

Ferromagnetism in LaCoO_3

J.-Q. Yan, J.-S. Zhou, and J. B. Goodenough

Texas Materials Institute, University of Texas at Austin, Austin, Texas 78712, USA

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A systematic investigation of the low-temperature magnetic properties of LaCoO_3 has demonstrated a ferromagnetism with $T_c \approx 85$ K from surface cobalt atoms. The experimental investigation involved comparison of the magnetic susceptibility of (1) a single crystal, (2) a powder ground from the same crystal, and (3) a cold-pressed pellet from the ground powder that was unannealed and annealed at 400 °C followed by a later anneal at 1000 °C. The low-temperature magnetic susceptibility was found to have three contributions: a Curie-Weiss paramagnetism, a thermally driven spin-state transition, and a surface-related ferromagnetism with $T_c \approx 85$ K. The ferromagnetic component has a remanence and coercivity at 5 K that increases dramatically with increasing surface/volume ratio of the different samples. The presence of the surface ferromagnetism explains the discrepancies of the low-temperature magnetic susceptibility reported by different groups. An anion coordination at surface Co(III) ions that differs from that of the bulk cobalt is shown to be capable of stabilizing higher spin states. A $T_c \approx 85$ K is argued to be too low for ferromagnetic coupling by oxidized clusters, and possible mechanisms for a ferromagnetic coupling between higher-spin Co(III) ions are discussed.

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INTRODUCTION

The rhombohedral ($R\bar{3}c$) perovskite LaCoO_3 undergoes an interesting evolution of its spin state with increasing temperature. Recent experiments have finally established that the bulk Co(III) ions are in their low-spin (LS) t^6e^0 ($S=0$) state at lowest temperatures, but change to a primarily intermediate-spin (IS) t^5e^1 ($S=1$) state in the interval $35 \text{ K} < T < 100 \text{ K}$ and then to a mixture of IS and high-spin (HS) t^4e^2 ($S=2$) states in the interval $300 \text{ K} < T < 600 \text{ K}$ before, at higher temperatures, undergoing a transition from localized e electrons to itinerant electrons in a narrow σ^* band of e -orbital parentage.¹⁻⁷ Nevertheless, all investigators have noted a Curie-Weiss paramagnetic component of unknown origin that persists to lowest temperatures. This component has been ascribed to impurities and to surface Co, but there has been no systematic investigation of its origin. In view of the universal observation of this component, it seems unlikely that it is due to substitutional impurities. Moreover, the suggestions concerning the origin of the low-temperature paramagnetism cannot persuasively explain the obvious inconsistency in reports of magnetic susceptibility in the interval $5 \text{ K} < T < 140 \text{ K}$. It has been observed that regrinding and refiring affects the low-temperature magnetic susceptibility of LaCoO_3 .^{8,9} However, the regrinding and refiring process cannot preclude a variation of oxygen stoichiometry or a change in the La/Co ratio due to the evaporation of Co ions when firing at high temperatures. Since we were in possession of a single crystal and have also observed that cold-pressed samples are cracked so as to create a large surface area that is removed only by annealing at higher temperatures, we have studied the low-temperature susceptibilities of (1) a single crystal, (2) a powder ground from the crystal, and (3) a cold-pressed pellet from the ground powder before and after annealing at 400 °C and 1000 °C. These varied treatments provided samples of widely different surface areas per unit volume and therefore allowed probing the influ-

ence of the surface on the low-temperature susceptibility.

Another related question that needs to be clarified is the origin of a nonlinear M - H curve and hysteresis loop first found by Menyuk *et al.*¹⁰ in both precipitated powder and a ground single crystal in view of the absence of any long-range magnetic order of the bulk LS Co(III). Menyuk *et al.* concluded they were observing isolated ferromagnetic regions dispersed in a nonmagnetic matrix, but the nature of the ferromagnetic phase was not identified. Androulakis *et al.*¹¹ reported two ferromagnetic phases, one with a $T_c < 10 \text{ K}$ and the other with $20 \text{ K} < T_c < 100 \text{ K}$ that they suggested were caused by the presence of Co(IV) ions associated with La^{3+} -ion vacancies.

In this paper, we report a temperature dependence of the magnetic susceptibility below 150 K that contains contributions from three sources: (1) the thermally activated LS to IS transition in the interval $35 \text{ K} < T < 150 \text{ K}$, (2) a ferromagnetic phase having a Curie temperature $T_c \approx 85 \text{ K}$ detected at low magnetic fields, and (3) the universally observed low-temperature Curie-Weiss paramagnetism. We argue that surface Co(III) ions retain a higher spin state, most probably an IS state. Possible mechanisms responsible for the observed ferromagnetism are discussed.

EXPERIMENTAL PROCEDURE AND RESULTS

A LaCoO_3 single crystal was grown by the floating-zone method in an IR image furnace as reported elsewhere.⁶ A part of the as-grown single crystal was ground into a fine powder, and then a part of the powder was cold pressed (CP) into a dense, 3 mm diameter pellet 1 mm thick by a technique reported elsewhere.¹² The particles of a CP sample are cracked, introducing more surface area; but a high-temperature anneal heals the cracks and yields a dense polycrystalline sample having transport properties of an isotropic material that are nearly equivalent to those of a single crystal.

Since the same bulk single crystal was used to prepare all three samples, any differences between the low-temperature

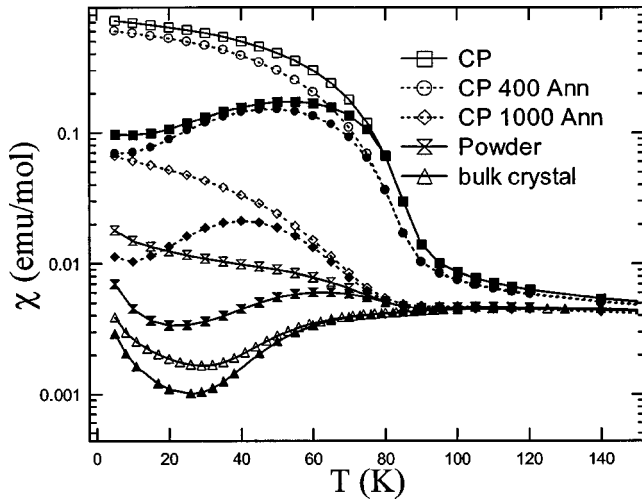


FIG. 1. Temperature dependence of magnetic susceptibility of LaCoO_3 single crystal (24 mg, bulk crystal), ground powder (powder), unannealed CP pellet (CP), and CP pellet annealed at 400°C (CP 400 Ann) and 1000°C (CP 1000 Ann) measured at 500 Oe in zero-field-cooled (ZFC, solid) and field-cooling (FC, open) modes.

magnetic susceptibilities of the three samples cannot be attributed to substitutional impurities, but they could reflect the spin state of surface cobalt because of the large difference in the surface/volume ratio of the samples. Moreover, x-ray powder diffraction did not reveal the appearance of any phase other than LaCoO_3 although the peaks of the CP sample were clearly broadened compared to those of the ground powder. This peak broadening indicates the smaller particle size of the CP pellet and possible residual strains in the CP sample. To eliminate any influence of internal strains resulting from the CP process, the powder and the CP pellet were annealed at 400°C for 15 h in flowing oxygen; at this temperature, little if any sintering occurs.

The temperature dependence of the magnetic susceptibility $\chi(T)$ of the single crystal was first compared to that of the ground powder and the CP pellet; a $\chi(T)$ curve of the CP pellet was then taken after the 400°C and 15 h anneal and after the 1000°C and 4 h anneal. The data were taken with a SQUID magnetometer (Quantum Design) from 5 K to 320 K in a field of 500 Oe in both field cooled (FC) and zero-field-cooled (ZFC) modes. Above 140 K, the $\chi(T)$ curves of all samples have the same magnitude and temperature dependence and were similar to those reported in the literature; below 140 K, the $\chi(T)$ curves differed significantly from one another as is shown in Fig. 1.

Four features of Fig. 1 are to be noted: (1) the single-crystal data exhibit a minimum susceptibility χ_{\min} at a temperature $T_{\min} \approx 26$ K and a divergence of the FC and ZFC curves below 70 K. The sharp decrease of $\chi(T)$ on cooling in the interval $T_{\min} < T < 80$ K (note logarithmic scale) reflects the transition from IS to LS Co(III) in the crystal bulk. (2) The ground powder, on the other hand, shows a divergence of the FC and ZFC curves below 85 K; the ZFC curve has a lower T_{\min} and a χ_{\min} four times larger than that of the single

crystal while the FC curve shows evidence of a weak ferromagnetism setting in below 85 K. The curve changed little after a 400°C anneal. (3) The CP pellet shows a much stronger ferromagnetic response of the FC curve and the ZFC curve has a T_{\min} shifted to 0 K; the ferromagnetic Curie temperature is $T_c \approx 85$ K. The magnitude of the ZFC $\chi(5$ K) jumps to 97×10^{-3} emu/mol compared with 2.51×10^{-3} emu/mol for the single crystal and 6.93×10^{-3} emu/mol for the powder. The anneal at 400°C changed the FC and ZFC by a minimal amount. (4) After the anneal at 1000°C , the magnitude of the ferromagnetic component was sharply decreased for the CP pellet. The thermoelectric power of the annealed sample $\alpha \approx 350 \mu\text{V/K}$ is close to that for the single crystal at room temperature; any change of the bulk oxygen content as a result of grinding into a powder, forming a CP pellet, and subjecting to anneals at 400°C and 1000°C is negligible. Therefore, we may conclude that the dramatic change in $\chi(T)$ below 85 K of the CP pellet before and after the 1000°C anneal reflects a change in the surface/volume ratio of the sample.

To confirm this conclusion, SEM photographs of the several samples were taken and compared. Figure 2 presents the surface images of the CP pellet after an anneal at 400°C (a) and (b) and at 1000°C (c) and (d). The irregular grain size of the CP pellet annealed at 400°C does not change noticeably from that of the unannealed CP pellets and is similar to the particle size of ground powders. However, many microcracks [see Fig. 2(b)] can be seen in some large individual particles in the CP pellet; these microcracks are not present in the particles of the ground powders and they were not significantly removed from the CP pellet annealed at 400°C . These microcracks increase greatly the surface/volume ratio of the CP pellet. After annealing at 1000°C , the microcracks are removed and grain connectivity was observed [see Fig. 2(c) and 2(d)]. A reduction in surface/volume ratio is clearly evident. Another direct evidence for surface involvement in the ferromagnetism is the dependence of $\chi(T)$ on the size of the single crystal. As shown in Fig. 3, the larger the size of the crystal, the smaller the χ_{\min} .

To demonstrate the existence of a ferromagnetic component in the $\chi(T)$ curve, M - H hysteresis loops were taken at 5 K over the range $-5 \text{ T} < H < 5 \text{ T}$; they are displayed in Fig. 4. They illustrate a dramatic increase in the remanence, M_r , and coercivity, H_c , with increasing surface/volume ratio. Saturation of the magnetization has not been reached in any of the samples, which signals a paramagnetic contribution from the bulk in addition to the presence of ferromagnetic regions on the surface. It is noticed that $M(5 \text{ K}, 5 \text{ T}) = 0.20 \mu_B/\text{f.u.}$ for the CP pellet is about 20 times that of the bulk single crystal, which is also direct evidence for the creation of more localized spins with increasing surface/volume ratio. After the anneal at 1000°C , the M - H curve of the CP pellet became like that of the ground powder.

Figure 5 shows FC and ZFC $\chi(T)$ curves for a 24 mg single crystal measured with different applied magnetic field strengths H . The separation between the FC and ZFC curves below 85 K decreases and the magnitude of χ_{\min} drops as H

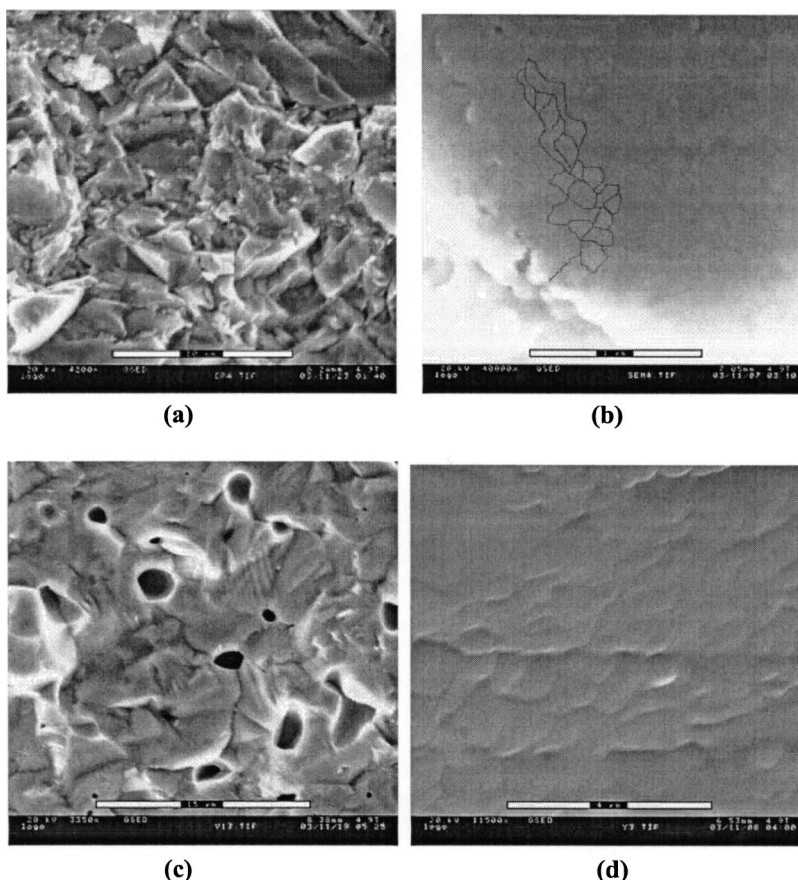


FIG. 2. SEM photograph for CP pellet annealed at 400 °C for 15 h (a) and (b) and at 1000 °C for 4 h (c) and (d). Curves in (b) highlight the microcracks.

increases; the FC and ZFC curves for $H > 1 \text{ T}$ (not shown) overlap over the entire interval $5 \text{ K} < T < 300 \text{ K}$. Below 120 K, three contributions to $\chi(T)$ can be identified as

$$\chi(T) = \chi_{\text{para}} + \chi_{\text{sst}} + M/H, \tag{1}$$

where χ_{para} is a Curie-Weiss paramagnetism, χ_{sst} is from the well-studied LS to IS transition on the bulk Co(III) ions, and M is a field-dependent magnetization of the ferromagnetic regions having a Curie temperature $T_c \approx 85 \text{ K}$ and a temperature dependence described by the Brillouin function. The first two terms of Eq. (1) are field-independent whereas the third term saturates at high fields. Since the divergence of the ZFC and FC curves is caused by the third term, it is expected that the FC and ZFC curves overlap at sufficiently high magnetic field. In low enough fields, the ferromagnetic contribution is comparable with χ_{para} and χ_{sst} or may even be dominant where the surface/volume ratio is large.

DISCUSSION

Our experiments have clearly identified the existence of unpaired localized spins at the surface of LaCoO_3 particles and a ferromagnetic coupling to give ferromagnetic surface regions with a $T_c \approx 85 \text{ K}$. Both the magnitude and the temperature dependence of $\chi(T)$ depend on the surface/volume ratio of the sample and the applied magnetic field, which can well account for the discrepancies in the reported low-temperature $\chi(T)$ behavior of LaCoO_3 .

The spin state in LaCoO_3 is determined by the competition between the crystal field splitting energy Δ_c and the

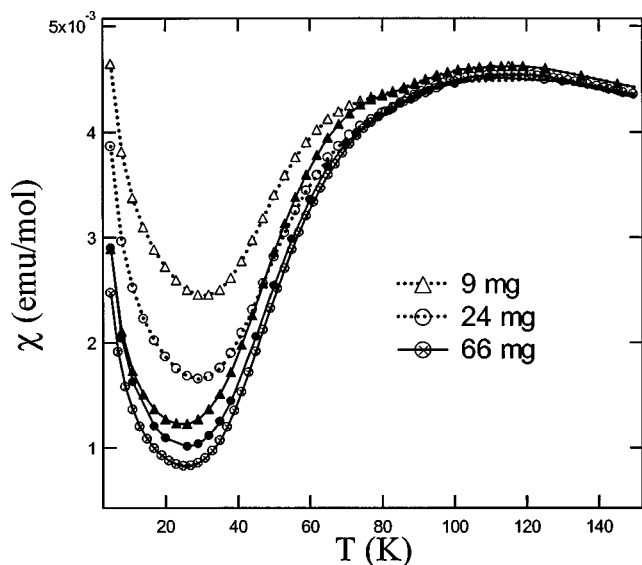


FIG. 3. The temperature dependence of magnetic susceptibility of LaCoO_3 bulk single crystals with different sizes measured at 500 Oe in ZFC (solid curve) and FC (dashed curve) mode. No FC mode was measured for the 66 mg sample.

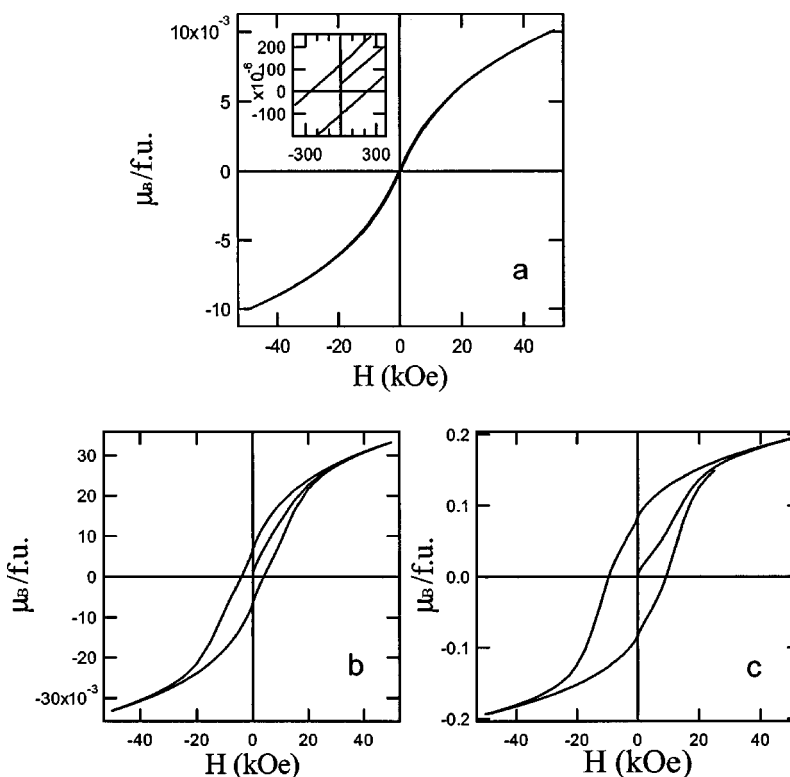


FIG. 4. M - H hysteresis loops at $T=5$ K of (a) bulk single crystal, (b) ground powder, and (c) CP pellet. Inset in (a) highlights the low remanence and coercivity for bulk single crystal (24 mg).

Hund exchange energy Δ_{ex} . In the bulk, a small $(\Delta_c - \Delta_{ex}) > 0$ stabilizes the LS state as the ground state at low temperatures. The spin-state transition can be induced not only by thermal energies of the order of a few meV, but also by any structural or chemistry change that influences the balance between Δ_c and Δ_{ex} . It has been predicted¹³ and verified later by experiment⁶ that the substitution of La by other rare-

earth ions with smaller radius will stabilize the LS state to higher temperatures because chemical pressure increases Δ_c . A fivefold-coordinated Co(III) ion on an ideal surface has a smaller Δ_c than an octahedrally coordinated bulk Co(III) ion, which stabilizes higher spin states even at the lowest temperatures.¹⁴

Fivefold, square-pyramidal oxygen coordination introduces a tetragonal site symmetry that favors the IS state since it removes the e -orbital degeneracy of that state. $\text{RBaCo}_2\text{O}_{5.5}$ is an oxygen-deficient perovskite with rare-earth R^{3+} and Ba^{2+} ions ordered into alternate (001) planes; the oxygen of the R^{3+} planes are removed, which stabilizes IS or HS Co(III) in square-pyramidal sites.¹⁵

With large surface/volume ratio, LaCoO_3 could lower the surface energy by either surface reconstruction or by adsorption of oxygen or moisture. Although a reconstruction of low-index surface of LaCoO_3 has been estimated to give a 76% reduction of the surface energy,¹⁶ oxides normally adsorb water at the surface oxygen vacancies; this bound water is present as surface hydroxyl anions OH^- . Oxide surfaces exposed to the atmosphere adsorb H_2O and/or O_2 to lower their surface energy. Bound water that releases a proton to a neighbor O^{2-} ion creates two surface OH^- ions without changing the valence state of the Co(III) ions. If H_2O from the air is chemically adsorbed on the surface, some surface Co(III) are coordinated with five oxygen and one OH^- ion. This coordination is similar to that in $\text{Sr}_2\text{CoO}_3\text{Cl}$ where IS or HS Co(III) ions are coordinated by five oxygen and one Cl^- ion.¹⁷ Therefore, the adsorption of H_2O can be expected to double the concentration of surface Co(III) ions in a higher spin state without changing the valence state of co-

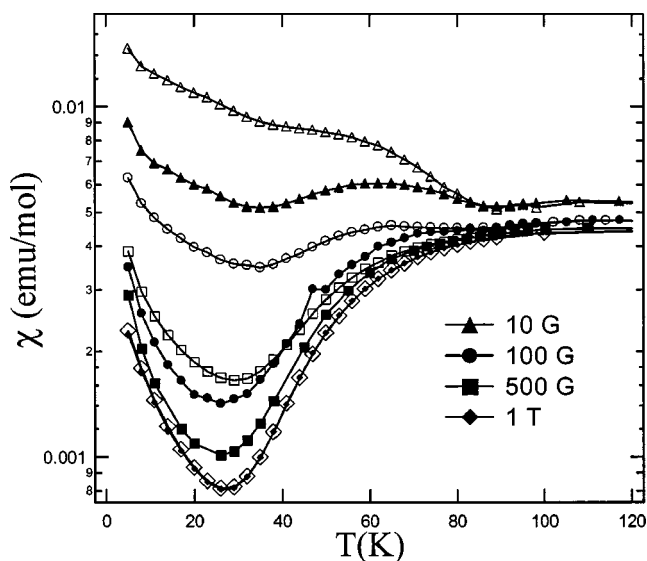


FIG. 5. Temperature dependence of magnetic susceptibility of bulk single crystal (24 mg) in ZFC (solid) and FC (open) modes at different magnetic fields.

balt. On the contrary, the chemical adsorption of an oxygen atom at a fivefold coordinated site would oxidize the surface cobalt to Co(IV) t^5e^0 with $S=1/2$. Therefore, some localized spins could be stabilized on the surfaces of LaCoO₃ no matter whether the surfaces are ideal or adsorb moisture and/or oxygen.

Given the presence of localized surface spins, we must next consider the possible magnetic couplings that can lead to a surface ferromagnetism. The LS Co(III): t^6e^0 ions with $S=0$ are diamagnetic. In lightly Sr-doped LaCoO₃, LS Co(IV): t^5e^0 ions with $S=1/2$ are known to create ferromagnetic clusters having IS cobalt configurations $t^5\sigma^{*n}(n < 1)$ in which the e electrons are no longer localized, but occupy molecular σ^* orbitals of e -orbital parentage; these magnetic clusters have a $T_c \approx 220$ K.¹⁸ Although oxidation of Co(III) to Co(IV) at the surface by adsorption of O₂ could explain the observed ferromagnetism by the double exchange interaction in $t^5\sigma^{*n}(n < 1)$ clusters, a $T_c \approx 85$ K seems too low to match this mechanism. Nevertheless, in order to find the evidence of surface oxidation, we ground pieces of single crystal in flowing O₂, flowing wet Ar, and in air, respectively, into fine powders with similar particle size and distribution; the magnetic susceptibility was measured immediately after grinding. The $\chi(T)$ of all three samples showed a similar temperature dependence, although the magnitude varied somewhat due to different particle size and distribution. This result argues against the oxidation of surface Co(III) to Co(IV) to give the observed ferromagnetism. Moreover, the unchanged thermopower of the CP pellet after annealing at 1000 °C for 4 h casts further doubt on the double exchange mechanism as the origin of the observed ferromagnetism.

Given a large cluster of surface cobalt ions having IS Co(III), the ferromagnetism could be induced by a vibronic e^1-O-e^0 superexchange between IS Co(III), but this coupling requires a dynamic Jahn-Teller distortion. Alternatively,

a static Jahn-Teller orbital ordering like that in the (001) planes of LaMnO₃ at neighboring IS Co(III) on the two-dimensional surface could give ferromagnetic e^1-O-e^0 interactions. Although antiferromagnetic ordering between surface HS Co(III) could give a weak canted-spin ferromagnetic moment, a sufficiently large magnetization observed makes this alternative less likely. However, our data do not provide an unambiguous distinction between these three alternatives.

CONCLUSIONS

Our experiments unambiguously demonstrate the presence of localized spins on the surface of LaCoO₃ particles and a ferromagnetism with $T_c \approx 85$ K. The ferromagnetism becomes observable if an applied magnetic field is small; it is enhanced as the surface/volume ratio of the sample increases. The surface ferromagnetism contributes to the low-temperature susceptibility in addition to the universally observed low-temperature Curie-Weiss paramagnetism and the paramagnetism due to the thermally driven spin-state transition. The ferromagnetic component from the surface states explains the discrepancies in different reports of the low-temperature magnetic susceptibility for LaCoO₃. A reduced oxygen coordination of the surface cobalt ions is responsible for the higher spin state of the surface cobalt even in the presence of bound water. Further experiments are needed to identify the magnetic coupling responsible for the surface ferromagnetism.

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