Ferromagnetic and antiferromagnetic interactions in lanthanum cobalt oxide at low temperatures

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Systematic dc and ac magnetic susceptibility studies have been performed on single-phase $LaCoO_3$ powder samples. Evidence is presented in support of the existence of ferromagnetic (FM1, FM2) and antiferromagnetic (AFM) interactions at low temperatures. FM1 and FM2 are ferromagnetic interactions that occur at different temperature regimes and their proposed origin is different. Specifically, FM1 interactions are observed at very low temperatures ($T<10$ K) and are attributed to superexchange interactions of the type Co^{IV}-O-Co^{s} (where $s=iii$ or $3+$). FM2 interactions are observed for $20<T<100$ K and are attributed to coupling of localized moments on Co^{IV} sites through RKKY interactions. The weak AFM interactions set in at $T\sim28$ K are attributed to the strong electron correlations in the system. The existence of the weak AFM may constitute evidence in support of the proposal that this system is a Mott-Hubbard insulator. The fact that the onset temperature of AFM is different from that of the metal-to-insulator transition is attributed to the presence of magnetic impurities (Co^{IV}). The existence of Co^{IV} is based on the results of iodometric titrations, and attributed to La vacancies. A consistent qualitative explanation is provided for available magnetic and transport data.

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I. INTRODUCTION

$LaCoO_3$ is a strongly correlated *p*-type semiconductor and exhibits a metal-to-insulator (MI) transition around $T\sim500$ K. [1–3] Moreover, it has interesting magnetic properties, one of which is its unusual, temperature-dependent magnetic susceptibility $\chi(T)$.[4–6]

It is interesting to point out that nearly all dc susceptibility measurements reported to date refer to an applied field of $H=1$ T.[7–9] These measurements have revealed that the magnetic susceptibility of $LaCoO_3$ exhibits a minimum at ~35 K and rises drastically at lower temperatures. This behavior has been observed for all types of samples studied to date, either polycrystalline powders or single crystals, and has been mainly attributed to the existence of paramagnetic impurities in the samples. The susceptibility increases abruptly above 35 K and exhibits a broad maximum around 90 K. At higher temperatures, χ exhibits a Curie-Weiss-like behavior for $T<400$ K and $T>600$ K, while in the temperature interval $400<T<600$ K, χ remains nearly constant.

Early neutron diffraction studies on polycrystalline $LaCoO_3$ samples have found no long-range magnetic order down to 4 K,[10–12] and inferred that the broad susceptibility peak at ~90 K cannot represent the onset of antiferromagnetic (AFM) order. This peak has been instead attributed to a thermally activated spin transition.[4,6] Specifically, Raccah and Goodenough[6] have originally suggested that all trivalent Co ions in $LaCoO_3$ are in the low-spin nonmagnetic ground state (LS, Co^{III}:$t_{2g}^6e_g^0$,$S=0$), and that thermal population of the high-spin state (HS, Co^{3+}:$t_{2g}^4e_g^2$,$S=2$) occurs with increasing temperature. Several recent spectroscopic studies have attempted to shed light on the puzzle of the 90 and 500 K transitions in $LaCoO_3$ without particular success since their conclusions are contradictory.[13–19] Nevertheless, the majority of new studies point towards the scheme LS→IS →(IS,HS) with rising temperature. (IS is Co^{iii}:$t_{2g}^5e_g^1$,$S=1$ intermediate spin state.) In particular, the first spin transition at ~90 K has been suggested to be from LS to IS and the second, at 500 K, from IS to a mixed state of IS and HS.

Recent polarized neutron scattering measurements on a $LaCoO_3$ ingot consisting of several large single crystals (10–700 K) have demonstrated that the paramagnetic scattering is almost zero at 10 K for the reciprocal lattice point (1.07, 0, 0).[13,14] Additionally, ^{59}Co and ^{159}La Knight shifts are temperature independent below ~30 K.[20] These results from both the neutron diffraction and NMR studies have been considered as strong evidence for the proposed nonmagnetic ground state of $LaCoO_3$. However, we should point out that there are other studies which conclude that the ground state is magnetic; e.g., Heikes *et al.* have interpreted their magnetic susceptibility and transport data by proposing a model with an IS state, with $S=1$ as the ground state of $LaCoO_3$.[1]

Korotin *et al.* have performed band-structure calculations using the local density approximation (LDA)+U method, which is a generalization of the local density approximation, and have found that the IS configuration has a lower excitation energy than the HS configuration.[21] These LDA+U calculations have also pointed out that the IS state should be metallic in variance to transport measurements. In order to explain the semiconducting nature of $LaCoO_3$, it has been proposed that the IS state develops orbital ordering due to the strong Jahn-Teller nature of the $t_{2g}^5e_g^1$ configuration which leads to an energy gap of ~2 eV. It is, according to these authors, the loss of orbital ordering that allows the broad e_g bands to cross the Fermi level and $LaCoO_3$ to become metallic at ~500 K. Generalized-gradient-corrected, density functional calculations using the supercell approach and the virtual crystal approximation have failed to predict a narrow-band-gap semiconducting behavior for $LaCoO_3$, and metallic behavior has been suggested.[22] Sarma *et al.* have proposed that, according to their band-structure calculations using the local spin density approximation (LSDA), $LaCoO_3$ shows a semimetallic nature with a direct gap of 0.04 eV.[23] It

is evident that, despite the numerous theoretical as well as experimental studies, the electronic structure of $LaCoO_3$ still remains debatable.

In a recent study, Tokura *et al.* have investigated the MI transition of $LaCoO_3$ by optical conductivity and transport measurements.[24] They report that the MI transition is characterized by a large energy-scale change of the electronic structure and a steep increase of the carrier density due to the closing of the charge gap. These features have been identified as characteristic of the Mott transition in strongly correlated electron systems.

Another challenging question evoked through numerous magnetic studies reported on $LaCoO_3$ is the existence of either long- or short-range magnetic order.[10–12] As has been mentioned, early neutron diffraction studies down to 4 K have excluded the possibility of long-range magnetic order. The polarized neutron measurements by Asai *et al.*, however, have revealed that the Q dependence of the magnetic scattering at 295 K exhibits a broad peak around (1, 0, 0), indicating a weak ferromagnetic correlation in the oxide.[14] It has been suggested that this weak ferromagnetic correlation in $LaCoO_3$ is due to short-range ferromagnetic interactions between neighboring high-spin Co^{3+} ions. Menuyk *et al.* have observed a hysteresis in the magnetization of $LaCoO_3$ at 1.9 K and suggested the existence of a small ferromagnetic component in this oxide.[11] They proposed that the remanent moment in $LaCoO_3$ is due to isolated regions of a magnetic phase dispersed in a nonmagnetic matrix and that the variation in the size and number of these regions is the cause of the discrepancies observed in the magnetic properties between different $LaCoO_3$ samples.

All recent neutron studies have been performed on ingots consisting of several large single crystals. However, such studies are not ideal for exploring the whole reciprocal lattice and, therefore, it is possible that they have missed the existence of short- or long-range magnetic order in $LaCoO_3$. It is worth noting that an early low-temperature neutron diffraction study by Menuyk *et al.* on powder samples revealed the existence of three magnetic peaks at low angles that were not identified.[11] Furthermore, there is no systematic study of either the dc susceptibility dependence on the magnetic field or the ac susceptibility dependence on temperature, magnetic field, and frequency, which could elucidate the magnetic properties of $LaCoO_3$ especially at low temperatures ($T < 100$ K). (We remind the reader that most of the reported magnetic data are taken at $H = 1$ T.) In addition, there is no complete study that addresses the question of the occurrence of any type of magnetic order in $LaCoO_3$ at low temperatures. Finally, there has not been given a definite explanation for the reported ubiquitous upturn in the dc susceptibility at very low temperatures ($T < 35$ K).

In this paper, a systematic study of the low-temperature magnetic properties of single-phase $LaCoO_3$ powder samples is presented. The origin and type of the earlier reported paramagnetic impurities, as well as their correlation to the magnetic and transport properties of the system, are examined. Concrete evidence is provided that establishes ferromagnetic (FM) and AFM interactions in $LaCoO_3$. A simple picture is suggested, which gives a qualitative explanation for the available magnetic and transport data on $LaCoO_3$.

II. EXPERIMENTAL PROCEDURE

$LaCoO_3$ powder samples were prepared by a coprecipitation method, using $La(NO_3)_3 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ as starting materials. The nitrates were first dissolved in water; coprecipitation of mixed lanthanum and cobalt hydroxides was achieved by adding aqueous NaOH solution as a precipitating agent keeping pH$\sim$11. The precipitates were carefully washed, dried, and finally decomposed at 1073 K. The precursor powders obtained were subsequently heated in air at 1273 K for 30 h, and cooled down slowly to room temperature (1 K/min).

The samples were characterized by x-ray powder diffraction using a Siemens D 500-diffractometer with Cu $K\alpha$ radiation and by differential optical reflectivity. There was no evidence for any impurity phase within the experimental error of both techniques used. Iodometric titrations were carried out to determine the trivalent Co concetration: the samples were dissolved in a concentrated HCl solution and the clorine produced was transferred via nitrogen gas into an acidified KI solution; the I_2 generated was then titrated against a standard 0.105N solution of sodium thiosulphate. The iodometric titrations have shown that the concentration of the trivalent Co in the samples is $\geqslant$100.9%.

The magnetic measurements were performed using a MagLab Exa susceptometer by Oxford Instruments. The dc magnetization was measured in the temperature range $1.8 \leqslant T \leqslant 300$ K and at several magnetic fields up to 7 T. The real and imaginary components χ' and χ'' of the ac susceptibility were measured as a function of temperature ($1.8 \leqslant T \leqslant 300$ K), dc magnetic field ($0 \leqslant T \leqslant 7$ T), and frequency ($100 \leqslant f \leqslant 10^4$ Hz). Data shown were collected on warming after zero-field cooling (ZFC) of the samples, unless otherwise indicated.

III. RESULTS

A. dc magnetization

The temperature dependence of the dc susceptibility χ of $LaCoO_3$ at several magnetic fields, ranging from 0.04 to 7 T, is depicted in Fig. 1. It is observed that $\chi(T)$ shows a strong field dependence for $T < 100$ K which indicates the possible existence of ferromagnetic interactions in $LaCoO_3$.

For $H = 0.04$ T, χ shows a minimum (χ_{min}) at $T_{min} \sim 16$ K. The position of χ_{min} shifts to higher temperatures with increasing magnetic field and reaches $\sim$35 K for $H = 1$ T. For higher magnetic fields, χ_{min} moves to lower temperatures and reaches $\sim$30 K for $H = 7$ T. At temperatures below T_{min}, χ increases abruptly with decreasing temperature for $H \leqslant 1$ T; however, χ rises slightly for $H = 5$ T, and remains almost constant for $H = 7$ T in accordance with the Knight shift data of Ref. 20. It seems that at very low temperatures ($T < 10$ K) there exist ferromagnetic interactions in $LaCoO_3$ which are suppressed by the application of high magnetic fields.

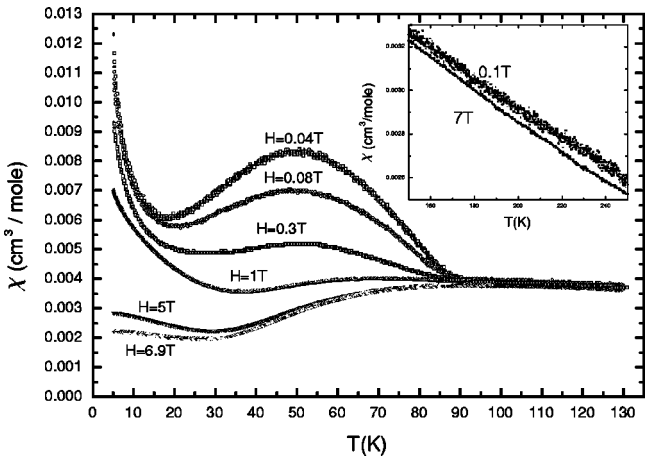

FIG. 1. Temperature dependence of the magnetic susceptibility for $LaCoO_3$ measured under ZFC conditions in several magnetic fields ($0.04 \leqslant H \leqslant 7$ T). The inset shows the high-temperature expansion of the magnetic susceptibility curves for $H=0.1$ and 7 T.

At temperatures above T_{min}, χ increases with rising temperature and exhibits a broad maximum (χ_{max}) between 50 and 100 K depending on the applied magnetic field. In particular, the position of χ_{max} shifts to higher temperatures with increasing field. The strong field dependence of χ_{max}, which is to our knowledge pointed out for the first time, indicates that the increase in χ is not only due to the earlier suggested thermally activated spin transition but also due to other magnetic interactions (*vide infra*).

Above 100 K, χ follows a Curie-Weiss-like behavior and continues to exhibit a slight magnetic field dependence (see the inset of Fig. 1). It is worth noting that the χ^{-1} vs T curve, shown in Fig. 2, is not linear. Both of these observations, i.e., the offset observed between $\chi(T)$ curves taken at different magnetic fields and the clear deviation from the ideal Curie-Weiss behavior, are in support of the polarized neutron diffraction measurements that have revealed the existence of ferromagnetic correlations in $LaCoO_3$ at 295 K.

Figure 3 shows magnetization versus dc magnetic field curves at several temperatures. A hysteresis loop is observed

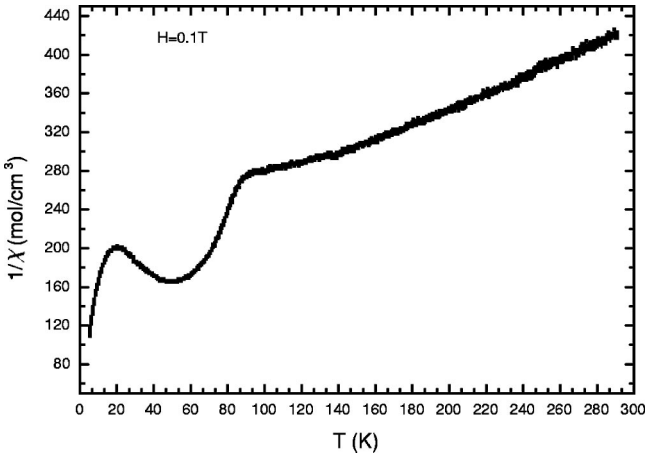

FIG. 2. Temperature dependence of the inverse magnetic susceptibility χ^{-1} for $LaCoO_3$ in $H=0.1$ T. Notice that for $T>100$ K the curve is not linear.

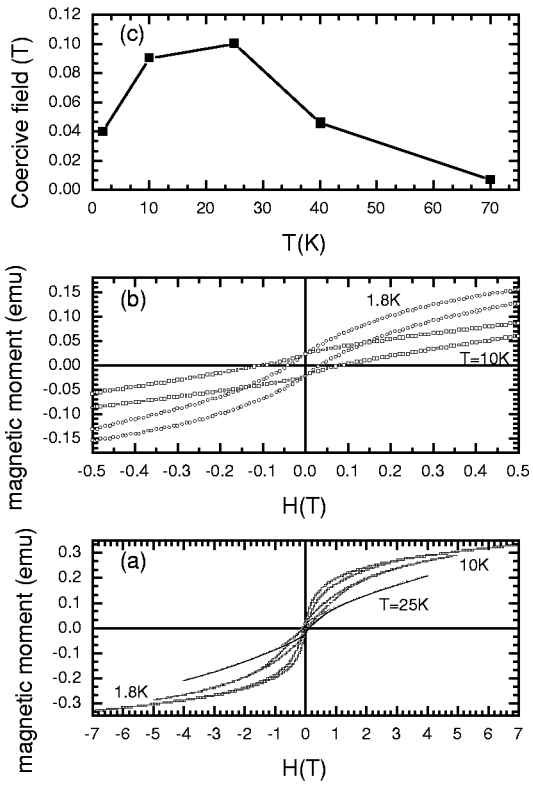

FIG. 3. (a) Magnetic field dependence of magnetization for $LaCoO_3$ at 1.8, 10, and 25 K. (b) Low-field expansion of the $M(H)$ hysteresis loops for 1.8 and 10 K. (c) Temperature dependence of the coercive field; notice that the curve is not monotonic.

at 1.8 K that clearly demonstrates the existence of ferromagnetic correlations in $LaCoO_3$. The coercive field observed is approximately 0.04 T. The nonsaturation of the $M(H)$ curve that is observed under the highest magnetic field applied ($H=7$ T) points out that no true long-range ferromagnetic order exists in $LaCoO_3$, in accordance with the neutron diffraction studies.[14] The hysteresis in $M(H)$ curves is clearly observed up to 100 K, indicating that ferromagnetic interactions occur also at higher temperatures. Notice that the coercive field is not a monotonic function of temperature [see Fig. 3(c)] which suggests that different mechanisms are responsible for the ferromagnetic interactions observed at different temperature regimes.

Figure 4 shows the temperature dependence of zero-field-cooled (M_{ZFC}) and field-cooled (M_{FC}) dc magnetization under the applied magnetic fields of 0.1, 1, and 7 T. There is a distinct difference between $M_{ZFC}(T)$ and $M_{FC}(T)$ below a certain characteristic temperature T_{irr}, which decreases with increasing applied field. It is, therefore, concluded that thermomagnetic irreversibility occurs in $LaCoO_3$.

B. ac susceptibility

The temperature dependences of the real and imaginary components χ' and χ'' of the linear ac magnetic susceptibility are shown in Fig. 5 and Fig. 6, respectively, as a function of the dc magnetic field. The linear component was measured with a driving ac field of amplitude $H_0=1$ Oe oscillating at

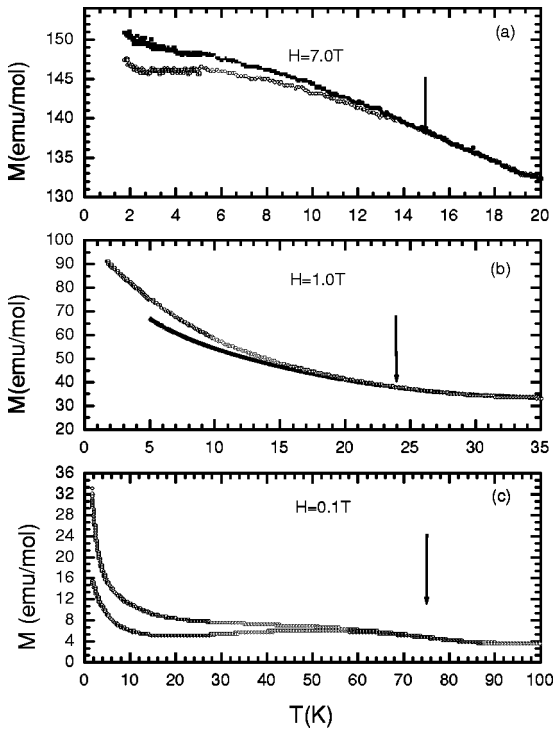

FIG. 4. Temperature dependence of the ZFC and FC magnetization of $LaCoO_3$ in $H=0.1$ T with $T_{irr}\approx 75$ K (a), $H=1$ T with $T_{irr}\approx 24$ K (b), and $H=7$ T with $T_{irr}\approx 15$ K (c). The arrows indicate the position of T_{irr}.

a frequency of 1 kHz. For $H_{dc}=0$ (i.e., under experimental conditions that reflect the true ground state of a magnetic system), an increase in χ' is observed at ~ 90 K, indicating the onset of a ferromagnetic phase (FM2). As the temperature is reduced, χ' exhibits a broad peak at ~ 62 K and then decreases abruptly, showing a minimum at ~ 22 K. Morover, it is observed that χ'' exhibits a broad hump at ~ 50 K which is most likely a consequence of superposition of several peaks. With increasing field the broad peak in χ' at ~ 62 K

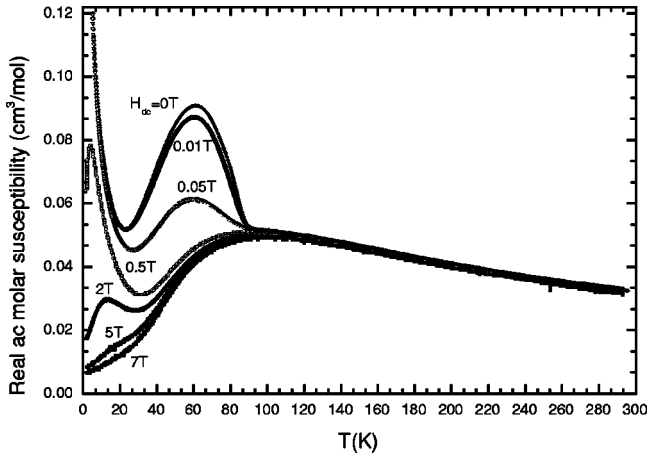

FIG. 5. Real part of the linear ac magnetic susceptibility χ' as a function of temperature for $LaCoO_3$ at several dc magnetic fields. Data were taken with a driving field of amplitude $H_0=1$ Oe oscillating at a frequency of 1 kHz.

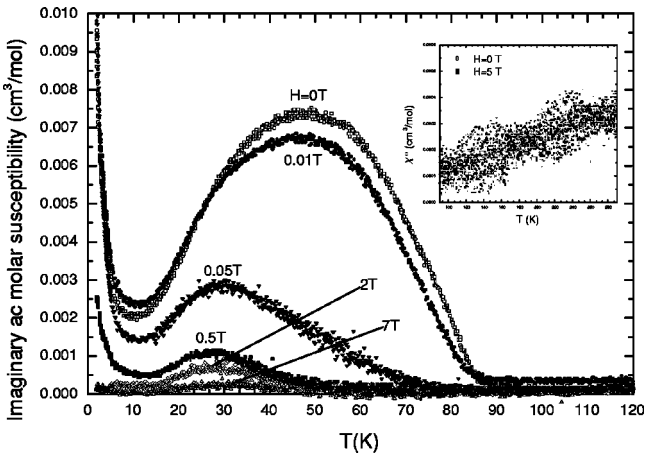

FIG. 6. Imaginary part of the linear ac magnetic susceptibility χ'' as a function of temperature for $LaCoO_3$ at several dc magnetic fields. Data were taken with a driving field of amplitude $H_0=1$ Oe oscillating at a frequency of 1 kHz. The inset shows the high-temperature expansion of χ'' at $H_{dc}=0$ and 5 T. Notice that $\chi''(T)$ is nonzero and has a positive slope.

is gradually suppressed, and for $H_{dc}\geqslant 5$ T both the broad maximum and minimum in χ' disappear. In addition, the application of $H_{dc}=0.05$ T supresses the broad hump in χ'', and a peak at ~ 28 K appears instead. The disappearance of the broad hump in χ'' implies that the ferromagnetic correlations observed in $LaCoO_3$ at $T>50$ K are easily suppressed by applying small dc fields. On the contrary, the peak at ~ 28 K persists up to the highest H_{dc} field applied even though its intensity gradually decreases. It is therefore suggested that the peak in χ'' at ~ 28 K implies the onset of AFM in $LaCoO_3$. It is worth noting that at $H_{dc}=7$ T the peak at ~ 28 K almost vanishes because the magnetic field provides the system with energy close to the ordering temperature (i.e., $\mu H\sim 30$ K).

At lower temperatures ($T<15$ K), χ'' exhibits a sudden increase, which indicates the existence of magnetic correlations. Furthermore, χ' exhibits a peak whose position shifts to higher temperatures and whose amplitude is steadily suppressed by the application of an external dc field. The above behavior of χ_{ac} is consistent with the existence of FM correlations. However, as can be readily seen from Fig. 5, the field dependence of χ_{ac} in this temperature regime is different from that for $T>25$ K, thus indicating that this type of FM interactions (FM1) is different from the ones for $T>25$ K (FM2).

It is also interesting to notice that χ'' is nonzero and has a positive slope for $T>100$ K, which indicates that the system possibly undergoes a magnetic transition at higher temperatures ($T>300$ K). This observation is in accordance with our dc susceptibility data which also indicate that ferromagnetic interactions exist up to 300 K (the maximum temperature at which measurements were taken during this study).

In Fig. 7, the frequency dependence of χ' is shown for $333\leqslant f\leqslant 5000$ Hz. It is observed that the broad peak at ~ 62 K is suppressed and shifts to higher temperatures with increasing frequency, indicating the existence of relaxation phenomena in $LaCoO_3$. This frequency dependence in con-

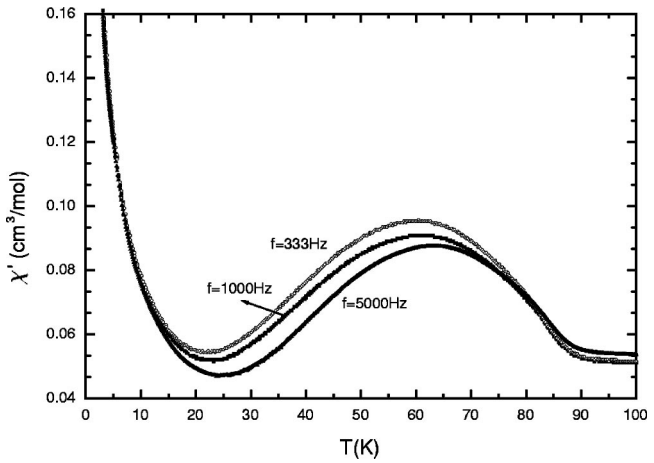

FIG. 7. Frequency dependence of the real part of the linear ac magnetic susceptibility χ' as a function of temperature for $LaCoO_3$ at several frequencies. Data were taken with a driving field of amplitude $H_0=1$ Oe and zero dc magnetic field.

juction with the irreversibility of χ_{dc} and the fact that χ' exhibits a cusp at $T<15$ K for $H_{dc}\leqslant 2$ T (Fig. 5), which shifts to lower temperatures with decreasing field, could be taken as evidence for spin-glass behavior. However, it is well known that a spin-glass phase should also exhibit a peak in the nonlinear susceptibility χ_3'. It is readily seen in Fig. 8 that the nonlinear susceptibility shows no peak below 15 K. Therefore, it is concluded that $LaCoO_3$ is not a spin-glass system.

IV. DISCUSSION

The result of the iodometric titrations, i.e., the concentration of trivalent Co being over 100%, is usually attributed to an excess of oxygen. However, there are experimental[25] and theoretical[26] studies, which indicate that the perovskite structure cannot accommodate oxygen atoms at interstisial sites.

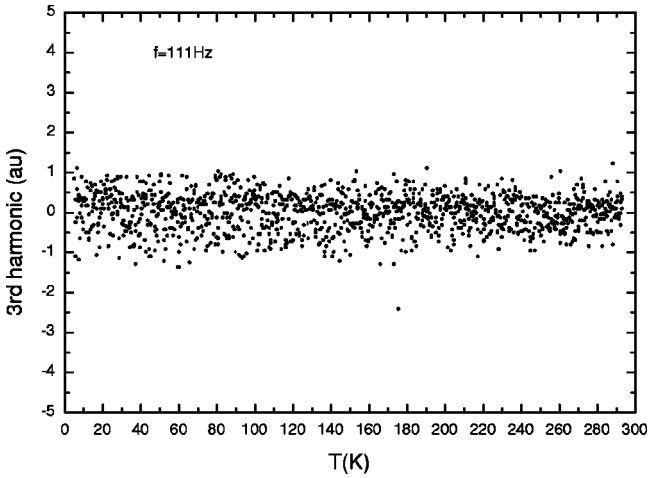

FIG. 8. Temperature dependence of the real part of the third-harmonic nonlinear ac susceptibility for $LaCoO_3$ in zero dc magnetic field. Data were taken with a driving field of amplitude $H_0=1$ Oe oscillating at a frequency of 111 Hz.

Therefore, we propose that $LaCoO_3$ has intrinsic structural defects, i.e., La vacancies, which have thermodynamic origin and their concentration depends on the preparation method. Due to the existence of vacant trivalent lattice sites, charge neutrality requires a number of Co atoms ($\sim 1\%$) to appear as Co^{IV}. These Co^{IV} ions are most likely randomly distributed in the lattice and constitute stable $S=1/2$ localized moments for the whole temperature range of interest. A similar explanation has been proposed by Ritter *et al.* (i.e., possible existence of Mn^{4+} sites dispersed in the lattice) in order to explain their magnetic measurements on $LaMnO_3$.[27]

The existence of intrinsic vacant lattice sites, even in the purest of samples, has been established in many materials. For example, one of the oxygen sites is systematically vacant in the chain layers of the high-T_c superconducting (HTS) compound $YBa_2Cu_3O_{7-\delta}$.[28] Similarly, in the mercury-based family of HTS compounds, defects in the mercury and oxygen sublattices are believed to play a crucial role for the superconducting behavior.[29]

It is worth noting that doping $LaCoO_3$ with divalent Sr ions can also induce the presence of tetravalent Co ions. There are important differences and similarities between the two systems. In the case of La-deficient $LaCoO_3$, the hole doping comes from oxygen $2p$ orbitals whereas in the case of Sr^{2+} doping the holes stem from Co $3d$ orbitals.[30] However, there exist remarkable similarities between the high-temperature electronic structure of $LaCoO_3$ and the metallic compound $La_{0.7}Sr_{0.3}CoO_3$.[24]

Optical conductivity measurements on $LaCoO_3$ have revealed a spectral change with increasing temperature that cannot be accounted by band-gap closing as in a narrow-band-gap semiconductor.[24] The deduced effective number of carriers, N_{eff}, which is a measure of the increase of the kinetic energy of the electronic system, is found to be nonzero for $T>9$ K. Based on these observations it has been suggested,[24] in accordance with other studies,[6,7,12] that $LaCoO_3$ is most likely a Mott-Hubbard insulator (i.e., a band metal which is insulating because of strong Coulomb interactions). We suggest that $LaCoO_3$, featuring a metal-like band structure, provides the holes doped in the system due to La deficiency with bands that cross the Fermi surface; hence, a small portion of these carriers can exhibit itinerant behavior affecting the observed magnetic and transport properties even at low temperatures.

In the temperature range 1.8–10 K, transport measurements indicate that *d*-electron correlations are dominant. Therefore, we suggest that the observed ferromagnetic correlations (FM1) are established due to superexchange interactions between Co^{IV} and IS and HS states of trivalent Co through the oxygen anions. This scheme has been suggested by J. B. Goodenough,[31] who has argued that Co^{IV} cations stabilize nearest-neighboring trivalent Co atoms in higher-spin states, which couple to give ferromagnetism according to Co^{IV}-O-Co^{s} (where $s=iii$ or $3+$). Because of the dependence of the ferromagnetic correlations on the concentration of Co^{IV}, we expect the magnitude of spontaneous magnetization to be strongly sample dependent. This could explain

the discrepancy among reported magnetic susceptibility data for $T<35$ K.

It is interesting to notice that in the study of Tokura *et al.*,[24] Sr^{2+} doping greatly increases the susceptibility upturn at low temperatures even at 2 parts per 1000 (ppt) Sr^{2+} ions concentration, while the qualitative behavior of χ does not change. At 5 ppt $[Sr^{2+}]$, the increase in χ is much greater due to the enhancement of the ferromagnetic interactions that dominate in the low-temperature region. In view of the fact that Sr^{2+} doping leads to the appearence of Co^{IV}, the aforementioned lends further support to our picture.

We suggest that a possible origin of AFM observed at ~ 28 K is e_g orbital ordering as has been discussed by Korotin *et al.*[21] The possible existence of AFM in $LaCoO_3$ is reported to our knowledge for the first time. $LaCoO_3$ being a Mott-Hubard insulator is expected to exhibit an AFM transition. The concurrence of AFM (T_N) and the metal-to-insulator transition (T_{MI}) is expected in the case of a pure sample. In case the sample contains magnetic impurities, as in our case (Co^{IV}), T_N is expected to be lower with respect to T_{MI} and even become zero at high concentrations of impurities.

In the temperature range 10–100 K, a second ferromagnetic transition (FM2) is observed. The broad peak centered at 62 K seems to be a superposition of several peaks, indicating the existence of domains of different size.[11] We propose that the few existing itinerant carriers, which exist, couple to Co^{IV} sites ferromagnetically through short-range RKKY interactions. The proposed picture of domains of variable size, within which Co^{IV} couples ferromagnetically through RKKY interactions, is consistent with the fact that ZFC and FC measurements result in a strong thermomagnetic irreversibility.

The magnetic susceptibility curve up to 100 K, therefore, is the superposition of four different contributions: FM1 for $T<10$ K, AFM for $T<30$ K, FM2 for $20<T<100$ K, and the last one coming from thermally activated spin transitions ($1.8<T<100$ K). In a dc field of 7 T the FM and AFM components are nearly suppressed. Thus, the increase in the susceptibility, observed from 30 K on, could be attributed to spin transitions to higher states. However, the Zeeman effect constitutes a strong perturbation in the system, rendering us unable to conclude on a specific spin state.

Above 100 K thermal effects oppose electron correlations more effectively. Thus, one should expect significant changes towards metallic behavior in the temperature regime 100–400 K. However, increasing temperature yields a large population of thermally excited Co^{III} to higher-spin states.[32] The odd number of electrons in e_g orbitals gives rise to the Jahn-Teller (JT) effect.[20,33] The JT effect breaks the O_h symmetry of cobalt cations, leading them into a D_{4h} symmetry. This lowering of the symmetry due to the JT effect is significant, because itinerant electrons are being exposed to the less-shielded cationic electrostatic potential of cobalt sites, thus further stabilizing the insulating phase.

The stabilization of the insulating phase up to 400 K is clearly depicted in the resistivity data of Ref. 34. It is interesting to notice the anomaly in the resistivity curve around 300 K. This plateau in the resistivity still remains unexplained. In our picture it is identified as a high-temperature Kondo-like effect. Specifically, we propose that the increase in the number of itinerant carriers with temperature results in an enhancement of the effective scattering process by the magnetic Co^{IV} sites, thus leading to higher resistivity. Resistivity data on $La_{1-x}Sr_xCoO_3$ for $x=0.002$, 0.005, and 0.01 exhibit a more extended plateau,[24] thus leading to further support to our proposal for increased magnetic scattering.

V. CONCLUSIONS

We have presented a systematic magnetic study of $LaCoO_3$. Here ac and dc magnetic susceptibility measurements provide strong experimental evidence for the existence of ferromagnetic (FM1, FM2) and antiferromagnetic (AFM) interactions at low temperatures. Specifically, FM1 interactions are observed at very low temperatures ($T<10$ K) and are attributed to superexchange interactions of the type Co^{IV}-O-Co^{s} (where $s=iii$ or 3+). FM2 interactions are observed for $20<T<100$ K and are attributed to coupling of localized moments on Co^{IV} sites through RKKY interactions. The weak AFM interactions set in at $T\sim 28$ K are attributed to orbital ordering in the system. The existence of the weak AFM may constitute the evidence in support of the proposal that this system is a Mott-Hubbard insulator. The fact that the onset temperature of AFM is different from that of the MI transition is attributed to the presence of magnetic impurities (Co^{IV}). The existence of Co^{IV} is based on the results of iodometric titrations and are attributed to La vacancies. A consistent qualitative explanation is provided for available magnetic and transport data.

When it comes to the $LaCoO_3$ system it becomes apparent that there are many complicated issues to consider regarding its interesting behavior. In-depth structural analysis and further theoretical and experimental work are needed in order to define all possible parameters that give rise to so many fascinating effects.

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