Spin-state driven ferromagnetic and spin glass states in layered LaSrCoO$_4$

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Abstract

Famous for its spin-state puzzle, LaSrCoO$_4$ (Co$^{3+}$) is an intermediate between antiferromagnetic (AFM) La$_2$CoO$_4$ (Co$^{2+}$) and ferromagnetic (FM) Sr$_2$CoO$_4$ (Co$^{4+}$). The appearance of the Co$^{3+}$ valence state (not present in the end compounds) is intriguing because of the spin-state transitions associated with it. In this work, we report two magnetic transitions in LaSrCoO$_4$: (i) a transition at $T = T_c \simeq 225$ K, from the paramagnetic state to a state with an inhomogeneous long-range ferromagnetic (FM) order wherein finite FM clusters coexist with infinite FM matrix in the percolation sense, and (ii) the transition to the cluster spin glass (CSG) state at $T = T_g \simeq 8$ K. Finite FM clusters (which at low temperatures give rise to the cluster spin glass state) and infinite FM matrix are formed due to the spin-spin interactions brought about by the inhomogeneously distributed Co$^{3+}$ high spin (HS) and Co$^{3+}$ low spin (LS) ions. A firm support to the presence of an unconventional (inhomogeneous) ferromagnetic order comes from the anomalous values of the critical exponents $\beta$, $\gamma$ and $\delta$ for the spontaneous magnetization, ‘zero-field’ magnetic susceptibility and the critical M - H isotherm, while the coexistence of HS Co$^{3+}$ and LS Co$^{3+}$ ions is confirmed by the results of the extended X-ray absorption fine structure spectroscopy.
INTRODUCTION

Low-dimensional magnetic orders are susceptible to a variety of external perturbations such as doping, magnetic field, strain, etc. [1] Much higher sensitivity to external stimuli compared to the 3D counterparts opens up room for many new applications, e.g., control of exchange bias has been possible in a single unit cell. [2] Moreover, in low-dimensional systems, control of spin moment can provide tremendous application opportunities for spintronics devices (layered cobaltates are potential candidates for such applications). LaCoO$_3$ (Co$^{3+}$), an often studied 3D compound, exhibits peculiar properties such as a metal-insulator transition, high-spin (HS) state to low-spin (LS) state transitions, magneto-electronic phase separation and ferromagnetic (FM) correlations [3]. A fascinating cobaltate and its 2D analog, La$_2$CoO$_4$ (Co$^{2+}$) is an antiferromagnetic insulator (AFI) [4], but not explored enough mainly due to its topotactic oxidation [5]. Its counterpart Sr$_2$CoO$_4$ (Co$^{4+}$) has a similar structure and shows FM and half-metallicity [6]. Intermediate between the above-mentioned end compounds, is LaSrCoO$_4$, which, in its unit cell structure, has LaCoO$_3$ 3D blocks separated by rock-salt LaO/SrO layers.

The Co$^{3+}$ ion, in general [7], can show the magnetically active, Co$^{3+}$ high spin (HS) S=2 state or intermediate spin (IS) S=1 state and non-magnetic low spin (LS) state S=0. However, the spin-state of the Co$^{3+}$ ions in LaSrCoO$_4$ compound has been discussed controversially, e.g., it is reported [8–10] that it exhibits the mixture of LS and thermally activated HS state of the Co$^{3+}$. Presence of homogeneous IS state of the Co$^{3+}$ is also claimed [11] but that has been challenged [12]. In our previous study [7], we probed the spin-states in La$_{2-x}$Sr$_x$CoO$_4$ (0.5 $\leq$ x $\leq$ 1) compounds and found existence of the HS and LS states together at room temperature and discarded the presence of IS state. Moreover, spin-state fraction quantified using recent x-ray absorption is in very close agreement with our results [13]. H. Wu [9] theoretically predicted that the ground state of LaSrCoO$_4$ can have mixed spin-states (HS and LS) of the Co$^{3+}$ ions but so far no experimental observation exists. As a matter of fact, it is well known that different spin states of the Co$^{3+}$ ions have different ionic radii, so experimentally spin state distribution estimate could be possible by extended X-ray absorption fine structure (EXAFS) spectroscopy as this method can provide information about minor local changes in the bond lengths and has been proven extremely useful in case of cuprates and manganites [14, 15].
In this report, the results of a detailed magnetization investigation of LaSrCoO$_4$ indicate the presence of ferromagnetic (FM) and spin-glass states. Observation of FM ordering and spin-glass (SG) behavior is consistent with the previous reports [16, 18]. The present work, further asserts that the FM and SG orders are spins-state (HS and LS) driven. We also provide experimental evidence for the inhomogeneous distribution of the HS and LS spin states by carrying out temperature-dependent EXAFS measurements across the Co K-edge. Our observations show that the present compound exhibits more complex SG behavior than encountered in normal cluster spin-glass systems.

**EXPERIMENTAL METHOD**

The details of sample synthesis and structural characterization are furnished elsewhere [7]. Magnetization measurements were carried out using a 7 Tesla Quantum design SQUID-VSM magnetometer. M(H) hysteresis loops were measured following the field-cooled (FC) protocol. Magnetization was measured as a function of temperature, M(T), over the temperature range extending from 5 K to 300 K at fixed fields, employing the FC and ‘zero-field-cooled’ (ZFC) protocols. For the virgin M(H) curves, first the sample was demagnetized and then data were taken. ZFC relaxation measurement has been performed by cooling the sample down to 150 K in zero field and after waiting for 100 s ($t_w$), a static magnetic field of 50 Oe was applied and the time evolution of magnetization at 150 K was measured upto $\sim 8000$ s. For constructing Arrott plots, the applied field has been corrected for the demagnetizing field to arrive at the internal effective magnetic field $H_{eff}$, in accordance with the relation, $H_{eff} = H_{applied} - (4\pi N)M$, where $N$ is the demagnetizing factor determined from the isothermal low-field M(H) data at $T < T_c$. EXAFS measurements were performed at the beamline P65 at PETRA III, DESY, Germany. The measurements were done in fluorescence and transmission on homogeneously mixed and pressed pellet of the sample and boron nitride (BN). The sample amount has been calculated for 1 absorption length. A liquid helium flow cryostat has been employed for low temperature EXAFS measurements. The Co K edge (7.7 keV) EXAFS has been measured up to high momentum transfer of about 16 Å$^{-1}$. *Athena* has been utilized for EXAFS data processing. In *Artemis*, the FEFF code was used to calculate theoretical scattering paths and the IFEFFIT has been used to fit the experimental spectra.
RESULTS AND DISCUSSION

Glassy nature and critical exponent analysis

Fig. 1(a) displays the ‘field-cooled’ (FC) and ‘zero-field-cooled’ (ZFC) thermomagnetic curves, M(T), in fixed magnetic fields (10 Oe - 10 kOe). A clear bifurcation between FC and ZFC M(T) is observed at low fields. Such bifurcations are the signature of spin-glass (SG) phase [20], cluster spin glass (CG) phase, magnetic anisotropy or super-paramagnetism (SPM) [21]. A closer look at the low-temperature ZFC M(T) data shows a clear cusp (inset (b) of Fig. 1) around \( T_g \sim 7-8 \) K. A similar feature was observed previously [16–18] and denoted as a freezing temperature. An interesting point to note is that on cooling below \( T_{Irr} \) (temperature at which FC and ZFC M(T) bifurcate), \( M_{FC} \) increases, which is taken to be a characteristic feature of cluster spin glass behavior in various systems [22]. The increase in \( M_{FC} \) with decreasing temperature, even below \( T_g \), points to the presence of a cluster spin glass (CSG) state [23] because \( M_{FC} \) normally exhibits a plateau for canonical spin glass [24]. It is noteworthy to mention that, for a typical re-entrant SG systems, the irreversibility occurs far below \( T_c \) while for CSG \( T_{Irr} \leq T_c \) [25]. In this connection, it is also reported [31] that if the bifurcation temperature \( T_{Irr} >> T_g \), the compound exhibits cluster glassy magnetism while for canonical SG [26] the \( T_{Irr} \) coincides with the \( T_g \). Thus, we conclude that the signatures discussed above basically reflect the CSG magnetism in LaSrCoO\(_4\) at low temperatures.

At first, we discuss the role of magnetic anisotropy as a possible source of bifurcation in M(T). Because of the elongated octahedra prevalent in the crystal structures similar to that in LaSrCoO\(_4\), the pseudo orbital moment of Co\(^{3+}\) HS, \( \tilde{L} = 1 \) [27], prefers to lie in-plane and forces the spin moment also to lie in the plane [28] due to the spin-orbit coupling. That, in these systems, magnetic moments are confined to the \( ab \) plane but can rotate within the plane, is clearly borne out by the neutron diffraction studies on iso-structural LaSrFeO\(_4\) [29] and half-doped La\(_{1.5}\)Sr\(_{0.5}\)CoO\(_4\) [30]. This is indicative of an XY-type anisotropy and hence \( c \)-axis may not be the easy axis of magnetization. We performed the analysis suggested by Joy et al. [21], according to which, if the decrease in \( M_{ZFC} \) is due to magnetocrystalline anisotropy, \( M_{ZFC} \) should follow the relation, \( \frac{M_{FC}}{H_{app}+H_c} \approx \frac{M_{ZFC}}{H_{app}} \). It is observed that, in the low temperature region and at low fields, \( \chi_{ZFC} \left( = \frac{M_{ZFC}}{H_{app}} \right) \) starts deviating from \( \chi'_{FC} \).
FIG. 1. (a) Thermomagnetic $M(T)$ curves taken at fixed magnetic fields. Inset (b) shows the enlarged view of ZFC $M(T)$ at low temperatures which facilitates the observation of the spin glass transition at $T_g$. (c-h) Temperature variations of the susceptibilities measured (solid circles) and calculated (open circles) at the different fixed magnetic fields. ($= \frac{M_{\text{FC}}}{H_{\text{app}} + H_c}$) (see Fig. 1(c-h)), indicating that, apart from the magnetocrystalline anisotropy, contributions from some other mechanisms could also be present.

Fig. 2(a) presents the isothermal $M(H)$ hysteresis loops, taken in the ‘field-cooled’ (7T) mode at temperatures below and above the paramagnetic (PM)-ferromagnetic (FM) transition temperature, $T_c \approx 225 \text{ K}$, (corresponding to the dip in $dM_{\text{ZFC}}(T)/dT$ at low fields $H = 10 - 100 \text{ Oe}$). With temperature decreasing from $T \gg T_c$, where the sample is in the PM state and as such the $M(H)$ isotherms are linear, the coercive field, $H_c$, increases from zero at $T = T_c \sim 225 \text{ K}$ to about 800 Oe at 5 K (the rate of increase in $H_c$ picks up for temperatures below 30 K); refer to the inset of Fig. 2(a). A steep increase in $H_c$ as the temperature falls below 30 K is indicative of an increase in the random magnetic anisotropy. The observation that magnetization does not saturate even in fields as high as 70 kOe and the presence of random magnetic anisotropy support the existence of cluster spin-glass state at low temperatures.

It is well-known that the critical-point (CP) analysis of magnetization, $M(T,H)$, data
FIG. 2. (a) ‘Field-cooled’ M(H) hysteresis loops. Inset shows the variation of $H_c$ with temperature. (b-f) Arrott ($M^{1/\beta}$ versus $(H/M)^{1/\gamma}$) plots with the choice of the critical exponents $\beta$ and $\gamma$ given by (b) the mean-field theory, and by the renormalization group calculations for the universality classes: (c) three-dimensional (3D) Heisenberg, (d) 3D-XY, (e) 3D Ising, and (f) mean-field tricritical (MFT).

This approach, taken in the critical region near $T_c$, provides a powerful means to unravel the true nature of magnetic ordering prevalent in a spin system. As elucidated below, the CP analysis makes use of the critical exponents $\beta$, $\gamma$ and $\delta$ for the spontaneous magnetization (order parameter), ‘zero-field’ susceptibility and the critical M(H) isotherm, (characterizing a continuous FM-PM phase transition at $T_c$), that are defined as:

$$M_s = B |\epsilon|^\beta \quad T < T_c, \quad H \to 0$$  \hspace{2cm} (1)
FIG. 3. (a) Arrott plots constructed using the presently determined critical exponent values. (b) $M^2$ versus $(H/M)$ plots in the low (5-30 K) temperature region demonstrate that no spontaneous magnetization, $M_s$, exists at such temperatures. (c) Linear log-log plot of the critical $M(H)$ isotherm at $T_c = 225$ K yields the value 1.825 for the critical exponent $\delta$. (d) Time evolution of the ZFC magnetization, $M(t)$, at 150 K measured in a static magnetic field of 50 Oe switched on with a time delay of 100 s. Note that $M(t)$ is normalized to its value at the time when the field was applied. The solid red curve through the data points (open circles) represents the fit to the stretched exponential function. (e) The scaling equation of state plot showing two different universal curves on which the $M(T,H)$ data, taken in the critical region at temperatures above and below $T_c$, collapse.

\[ \chi_0 = A \epsilon^{-\gamma} \quad T > T_c, \quad H \rightarrow 0 \]  
\[ M = M_0 H^{1/\delta} \quad T = T_c \]  

where $\epsilon = (T - T_c)/T_c$, A, B and $M_0$ are the critical amplitudes [31, 32]. The critical
exponents $\beta$, $\gamma$ and $\delta$ have exactly the same values for diverse systems belonging to a given universality class. Universality class is governed by the order parameter (spin) dimensionality and spatial dimensionality \[31\] as long as the interaction coupling the spins is of short range. The presence of different valence and spin states in the present system is expected to have a profound effect on the critical behavior. This expectation prompted us to undertake a detailed study of the critical behavior of LaSrCoO$_4$ at temperatures in the vicinity of the FM-PM phase transition. To this end, we have analyzed the virgin M(H) isotherms in the critical region using the scaling equation of state (SES) method, detailed in the reference \[31\]. Instead of following the customary practice of using, at first, the Arrott \[34\] scaling equation of state (SES), we use the generalized form of the Arrott SES, given by Arrott and Noakes \[35\] (AN), i.e.,

\[
(H/M)^{1/\gamma} = a[(T - T_c)/T_c] + bM^{1/\beta}
\]

(4)

to arrive at the correct choice of the critical exponents that makes the AN, $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$, plots a set of parallel straight lines in the critical region near $T_c$. The temperature at which the linear AN plot isotherm passes through the origin marks the $T_c$. To begin with, we ascertain if the values of critical exponents $\beta$ and $\gamma$, theoretically predicted for any universality class, make the AN plot isotherms at temperatures close to $T_c$ linear. The data presented in Fig. 2(b-f) clearly demonstrate that none of the universality class exponent choices: (b) mean-field, $\beta = 0.5$, $\gamma = 1.0$; (c) three-dimensional (3D) Heisenberg, $\beta = 0.365$, $\gamma = 1.386$; (d) 3D-XY, $\beta = 0.345$, $\gamma = 1.316$; (e) 3D Ising, $\beta = 0.325$, $\gamma = 1.241$; and (f) mean-field tricritical, $\beta = 0.25$, $\gamma = 1.0$; yields linear AN plot isotherms. This result prompted us to look for even the non-universal exponent values that could lead to the desired linear AN plot isotherms in the present system.

By varying the values of $\beta$ and $\gamma$ in Eq. (4), we succeeded in making the AN plot isotherms nearly straight over a wide field range but with anomalous critical exponent values, $\beta = 1$, $\gamma = 0.8$. From the modified Arrott plot (Fig. 3(a)), it is evident that the transition temperature $T_c \simeq 225$ K. Using Widom scaling relation \[36\] $\delta = 1 + \gamma/\beta$, the value of critical isotherm critical exponent $\delta$ comes out to be 1.8. To crosscheck this value, the relation (Eq. 3) is fitted to the virgin M(H) isotherm at $T_c = 225$ K. Fig. 3(c) shows the critical M(H) isotherm plotted as the ln M versus ln H$_{eff}$ plot. As expected from Eq. 3, this log-log plot is linear with inverse slope $\delta = 1.825$. This value of $\delta$ is in close agreement with that obtained through
the Widom scaling relation.

To ascertain whether or not the above-mentioned anomalous values of $\beta$ and $\gamma$, yielded by the AN SES (Eq. (4)), are reliable, we use these exponent values in constructing the $M|\epsilon|^{-\beta}$ versus $H|\epsilon|^{-\beta\delta}$ plot, which is based on the generalized SES of the form

$$M(H, \epsilon) = |\epsilon|^{-\beta} f_{\pm}\left[H/|\epsilon|^{\beta\delta}\right]$$

(5)

According to this SES, the M(H) isotherms taken in the critical region should fall onto two universal curves: $f_{-}$ for $T < T_c$ and $f_{+}$ for $T > T_c$, if the choice of critical exponents $\beta$ and $\gamma$ is correct. The $M|\epsilon|^{-\beta}$ versus $H|\epsilon|^{-\beta\delta}$ plots, shown in Fig. 3(e), testify to the correctness of the presently determined exponent values. The anomalous and non-universal critical exponent values signal the presence of an inhomogeneous FM order in LaSrCoO$_4$ at $T < T_c$.

With a view to gain more insight into the nature of magnetism at temperatures intermediate between the spin glass transition temperature $T_g \simeq 8$ K and $T_c \simeq 225$ K, the time ($t$) evolution of the ZFC magnetization, $M_{ZFC}(t)$, at 150 K was measured in a static magnetic field of 50 Oe switched on with a time delay of 100 s. The $M_{ZFC}(t)$ data, so obtained, were fitted to the stretched exponential function given by expression

$$M(t) = M_o - M_r \exp(-(t/t_r)^x)$$

(6)

where $M_o$ represents the FM component while $M_r$ and $t_r$ are associated with the spin glass behavior. The value of exponent $x$ reflects the type of energy barriers present. For instance, $x = 1$ describes the relaxation behavior of a FM system with a single anisotropy energy barrier separating the ZFC and FC states. $x \simeq 0.5$, on the other hand, is associated with the stretched exponential relaxation, caused by hierarchical energy barriers in spin glasses. From the fit (solid red curve through the data points), based on the above expression (Eq.(6)), to the $M(t)$ data (Fig. 3(d)), we obtain $x = 0.455$, which is in good agreement with the values generally reported for spin glass systems. Note that $M(t)$ is normalized to its value at the time when the field was applied. This result provides an evidence for the coexistence of the cluster spin glass like phase and ferromagnetic order at intermediate temperatures.

Furthermore, in the low temperature region ($T \lesssim 30$ K), the Arrott ($M^2$ versus H/M)
FIG. 4. (a-c) Schematics of the evolution of magnetic order in LaSrCoO$_4$ as the temperature changes the relative concentration of the Co$^{3+}$ ions in the high-spin (HS) and low-spin (LS) states. Solid patches (red) represent FM clusters (which eventually form a cluster spin glass state at low temperatures) and orange arrows indicate ferromagnetically interacting Co$^{3+}$ HS moments. (a) The magnetic state at $T \sim T_c$ wherein finite FM clusters coexist with an infinite FM matrix. (b) The magnetic state at intermediate temperatures, $T_g < T \ll T_c$, comprises randomly oriented smaller FM clusters coexisting with the infinite FM matrix. (c) At temperatures $T \sim T_g$, the long-range FM order is completely absent and the transition to the cluster spin glass state occurs. (d) The model depicting the inhomogeneous (HS+LS) spin state distribution of the Co$^{3+}$ ions that describes the observed EXAFS spectra the best.

plots, when extrapolated to $H = 0$, do not yield any intercept on the ordinate axis (see, Fig. 3(b)). It immediately follows that no spontaneous magnetization, and hence no long-range FM order, exists at these temperatures. Moreover, a steep rise in random magnetic anisotropy (reflected in a sharp increase in the coercive field, refer to the inset of Fig. 2(a)) as the temperature falls below 30 K destroys long-range FM order and instead establishes
the spin glass state at low temperatures.

For a better understanding of the nature of magnetic order in different temperature regimes in LaSrCoO$_4$, the present results must be viewed against the backdrop of those reported [40, 41] earlier. Before proceeding further, the pertinent points are briefly summarized below. (i) In the ground state, a mixture of low-spin (LS with $S = 0$) and high-spin (HS with $S = 2$) states of Co$^{3+}$ ions exists. (ii) As the temperature is raised, the concentration of HS Co$^{3+}$ ions increases [40–42] at the expense of that of LS Co$^{3+}$ ions. (iii) Co$^{3+}$ HS - O$^{2-}$ - Co$^{3+}$ HS superexchange gives rise to antiferromagnetic (AFM) interaction between the spins of neighboring Co$^{3+}$ HS ions. (iv) By contrast, Co$^{3+}$ HS - O$^{2-}$ - Co$^{3+}$ LS - O$^{2-}$ - Co$^{3+}$ HS superexchange (involving correlated hopping [40, 41] of $t_{2g}$ and $e_{g}$ electrons between Co$^{3+}$ LS and its Co$^{3+}$ HS neighbors, without charge transfer) leads to ferromagnetic (FM) interaction between the spins of the Co$^{3+}$ HS ions. Invoking percolation ideas, the physical picture of magnetism at different temperatures in LaSrCoO$_4$ that emerges as a consequence of presence of the above mentioned AFM and FM competing interactions is as follows. At $T \gg T_c$, thermally-excited spin fluctuations randomize the magnetic moments associated with the Co$^{3+}$ HS ions and hence the system is in the PM state. At $T \lesssim T_c$, finite FM clusters coexist with an infinite FM matrix. So far as the finite spin clusters are concerned, the intra-cluster FM interaction competes with the inter-cluster AFM interaction so as to frustrate spins at the periphery of the finite clusters. A further reduction in the temperature results in (I) a decrease in the cluster size due to the diminishing concentration of HS Co$^{3+}$ ions, and (II) freezing in random orientations of bigger clusters with slower relaxation rate at a higher temperature followed by the freezing of smaller clusters at lower temperatures (i.e., hierarchical freezing/blocking of the clusters of different sizes). Thus, at intermediate temperatures, a long-range FM order coexists with a cluster spin glass like phase (as inferred from the stretched exponential time evolution of ZFC magnetization (Eq.(6)) shown in Fig. 3(d)). By the time temperature nears 30 K, most of the finite clusters have frozen in random directions. The random anisotropy field, produced by the frozen clusters, in turn, destroys the long-range FM order at $T \lesssim 30$ K. In the process, a spin glass state (involving finite FM clusters of very small size, or even individual spins of HS Co$^{3+}$ ions, in a non-magnetic matrix of LS Co$^{3+}$ ions) is formed at $T \lesssim 8$ K.
Investigation of the Spin-state inhomogeneity

In the following, we will present the evidence for the presence of the Co\(^{3+}\) HS and LS distribution which is responsible for the formation of FM spin clusters and infinite FM matrix, as elucidated in the previous paragraph. In the unit cell we have tetragonal octahedral symmetry around the Co ions with four equatorial (Co-O2) and two axial (Co-O1) bonds. Because of the different radii of cobalt ions in different spin states (Co\(^{3+}\) HS (0.61 Å) and Co\(^{3+}\) LS (0.545 Å)) we expect different bond lengths between the cobalt ion and the oxygen ions. Therefore, we assume a simple model (see Fig. 4(d)) that in case of spin-state inhomogeneity we should observe a difference between the lattice constant \(a\) and twice the of bond length between the Co ions and the oxygen ions (Co-O2) i.e. \(a \neq 2 \times \text{Co-O2}\).

We have measured temperature dependent Co K-edge EXAFS and analyzed the data...
FIG. 6. (a) Fourier transformed $k^2 \chi(k)$ vs $R$ at 7 K. (b) $k^2 \chi(k)$ vs $k$ at 7 K, empty circle represents the data while continuous line is the fit to data. (c) Comparison of lattice parameter $a$ extracted from EXAFS (filled circle) and from literature (empty circle) (d) MSRD as function of temperature for inplane and out of plane Co-O bonds. (e) Bond lengths as function of temperature for inplane and out of plane Co-O bonds.

following a standard protocol [43]. Using the relation $\chi(k) = (\mu(k) - \mu(k_o))/\Delta\mu$, one may get the fine structure (EXAFS oscillations) where $k$, momentum, is defined as $k = \sqrt{2m(E - E_o)/\hbar}$, $E_o$ is deduced from the first inflection point on the edge and other symbols have their usual meaning [43]. Fig. 5 displays the $k^2$ weighted $\chi(k)$ oscillations measured at various temperatures (4 K to 300 K). The Fourier transformation of these gives us the radial distribution of shells. EXAFS spectra were fitted in R-space using the range $0.9 < R < 4 \text{ Å}$. We used a model with 4 equatorial and 2 axial oxygen neighbors [44] for a first shell to distinguish the equatorial and axial bond length in the CoO$_6$ octahedra and higher shells to independently measure the Co-Co = $a$. We have utilized the trigonometric constraints (see Table I) to fit the data. Fig. 6(a) and (b) show the fit of the spectrum measured at 7 K in R and $k$ space. Fig. 6(c) shows the agreement between the reported [45] and fitted lattice parameter, $a$, Fig. 6(e) shows the temperature dependence of the determined Co-O
distances, for Co-O1 and Co-O2. Fig. 6(c) and (e) clearly show that $a \neq 2 \times \text{Co-O2}$. This is the first experimental evidence of the theoretical study done by W. Hu. [9], who proposed mixed spin states. Our measurement on a polycrystalline sample is not sensitive to atom pair bond length of particular orientation/plane. Rather these results are a distribution and average of different bond lengths so it is not possible to quantify the fraction of a particular spin state. Further measurements on single crystals can enable quantification of the fractions of the two spin states.

Fig. 6(d) displays the mean square relative displacement (MSRD) ($\sigma^2 = \langle (R - \langle R \rangle)^2 \rangle$) for atoms in the equitorial and axial places of the octahedron. Clear anomalies are observed in MSRD in the low temperature and same are also found in bond lengths, indicating the distortion (Co-O1/Co-O2) in the octahedra (see Fig. 4(d)). The first anomaly appears at $\sim 75$ K and second appears at $\sim 48$ K. These two anomalies could be explained from our previous Seebeck coefficient results [7], that coupling of electron-phonon and electron-magnon freezes at these respective temperatures and produces static distortion at the cost of freezing of low energy excitations. It is interesting to note that these dynamics are observable in the fast time scale of EXAFS ($10^{-15}$ sec).

**CONCLUSION**

In summary, a detailed investigation of the LaSrCoO$_4$ compound has been carried out by measuring bulk DC magnetization over wide ranges of temperature and magnetic field and by using EXAFS, a local structural probe. The existence of a highly inhomogeneous ferromagnetic (FM) ordering at temperatures close to, but below, the Curie temperature, $T_c \simeq 225$ K, is inferred from the critical point analysis. The physical picture that emerges is that finite FM clusters are embedded in the infinite FM matrix at $T \lesssim T_c$. On lowering the temperature down to $T \simeq 30$ K, freezing of FM clusters in random orientations gives rise to the random anisotropy field, which, in turn, destroys long-range FM ordering and instead establishes the cluster spin glass state at $T_g \simeq 8$ K. Presence of a spin-state inhomogeneity is confirmed through the EXAFS analysis.

To conclude, with lowering temperature from 300 K, (i) the system undergoes a continuous phase transition from the paramagnetic (PM) state to the inhomogeneous FM state at $T_c \simeq 225$ K, (ii) long-range FM order coexists with finite FM clusters at intermediate
TABLE I. Scattering paths and used constraints during EXAFS fitting

| Path                        | $R_{eff}$ (Å) | Constraints               |
|-----------------------------|---------------|---------------------------|
| Co ↔ O2                    | 1.903         | o2                        |
| Co ↔ O1                    | 2.009         | o1                        |
| Co ↔ La                    | 3.197         | –                         |
| Co ↔ Co                    | 3.806         | $a$ = Lattice parameter   |
| Co → O2 → O2 → Co          | 3.806         | $2p = 2(a \tan(\angle O2-Co-Co))$ |
| Co → O2 → Co ↔ Co          | 3.806         | –                         |
| Co ↔ O2 (second shell)     | 4.255         | $o2' = (a^2 + o2^2)^{1/2}$ |

temperatures (between $\sim$ 225 K and $\sim$ 8 K), and (iii) a transition to the cluster spin glass state occurs at $T_g \simeq 8$ K.

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[1] C. Gong and X. Zhang, Science 363 (2019).
[2] A. Ahad, K. Gautam, K. Dey, S. Majid, F. Rahman, S. Sharma, J. Coaquira, I. da Silva, E. Welter, and D. Shukla, Phys. Rev. B 102, 094428 (2020).
[3] J. Wu and C. Leighton, Phys. Rev. B 67, 174408 (2003).
[4] R. A. M. Ram, P. Ganguly, and C. N. R. Rao, Mat. Res. Bull. 23, 501 (1988).
[5] A. Nemudry, P. Rudolf, and R. Schollhorn, Solid State Ionics 109, 213 (1998).
[6] P. K. Pandey, R. J. Choudhary, and D. M. Phase, Appl. Phys. Lett. 103, 132413 (2013).
[7] A. Ahad, D. K. Shukla, F. Rahman, S. Majid, Tarachand, G. S. Okram, and D. M. Phase, Acta Mater. 135, 233 (2017).
[8] J. Wang, W. Zhang, and D. Y. Xing, Phys. Rev. B 62, 14140 (2000).
[9] H. Wu, Phys. Rev. B 81, 115127 (2010).
[10] N. Hollmann, M. W. Haverkort, M. Cwik, M. Benomar, M. Reuther, A. Tanaka, and T. Lorenz, N. J. Phys. 10, 023018 (2008).
[11] R. Ang, Y. P. Sun, X. Luo, C. Y. Hao, and W. H. Song, J. Phys. D: Appl. Phys. 41, 045404 (2008).
[12] G. Subías, J. Blasco, S. Lafuerza, V. Cuartero, M. C. Sánchez, R. Boada, S. Díaz-Moreno, F. Fauth, and J. García, Inorg. Chem. 59, 15757 (2020).
[13] S. C. Haw, Z. Hu, H. J. Lin, J. M. Lee, H. Ishii, N. Hiraoka, A. Melendez-Sans, A. C. Komarek, L. H. Tjeng, K. Chen, et al., J. Alloys Compd., 158050 (2020).
[14] C. Zhang and H. Oyanagi, Phys. Rev. B 79, 064521 (2009).
[15] A. Bianconi, N. Saini, A. Lanzara, M. Missori, T. Rossetti, H. Oyanagi, H. Yamaguchi, K. Oka, and T. Ito, Phys. Rev. Lett. 76, 3412 (1996).
[16] Y. Shimada, S. Miyasaka, R. Kumai, and Y. Tokura, Phys. Rev. B 73, 134424 (2006).
[17] Y. Y. Liu, X. M. Chen, and X. Q. Liu, Solid State Commun. 136, 576 (2005).
[18] H. Guo, Z. Hu, T.-W. Pi, L. H. Tjeng, and A. C. Komarek, Crystals 6, 98 (2016).
[19] S. Srinath and S. N. Kaul, Phys. Rev. B 60, 12166 (1999).
[20] M. Kriener, C. Zobel, A. Reichl, J. Baier, M. Cwik, K. Berggold, H. Kierspel, O. Zabara, A. Freimuth, and T. Lorenz, Phys. Rev. B 69, 094417 (2004).
[21] P. A. Joy, P. S. A. Kumar, and S. K. Date, J. Phys.: Condens. Matter 10, 11049 (1998).
[22] R. S. Freitas, L. Ghivelder, F. Damay, F. Dias, and L. F. Cohen, Phys. Rev. B 64, 144404 (2001).
[23] S. N. Kaul and S. Srinath, J. Phys.: Condens. Matter 10, 11067 (1998).
[24] D. A. Pejaković, J. L. Manson, J. S. Miller, and A. J. Epstein, Phys. Rev. Lett. 85, 1994 (2000).
[25] S. Mukherjee, R. Ranganathan, P. S. Anilkumar, and P. A. Joy, Phys. Rev. B 54, 9267 (1996).
[26] J. Mydosh, Rep. Prog. Phys. 78, 052501 (2015).
[27] M. W. Haverkort, Z. Hu, J. C. Cezar, T. Burnus, H. Hartmann, M. Reuther, C. Zobel, T. Lorenz, A. Tanaka, N. B. Brookes, et al., Phys. Rev. Lett. 97, 176405 (2006).
[28] S. Csiszar, M. Haverkort, Z. Hu, A. Tanaka, H. Hsieh, H.-J. Lin, C. Chen, T. Hibma, and L. Tjeng, Phys. Rev. Lett. 95, 187205 (2005).
[29] N. Qureshi, H. Ulbrich, Y. Sidis, A. Cousson, and M. Braden, Phys. Rev. B 87, 054433 (2013).
[30] L. M. Helme, A. T. Boothroyd, R. Coldea, D. Prabhakaran, C. D. Frost, D. A. Keen, L. P. Regnault, P. G. Freeman, M. Enderle, and J. Kulda, Phys. Rev. B 80, 134414 (2009).
[31] S. N. Kaul, J. Magn. Magn. Mater. 53, 5 (1985).
[32] N. Khan, A. Midya, K. Mydeen, P. Mandal, A. Loidl, and D. Prabhakaran, Phys. Rev. B 82, 064422 (2010).
[33] R. Reisser, R. Kremer, and A. Simon, Physica B 204, 265 (1995).
[34] A. Arrott, Phys. Rev. 108, 1394 (1957).
[35] A. Arrott and J. E. Noakes, Phys. Rev. Lett. 19, 786 (1967).
[36] J. Lago, S. J. Blundell, A. Eguia, M. Jansen, and T. Rojo, Phys. Rev. B 86, 064412 (2012).
[37] N. Khan, A. Midya, P. Mandal, and D. Prabhakaran, J. Appl. Phys. 113, 183909 (2013).
[38] A. Ahad, K. Gautam, S. Majid, K. Dey, F. Rahman, R. Choudhary, and D. Shukla, Physica B (2019).
[39] S. P. Mathew and S. N. Kaul, J. Phys.: Condens. Matter 24, 256008 (2012).
[40] M. Merz, D. Fuchs, A. Assmann, S. Uebe, H. V. Löhneysen, P. Nagel, and S. Schuppler, Phys. Rev. B 84, 014436 (2011).
[41] M. Merz, P. Nagel, C. Pinta, A. Samartsev, H. v. Löhneysen, M. Wissinger, S. Uebe, A. Assmann, D. Fuchs, and S. Schuppler, Phys. Rev. B 82, 174416 (2010).
[42] S. R. Sehlin, H. U. Anderson, and D. M. Sparlin, Phys. Rev. B 40, 11681 (1995).
[43] B. K. Teo, *EXAFS: basic principles and data analysis*, Vol. 9 (Springer Science & Business Media, 2012).

[44] R. Bindu, S. Pandey, A. Kumar, S. Khalid, and A. Pimpale, J. Phys.: Condens. Matter 17, 6393 (2005).

[45] M. Cwik, *The Interplay of Lattice, Spin, and Charge Degrees of Freedom in Layered Cobaltates*, Ph.D. thesis, University of Cologne (2007).