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Huge anisotropic magnetostriction in $La_{1-x}Sr_xCoO_{3-\delta}$ $(x \geq 0.3)$: Field-induced orbital instability

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Magnetostriction parallel and perpendicular to the applied magnetic field has been measured for $La_{1-x}Sr_xCoO_3$ $(x=0.3,\ 0.5)$ over a wide temperature range $(4.2 \leq T \leq 300$ K) and up to a maximum field of 14.2 T. We find a huge anisotropic magnetostriction (λ_t) with values as large as 2.2×10^{-3} for $x=0.3$ and 1×10^{-3} for $x=0.5$ at 14.2 T and temperatures below 100 K. The volume magnetostriction has been found to be negligible. The large value of λ_t cannot be explained on the basis of the usual spin-orbit-coupling contribution. We propose that such a huge anisotropic magnetostriction has its origin in the orbital instability of the trivalent Co ions under the magnetic field, giving rise to a transition from a nondegenerated low-spin state to an orbital degenerated intermediate-spin state.

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During the last few years there has been an upsurge of research activities on oxides due to the discovery of colossal magnetoresistance (CMR) in manganates $(R^{3+}_{1-x}A^{2+}_x MnO_3$, where R is a rare-earth ion and A is an alkaline ion).[1,2] However, among the perovskite oxides other than manganates only cobaltates $(R^{3+}_{1-x}A^{2+}_x CoO_3)$ have been found so far to show magnetoresistance exceeding 30%.[3–5] The hole doping (substitution of R^{3+} by A^{2+}) in the parent compounds $LaMnO_3$, as well as in $LaCoO_3$, creates mixed valence (in Mn and Co ions) and ferromagnetic metallic state for $x \geq 0.25$. However, these two systems are fundamentally different in many respects.[3–8] The magnetic behavior of the cobaltates is rather unusual. The insulating $LaCoO_3$ $(x=0)$ is diamagnetic below 90 K and paramagnetic above this temperature. Because of the comparable magnitude of the crystal field (Δ_{CEF}) and intra-atomic exchange (J_{ex}) energies, the Co^{3+} ions, which are predominantly in a low-spin (LS) configuration $(t^6_{2g},\ S=0$, diamagnetic state), transform into a high-spin (HS) configuration $(t^4_{2g}e^2_g,\ S=2$, paramagnetic state) (see Fig. 1).[6–9] It has also been proposed recently that the transition occurs from the LS state to an intermediate-spin (IS) state $(t^5_{2g}e^1_g,\ S=1)$, which lies closer in energy than the HS state (see Fig. 1).[10] Upon hole doping the compounds phase segregate into a hole poor (rich in LS-Co^{3+} state) matrix and hole rich regions.[6,7] For low doping levels $(x<0.2)$ the hole rich regions are magnetic clusters with predominantly HS-Co^{3+} $(t^4_{2g}e^2_g)$ and LS-Co^{4+} (t^5_{2g}). These ions interact ferromagnetically via superexchange or double exchange mechanisms.[6] For higher hole doping levels $(x>0.2)$ the Co^{3+} and CO^{4+} ions in intermediate spin configuration ($t^5_{2g}e^1_g$ and $t^4_{2g}e^1_g$, respectively)[7] and the HS-Co^{3+} ions are localized on the interface between the magnetic clusters and the matrix.[6] The ferromagnetism within the clusters is believed to be of itinerant electron type.[6,7] The antiferromagnetic interaction between high-spin ions on the surface of the clusters competes with the ferromagnetic interaction within the clusters. These competing interactions give rise to a spin-glass state for $x \leq 0.2$ and cluster-glass state for $0.25 \leq x \leq 0.5$.[6,8,9,11] Metallic conduction in these materials arises when the ferromagnetic clusters percolate electrically.

The unusual magnetic and magnetotransport properties of the cobaltates provoked us to study their magnetoelastic properties mainly because the change of the orbital state could dramatically influence the magnetoelastic deformation of the lattice. In this paper we will concentrate on the compositions $x=0.3$ and 0.5 which show thermal induced paramagnetic metal to cluster-glass metal transition. Nevertheless, for a comparison we have also measured the compounds $x=0$ and 0.8.

The $La_{1-x}Sr_xCoO_3$ samples $(x=0,0.08,0.3,0.5)$ were prepared by the citrate route to ensure more homogeneity. Stoichiometric amounts of La_2O_3, $SrCO_3$, and Co were dissolved in nitric acid together with citric acid and ethyleneglycol. The gel obtained after the solution evaporation was fired overnight at 800 °C in an oxygen current flow. The resulting powder was pressed into bar shape and sintered at 1000 °C in oxygen flow for 3 days with intermediate grindings. Oxygen content was determined by thermogravimetric analysis in a reducing atmosphere. Samples with $x=0$ and 0.08 resulted in stoichiometric oxygen while $x=0.3$ and 0.5 showed a slight oxygen deficiency $(\delta=0.05)$. The crystal structures of $x=0.3$ and 0.5 are rhombohedral and cubic, respectively.

We have measured resistivity and magnetoresistance in the temperature range $4.2 \leq T \leq 300$ K and in magnetic fields up to $H=12$ T using a superconducting solenoid. In the same temperature range we also measured the thermal expansion and magnetostriction using the strain gauge technique. Magnetostriction measurements were performed along two directions, parallel $(\lambda_\parallel)$ and perpendicular $(\lambda_\perp)$ to the field. We used pulsed fields up to 14.2 T within the temperature range 4–300 K.

In Fig. 2 we show the resistivities (ρ) of the $x=0.3$ and 0.5 samples. It should be noted that for $x=0.5$, ρ is two orders of magnitude lower than for $x=0.3$, due to the better electrical connectivity between the ferromagnetic metallic clusters. The maximum magnetoresistance (MR) values, found near T_c at 12 T, are 12% and 7.5% for $x=0.3$ and 0.5, respectively (not shown in the figure). These values are

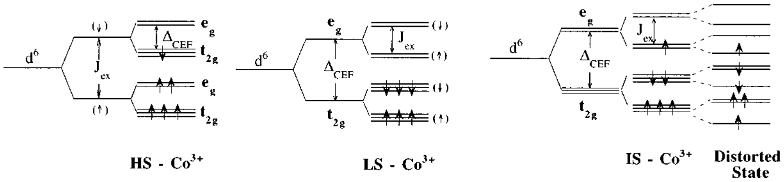

FIG. 1. Schematic diagram of the spin state of trivalent Co ions: (a) high-spin (HS) Co^{3+} ion with $J_{ex} \gg \Delta_{CEF}$, where J_{ex} is the intra-atomic exchange energy and Δ_{CEF} is the crystal field energy; (b) low-spin (LS) Co^{3+} ion ($\Delta_{CEF} \gg J_{ex}$); and (c) intermediate-spin (IS) Co^{3+} ion with Jahn-Teller distortion.

slightly higher than those previously reported for lower fields ($H<8$ T).[3–5] In the inset we show the thermal expansion coefficient, $\alpha[=1/T(dL/L)]$, for all the samples. The results obtained for $x=0$ and 0.8 are in good agreement with the earlier report,[9] based on neutron diffraction data. The large increase of α observed upon cooling in $LaCoO_3$ was associated with the LS-HS transition. As mentioned before, this transition has been interpreted recently as a LS-IS transition.[10] The Co ion in the IS state is a Jahn-Teller (JT) ion. However, the JT interaction is not cooperative, as suggested by the absence of any discontinuous change in the lattice parameters[9] and from infrared studies.[12] There is ambiguity in the literature about the existence of such a spontaneous spin-state transition in the hole-doped compositions. The coefficient α does not show any clear anomaly for $x>0$, which has been taken as the evidence for the absence of the spontaneous spin-state transition.[8]

The magnetostriction in the compounds with $x=0$ and $x=0.08$ was found to be negligible. Here we will report on the results obtained for the $x=0.3$ and 0.5 compositions, where large effects have been found. In Fig. 3 we illustrate the field dependence of the parallel ($\lambda_{\parallel}$) and perpendicular ($\lambda_{\perp}$) isotherms for $x=0.5$. As these $\lambda_{\parallel}$ and $\lambda_{\perp}$ magnetostrictions present opposite signs and display large values, a huge anisotropic magnetostriction ($\lambda_t \approx \lambda_{\parallel} - \lambda_{\perp}$) is obtained. To avoid complexity arising from the remanence and hysteresis showed by the magnetostriction isotherms the samples were heated above T_c (>250 K) before each new measurement. Only the data for the increasing strength of magnetic field are shown in this figure. The maximum volume magnetostriction ($\omega = \lambda_{\parallel} + 2\lambda_{\perp}$) for this composition is found near T_c ($\approx$250 K) and it is about -140×10^{-6} for $H=14.2$ T, which is one order of magnitude lower than found in manganates.[13] This finding suggests a very different nature of the magnetovolume effect in cobaltates compared to manganates. In the latter, the magnetostriction is isotropic ($\lambda_{\parallel} \approx \lambda_{\perp}$), and the large spontaneous or field induced magnetovolume effect observed was associated with the metal-insulator transition;[14] instead, the cobaltates retain their metallic behavior. On the following we will concentrate on the large anisotropic magnetoelastic effects that we have found in the cobaltates.

In Figs. 4(a) and 4(b) we show the anisotropic magnetostriction isotherms, λ_t, for $x=0.3$ and 0.5, respectively. As one can see, λ_t values obtained are huge (10^{-3} for $T \leqslant 100$ K), two orders of magnitude higher than those of ferromagnetic $3d$ oxides such as manganates[13] and $3d$ ferromagnetic metals.[15] Notice that λ_t does not show saturation even at a field as high as 14.2 T. This behavior is again different from ferromagnets, in which λ_t nearly saturates after the domain wall and domain rotation process are completed. It is also surprising that while the magnetic behavior[6,11] is typical of a ferromagnet, with sharp rise at low fields ($H<900$ Oe for $x=0.5$), λ_t shows only a gradual change from low to high field.

The largest anisotropic effects ever observed in magnetostriction are found in rare-earth intermetallics. For example, in $TbFe_2$, $\lambda_t \approx 4 \times 10^{-3}$ at $T=300$ K and $H=2.5$ T.[14] The origin for this magnetostriction is the large anisotropy of the $4f$ electronic charge cloud, which gives a large electric quadrupolar moment, and the strong spin-orbital coupling in relation to the crystal electric field (CEF) interaction. However, in most of the $3d$ oxides the lack of orbital degeneracy makes the orbital momentum negligible. As a consequence, the anisotropic magnetostriction is quite small, as happens in

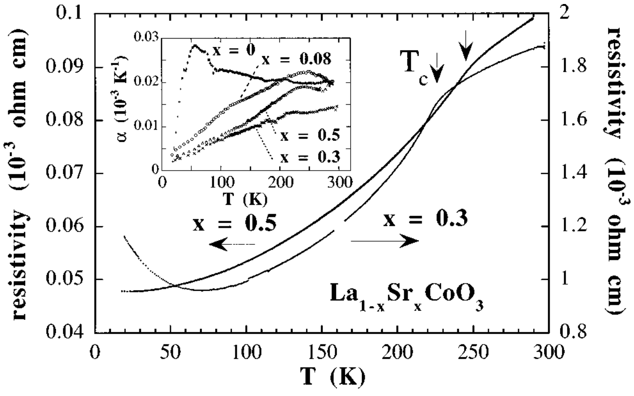

FIG. 2. Resistivity vs temperature for the $x=0.3$ and 0.5 compositions. The arrow indicates T_c. The inset shows the thermal dependence of the linear thermal expansion coefficient, α, for several compounds of the series $La_{1-x}Sr_xCoO_3$.

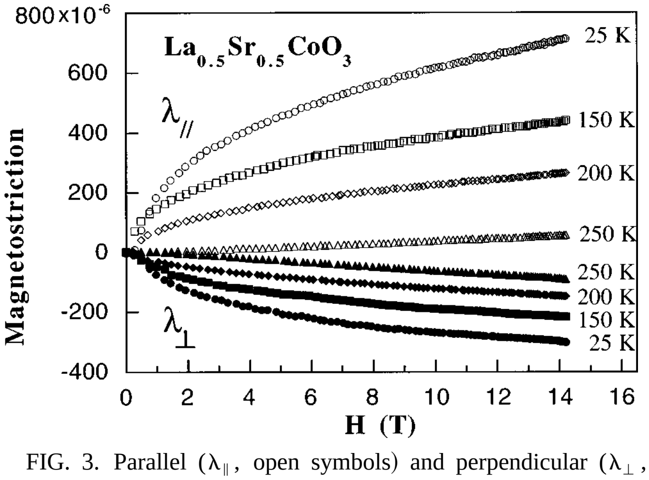

FIG. 3. Parallel ($\lambda_{\parallel}$, open symbols) and perpendicular ($\lambda_{\perp}$, closed symbols) magnetostriction isotherms of $La_{0.5}Sr_{0.5}CoO_3$ at selected temperatures.

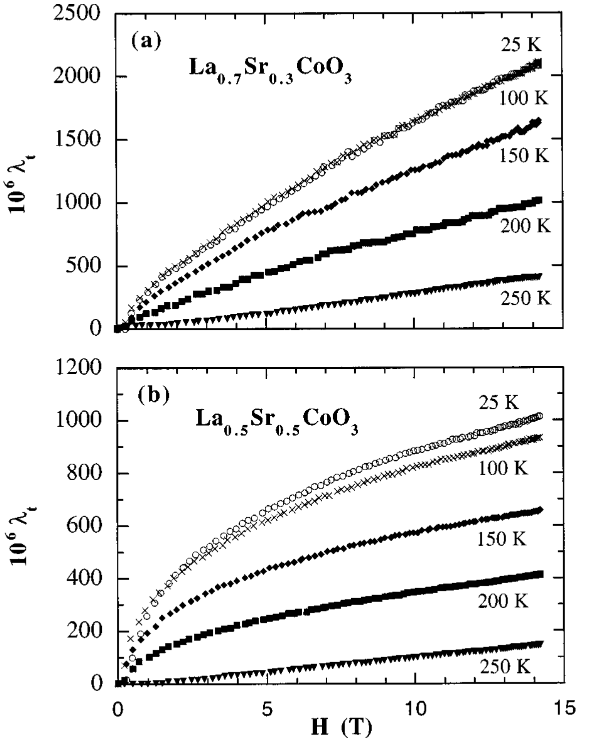

FIG. 4. Anisotropic magnetostriction (λ_t) isotherms in $La_{1-x}Sr_xCoO_3$ at selected temperatures: (a) $x=0.3$; (b) $x=0.5$.

manganites (in $La_{0.67}Ca_{0.33}MnO_3$, $\lambda_t \approx 60 \times 10^{-6}$ at 4 K). In view of this, we have to look for a different explanation to account for the large λ_t observed in cobaltates.

We suggest that a spin-state transition induced by the magnetic field is the cause of this large effect. The LS-Co^{3+} (t_{2g}^6) in the insulating matrix of the $x=0.3$ and 0.5 compositions has no orbital degeneracy and cannot give rise to the large value observed for λ_t. These LS ions are under the influence of the local magnetic field due to the ferromagnetic clusters and the externally applied magnetic field. As the external field increases, the magnetization within the clusters increases and hence the effective field at LS-Co^{3+} sites. This transforms the LS-Co^{3+} ion into the close energetic configuration of IS-Co^{3+}, which is a Jahn-Teller ion (see Fig. 1). Under JT distortion, the doubly degenerated e_g level of IS-Co^{3+} splits into two singlets ($L=0$), and the triplet t_{2g} into a singlet and a doublet ($L=1$). The singlet states of the t_{2g} level are occupied by two electrons with opposite spins and the doublet level by three electrons [see Fig. 1(c)]. Due to the degeneracy of the doublet level with nonzero angular momentum, a strong intra-atomic spin-orbit coupling is created which couples to the lattice strain to give rise to a large anisotropic magnetostriction. From our magnetostriction measurements we cannot elucidate whether the JT distortion induced by this field is cooperative or not. In the case of a completely nondegenerated orbital ground state ($L=0$), only a cooperative JT effect could produce a large λ_t. However, in the model proposed (see Fig. 1) the remaining orbital (t_{2g}) degeneracy can give rise to an orbital ordering by the field, due to the spin-orbit coupling. As we described above, we consider this effect as the main source of λ_t in the studied compounds.

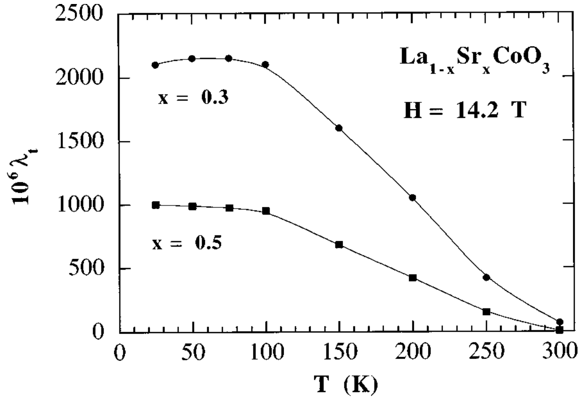

FIG. 5. Thermal dependence of the anisotropic magnetostriction at 14.2 T for the compounds $La_{1-x}Sr_xCoO_3$ ($x=0.3$ and 0.5).

A contribution to λ_t should also be expected to arise from the ferromagnetic clusters. However, due to the itinerant nature of the ferromagnetism in these clusters[6,7] this contribution is negligible. Nevertheless, these clusters play an important role in providing a large local magnetic field at LS-Co^{3+} ions. It should be mentioned that high-field magnetization measurements for the $x=0.5$ composition support the existence of an intercluster matrix in the intermediate-spin configuration.[6]

Figure 5 shows the temperature dependence of λ_t. The anisotropic magnetostriction is nearly constant below 100 K and decreases at a faster rate with increasing temperature. Such a temperature dependence can be explained with the proposed model due to the increasing population of the LS-CO^{3+} state, which is maximized below 100 K (the spontaneous spin-state transition temperature)[6] and hence the effect is larger. The field dependence above 250 K is similar to that of a paramagnet. From the above considerations we think that the plausible explanation for the large λ_t values observed is the field induced spin-state transition of the trivalent ions within the insulating matrix. The larger value of λ_t observed for lower strontium content (and hence the higher fraction of the LS-CO^{3+} matrix) also supports our hypothesis.

In conclusion, we have found a huge anisotropic magnetostriction in the cluster glass state cobaltates. We have explained this effect as arising from the field induced orbital instability as a consequence of the spin-state transition of trivalent Co ions in the intercluster matrix. The magnetostriction behavior of cobaltates is found to be different from that of the manganates, which suggests that the fundamental mechanism governing the magnetotransport properties is different in both systems.

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