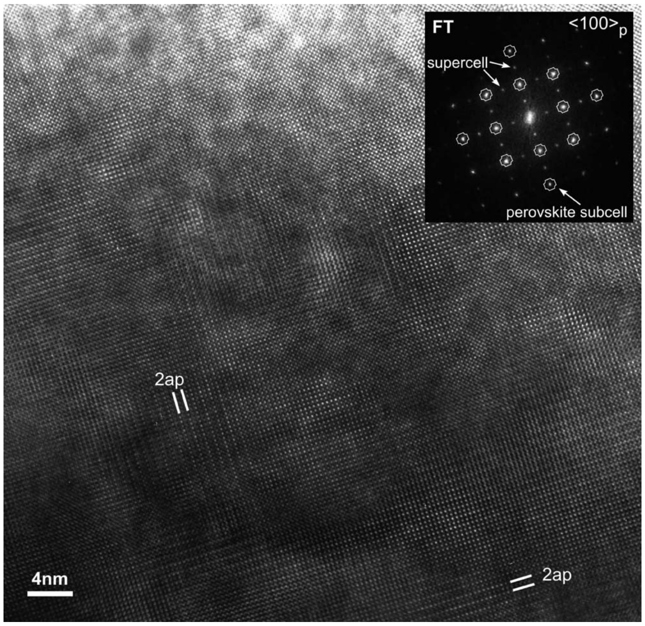

FIG. 1. HREM image corresponding to one of the perovskite {100} planes showing the nanostructurally ordered $LaBaCo_2O_6$ has 90° oriented domains in the 112-type ordered phase. The inset figure shows FT of the main figure and the strong reflections related to the perovskite subcell. Two supplementary sets of reflections are observed and related to the existence of 90° oriented domains having the $a_p \times 2a_p$ 112-type ordered structure.

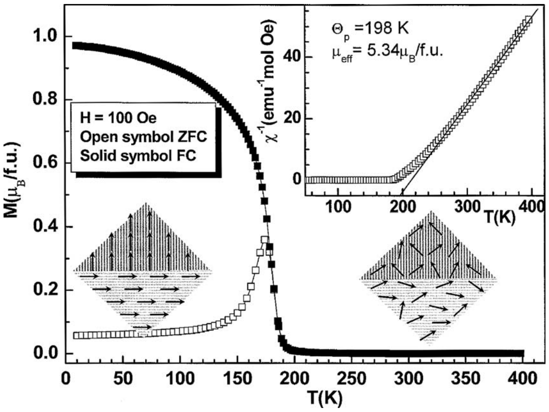

FIG. 2. Temperature dependence of ZFC (open symbol) and FC (solid symbol) magnetizations M of nanoscale ordered $LaBaCo_2O_6$ (H=100 Oe), and the schematic diagrams show the existence of magnetic spins in the 90° oriented nanodomains during ZFC (below and above T_C). The inset figure shows inverse susceptibility χ^{-1} vs temperature plot.

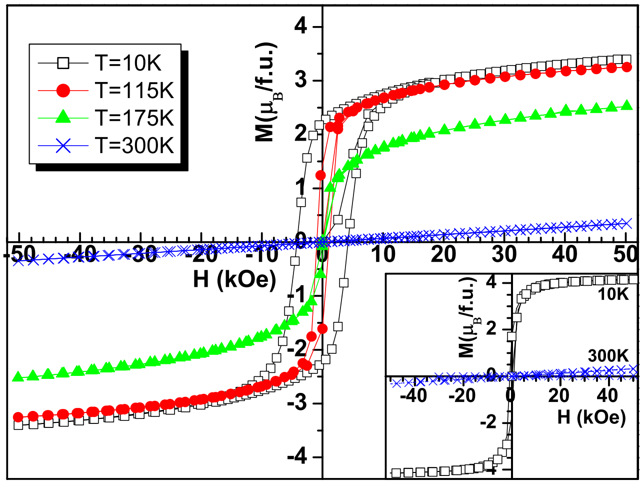

FIG. 3. (Color online) Field variation of magnetization $M(H)$ for nanoscale ordered $LaBaCo_2O_6$ at four different temperatures. The inset figure shows typical hysteresis curves at two different temperatures for completely disorder $La_{0.5}Ba_{0.5}CoO_3$ phase.

data around 179 K, indicating that the system is magnetically ordered and attains a spontaneous magnetization. With decreasing temperature, the magnetization value increases rather slowly but does not saturate. This behavior has been observed previously for both disordered and ordered phases[13,14] and suggests a competition between ferromagnetism and antiferromagnetism. The existence of long range FM ordering was indeed observed by neutron diffraction for the disordered phase $La_{0.5}Ba_{0.5}CoO_3$.[13] Just below the FM transition, T_C (179 K; calculated from the minimum position of the dM_{FC}/dT vs temperature plot), a strong irreversibility between the ZFC and FC data appears. The ZFC curve shows a sharp peak at T_C and below this, the magnetization value decreases rapidly to a lower value. By increasing the applied magnetic field (H=1 and 5 kOe, not shown), the peak in the ZFC curve broadens and shifts toward lower temperatures. The irreversible temperature between ZFC and FC T_{irr} also decreases for a lower field $T_{irr} \sim T_C$, whereas for higher applied fields $T_{irr} < T_C$ (e.g., $T_{irr} \sim 100$ K for H=5 kOe), a behavior similar to that of spin or cluster glass material.

The strong magnetic irreversibility of this nanostructured form is also supported by the field variation of isotherm magnetization $M(H)$ at four different temperatures (Fig. 3). A large hysteresis loop manifests at 10 K, with a remanent magnetization (M_r) value of $\sim 2.3\mu_B$/f.u. and a coercive field (H_C) of ~4.2 kOe. The highest value of the magnetic moment is only $\sim 3.4\mu_B$/f.u., which is less than the theoretical spin-only value of Co ions in HS state. At low temperature, the relatively higher value of H_C signifies a typical hard ferromagnet, and with increasing temperature, H_C decreases gradually. Finally, at temperatures higher than T_C, the $M(H)$ behavior is linear corresponding to a PM state. The obtained M_r and H_C values of this nanostructure ordered perovskite are much higher than those previously observed for the disordered perovskite $La_{0.5}Ba_{0.5}CoO_3$, i.e., $1.7\mu_B$/f.u. (to compare, we have calculated μ_B for 2 f.u.) and 0.8 kOe, respectively (inset of Fig. 3), as well as for the ordered perovskite $LaBaCo_2O_6$.[14] Nevertheless, the magnetic moment of the present perovskite is significantly smaller than that of the disordered form. Oriented domains have previously been observed in $GdBaCo_2O_{5.4}$ (Ref. 8) but not related to a different magnetic behavior due to the presence of 90° oriented domains as observed for this nanoscale ordered perovskite cobaltite.

Thus, the large divergence between the ZFC and FC magnetizations at low fields and the high coercivity can be explained in the scenario of short range FM ordering in 90° oriented nanostructured domains extended all over the material. During the ZFC magnetization, the magnetic spins will lock or freeze in the 90° oriented nanodomains. Therefore, at low temperature, the applied magnetic field is not sufficient to align the spins in its direction and it may be due to magnetostatic coupling. However, during the FC process, the spins are forced to align in the direction of the applied field at room temperature. Hence, ideally, there will be no disorderliness in the spin orientation below T_C as reflected in the observed value of a spontaneous magnetization. Due to this, a strong magnetic anisotropy appears in the ZFC and FC data, correlatively the pinning close to the boundaries of the nanodomains, will increase the H_C value.

To characterize the magnetic interaction in the PM region, we have plotted the inverse of magnetic susceptibility with the variation of temperature in the 75–400 K range (inset of Fig. 2). The data follow the Curie-Weiss behavior (for $T > 250$ K) and a linear fit to the Curie-Weiss law yields a PM Weiss temperature (θ_p) of ~198 K and an effective magnetic moment (μ_{eff}) of $\sim 5.34\mu_B/\text{f.u.}$ The obtained value of θ_p is higher than the T_C (179 K) value, and the positive value of θ_p is consistent with FM interactions in the high temperature region.

The FM transition temperature is close to that of the disordered and ordered phases, which was explained by positive double exchange interactions between Co^{3+} and Co^{4+} ions.[13,14] The low temperature FM phase is described by the latter authors as a cluster glass, but there is no supportive information. Therefore, we have studied this low temperature phase in detail to understand the nature of FM ordering or to establish the cluster glass behavior. The lack of magnetic saturation below the transition temperature may be due to short range FM ordering. This behavior is similar to the magnetically frustrated or glassy FM cobaltite reported in the literature.[15] This is supported by the $M(H)$ curve at higher fields (Fig. 3).

To establish this behavior, we have carried out ac susceptibility measurements below Curie temperature (T_C) at different frequencies. Figure 4 shows the in phase $\chi'(T)$ component of the magnetic ac susceptibility measured at four different frequencies. The $\chi'(T)$ data are similar to the low field ZFC magnetization curve, which shows a sharp peak around 179 K. A distinct peak appears corresponding to FM ordering, and, below this temperature, a weak frequency dependent behavior is observed and the out of phase component $\chi''(T)$ also confirms this feature (inset of Fig. 4). Below the peak position, the magnetization value decreases with an increase in frequency. The magnetic ac susceptibility behavior observed for nanostructure ordered $\text{LaBaCo}_2\text{O}_6$ is quite similar to glassy FM materials.[15]

Temperature dependence of electrical resistivity (ρ) in the presence (70 kOe) and absence (0 kOe) of applied magnetic field for our nanostructure ordered $\text{LaBaCo}_2\text{O}_6$ is shown in Fig. 5. The zero field resistivity curve shows a clear similarity with that of SrRuO_3 (Ref. 16) and $\text{SrRu}_{1-x}\text{M}_x\text{O}_3$ (Ref. 17) perovskites, attesting to the metallic behavior of these oxides in the PM as well as in the FM region. With a change in slope ($d\rho/dT$) at T_C, the resistivity decreases more rapidly. Similar to the ruthenates, one also observes an upturn in the resistivity at low temperature, i.e., below 35 K. This was explained in SrRuO_3 as a weak localization contribution associated with an electron-electron interaction,[18] whereas it was interpreted as a partial orbital ordering for the ordered $\text{LaBaCo}_2\text{O}_6$.[14] Another explanation is that it may be due to the grain boundary effects at the domain walls. Further investigations will be needed to understand this effect.

The material is FM and semimetallic below T_C as revealed from the magnetization and electrical resistivity results. The inset of Fig. 5 depicts the magnetic field dependence on isotherm resistivity behavior at four different temperatures (selected from the magnetic transitions). The MR is calculated as $\text{MR}(\%) = [\{\rho(7) - \rho(0)\}/\rho(0)] \times 100$, where $\rho(0)$ is the sample resistivity at 0 kOe and $\rho(7)$ in an applied field of 70 kOe. The highest value of MR is observed

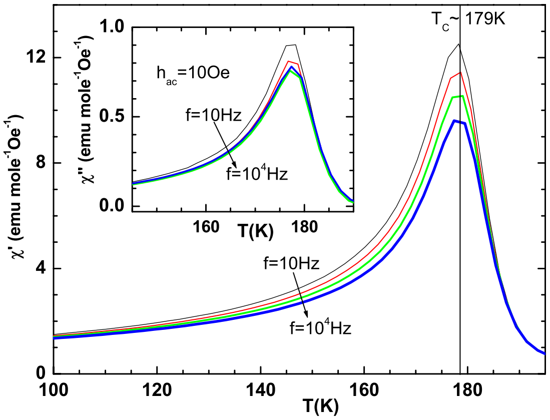

FIG. 4. (Color online) The temperature dependence in phase component of ac susceptibility χ' of nanoscale ordered $\text{LaBaCo}_2\text{O}_6$ at four different frequencies ($H_{\text{ac}} = 10$ Oe) and corresponding out of phase component $\chi''(T)$ data is shown in inset figure.

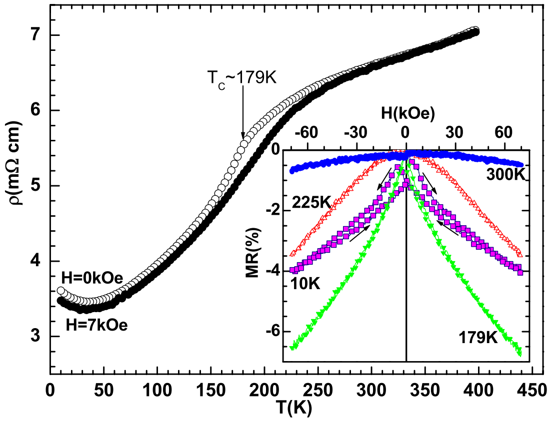

FIG. 5. (Color online) Temperature dependence of electrical resistivity ρ of nanoscale ordered $\text{LaBaCo}_2\text{O}_6$ in the presence (solid symbol) and absence (open symbol) of magnetic field (70 kOe). The inset figure shows magnetoresistance [(MR) (%)] at four different temperatures.

near T_C ($\sim$6.5%), similar to what is observed for the disordered phase $La_{0.5}Ba_{0.5}CoO_3$ by Fauth *et al.*[13] ($\sim$8%) and for the ordered phase $LaBaCo_2O_6$ by Nakajima *et al.*[14] ($\sim$7.5%). Such behavior is also similar to that observed for the ruthenates.[17] Nevertheless, the discrepancies between the results obtained by these two groups, about the MR values of the disordered phase, will require further investigations. Interestingly, the field dependent isotherm resistivity behavior at 10 K exhibits an anisotropic effect similar to those of magnetization behavior (see Fig. 3), also present in the 50 K isotherm resistivity data (not shown here). Also, near or above the FM transition, the irreversibility nature in the resistivity almost disappears. The low temperature isotherm MR data exhibit hysteresis effects, which resemble the "butterflylike" feature, MR being approximately isotropic for temperatures well above T_C (at 225 and 300 K). Hence, the butterflylike feature appears only at low temperatures (studied at 10 and 50 K) with a smaller value of MR compared to 179 K. The occurrences of anisotropic MR behavior nearly at similar temperatures as those for isotherm $M(H)$ studies suggest the strongly correlated nature of field-induced magnetic and electronic transitions.

In conclusion, the present study demonstrates a high magnetic anisotropy in the nanoscale ordered perovskite $LaBaCo_2O_6$, in contrast to the disordered and ordered phases.[13,14] Our results can be explained by the locking of the cobalt spins due to the existence of 90° oriented nanostructure domains. Both the enhanced bifurcation between the ZFC and FC magnetizations and the weak frequency dependence just below T_C indicate the glassy FM or cluster glass behavior, which signifies the competition between FM and antiferromagnetic (AFM) interactions. This suggests that the system is phase separated into large FM domains within the AFM matrix due to the presence of both Co^{3+} and Co^{4+} ions.[15] The unsaturated values of $M(H)$ measurements also support this assumption. The derived effective magnetic moment ($\sim 5.34\mu_B$/f.u.) from the experimental data corresponds to a situation where Co^{3+} and Co^{4+} are in LS and IS states, respectively. The obtained higher values of magnetic moment for the disordered phase compared to nanoscale ordered phase may be due to the crystal field splitting.

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