Persistence of antiferromagnetic order upon La substitution in the 4d$^4$ Mott insulator Ca$_2$RuO$_4$

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The chemical and magnetic structures of the series of compounds Ca$_{2-x}$La$_x$RuO$_4$ [x = 0, 0.05(1), 0.07(1), 0.12(1)] have been investigated using neutron diffraction and resonant elastic x-ray scattering. Upon La doping, the low-temperature S-Pbca space group of the parent compound is retained in all insulating samples [x ≤ 0.07(1)], but with significant changes to the atomic positions within the unit cell. These changes can be characterized in terms of the local RuO$_6$ octahedral coordination: with increasing doping, the structure, crudely speaking, evolves from an orthorhombic unit cell with compressed octahedra to a quasitetragonal unit cell with elongated ones. The magnetic structure on the other hand, is found to be robust, with the basic a-axis antiferromagnetic order of the parent compound preserved below the critical La doping concentration of x ≈ 0.11. The only effects of La doping on the magnetic structure are to suppress the A-centred mode, favoring the B mode instead, and to reduce the Néel temperature somewhat. Our results are discussed with reference to previous experimental reports on the effects of cation substitution on the d$^4$ Mott insulator Ca$_2$RuO$_4$, as well as with regard to theoretical studies on the evolution of its electronic and magnetic structure. In particular, our results rule out the presence of a proposed ferromagnetic phase, and suggest that the structural effects associated with La substitution play an important role in the physics of the system.

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I. INTRODUCTION

Doped Mott insulators host a plethora of novel electronic phases including unconventional superconductivity, pseudogap states, charge density wave order, etc. [1]. Elemental substitution offers the unique possibility to tune two of the fundamental parameters of a strongly correlated electron system, i.e., the one-electron bandwidth (bandwidth control) and the band filling (filling control), and thus allows a rich phase diagram of electronic and magnetic states to be accessed [2]. The doping evolution of the magnetic ground state of the parent compound, which is usually dictated by oxygen-mediated superexchange interactions, varies between different systems. In perovskite manganites, the parent antiferromagnetic (AFM) order order develops into a ferromagnetic (FM) phase hosting giant magnetoresistance [2]. On the other hand, in both cuprates [1] and J$_{\text{eff}}$ = 1/2 iridates [3–6], doping suppresses long-range AFM order leading to the formation of incommensurate spin-density wave order [7–10] with a conventional paramagnetic (PM) metal eventually emerging.

Particularly interesting is the case of Mott insulators containing d$^4$ transition metal ions (such as Ru$^{4+}$, Os$^{4+}$, and Ir$^{5+}$), where moderate spin-orbit coupling (SOC) λ(S · L) is expected to stabilize a nonmagnetic J$_{\text{eff}}$ = 0 singlet [11]. In this case, magnetic order can result from the condensation of magnetic excited states driven by intersite interactions [12,13], provided that the exchange coupling is strong enough to overcome the energy of promotion of the ion to the excited state (separated from the ground state by $\lambda$). This unusual singlet magnetism has been recently predicted to give rise to a rich phase diagram as a function of electron doping [14]: here, the magnetic ground state was found to strongly depend on the relative strength of the hopping integral $t_0$, the SOC constant $\lambda$, and the correlation energy $U$. In particular, through electron doping of the parent AFM phase, the system is expected to evolve towards either a FM or a PM phase depending on the size of $\lambda$, with possibility of triplet superconductivity in the former case.

Ca$_4$RuO$_4$ is a prominent candidate for the realization of J$_{\text{eff}}$ = 0 (L$_{\text{eff}}$ = 1, S = 1) singlet magnetism [13–15]. However, there is still controversy as to the precise role played by SOC in the exchange between Ru$^{4+}$ (4d$^4$) magnetic moments. Evidence supporting the proximity of Ca$_3$Ru$_2$O$_4$ to a J$_{\text{eff}}$ = 0 ground state was provided by a recent inelastic neutron investigation [15], which reported the existence of the amplitude (Higgs) mode in the magnetic excitations spectrum expected to arise from the condensation of the excited J$_{\text{eff}}$ = 1 triplet. Other studies accounted for the spin-wave spectrum by a more conventional S = 1 Heisenberg-like magnetic-exchange model, where a finite spin-wave gap is opened by the SOC-induced

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single-ion anisotropy [16–18]. Neutron diffraction [19] also reveal that Ca$_2$RuO$_4$ orders at low temperature in a canted antiferromagnetic (C-AFM) structure with propagation vector $\mathbf{k} = (0, 0, 0)$; the latter consists of two coexisting magnetic modes [A-centred (dominant) and B-centred], where the Ru$^{4+}$ magnetic moments predominantly lie along the elongated $\mathbf{b}$ axis of the Pbca orthorhombic lattice (see Fig. 1). The finite Dzyaloshinskii-Moriya interaction (DMI) (stemming from significant distortion of the RuO$_6$ octahedra [19]) causes a small net magnetization along the $\mathbf{a}$ axis, which is coupled antiferromagnetically (A-centre mode) or ferromagnetically (B-centred mode) between neighboring RuO$_2$ layers [19].

The doped system Ca$_{2-x}$La$_x$RuO$_4$, where divalent Ca is replaced by trivalent La, has been recently suggested as a candidate material for the investigation of the impact of electron doping on the parent compound C-AFM order [14]. In particular, the emergence of an FM phase upon doping was predicted based on previous estimates of $\lambda$ [11,20]. Experimental studies of doped Ca$_2$RuO$_4$, however, have mainly focused on the bandwidth control achieved by substitution of divalent Sr for isovalent Ca [21–26]. The investigation of the magnetic properties of the La-doped compounds have been limited to bulk magnetization measurements [27–29]. The magnetization data, however, are not conclusive and have been subject to two conflicting interpretations: Fukazawa et al. [27] interpreted the observed net magnetization as resulting from the canting of antiferromagnetically coupled moments analogous to the parent case [19] (Fig. 2), while Cao et al. [28,29] proposed the presence of FM ordering, consistent with the theoretical predictions of Chaloupka and Khaliullin [14]. Despite its relevance in light of the unusual doping effects predicted for a $d^4$ Mott insulator with singlet magnetism [14], the magnetic structure of doped Ca$_2$RuO$_4$ is thus still unresolved.

In this paper, we report on a resonant x-ray scattering (REXS) investigation of the magnetic structure of Ca$_{2-x}$La$_x$RuO$_4$ at the Ru $L_3$ and $L_2$ absorption edges. Our measurements clearly show that the AFM structure of the parent compound is retained in the doped crystals up to $x = 0.07(1)$. Long-range magnetic order is destroyed at a doping level between $x = 0.07(1)$ and $0.12(1)$, at which value the system is PM. The effect of La substitution is mainly to suppress the A-centred AFM mode of the parent compound and stabilize the B-centred one. Our findings, supported by a detailed structural characterization by means of neutron diffraction, are compared with the results observed upon Sr doping and discussed in relation to the structural changes induced by doping.

II. METHODS

The REXS measurements were performed using the six-circle kappa diffractometer at the I16 beamline [31] of the Diamond Light Source (Didcot, UK). The scattered signal of several space-group forbidden reflections was measured tuning the incident x-ray energy to the Ru $L_3$ ($E = 2.838$ keV) and $L_2$ ($E = 2.967$ keV) absorption edges by means of a channel-cut Si (111) crystal. Given the relatively low photon energy, the beamline was used in a nonstandard setup and extra-care was taken to minimize air absorption. The data were collected in vertical scattering geometry, using horizontal linear incident polarization (referred to as $\sigma$ polarization [32]). The samples were mounted with the $c$ axis of the Pbca structure in the scattering plane for diffractometer angles set to zero; different values of the sample azimuth $\psi$ were used, where $\psi = 0^\circ$ corresponds to having $\mathbf{b}$ in the scattering plane. Polarization analysis of the diffracted beam was achieved by means of
also synthesised between 1400 °C and 1500 °C (the temperature was increased with the La content) and 1% O2 atmosphere. The conditions were adapted from Ref. [34]. The parent compound (x = 0) displays a well-documented metal to insulator transition (MIT) at $T_{\text{MIT}} = 357$ K concomitant to a first-order structural transition from a high-temperature quasitetragonal metallic phase ($L\text{-Pbca}$) to the low-temperature orthorhombic one ($S\text{-Pbca}$) [27,34–36]. Below $T_N \approx 110$ K, a phase transition to the basal plane C-AFM state also occurs [19,27–29,34,35,37]. La substitution causes the MIT and Néel temperature to decrease and be ultimately completely suppressed at a doping concentration slightly higher than $x = 0.11(2)$ [27]. The corresponding temperature-doping phase diagram is shown in Fig. 2. Here, we report the Néel temperature derived from our bulk magnetization measurements (large filled circles with errorbars) [30] along with the results of the magnetization (small filled circles) and resistivity (filled squares) data collected by Fukazawa et al. [27].

IV. RESULTS

A. Structural characterization

The structural properties of Ca$_{2-x}$La$_x$RuO$_4$ as a function of the doping level were investigated by means of single crystal neutron diffraction at $T = 10$ K. The doped samples retain the same space group ($Pbca$, No.61) of the parent compound. However, the different Shannon radii of the La$^{3+}$ ($r = 1.22$ Å) and Ca$^{2+}$ ($r = 1.18$ Å) ions [27,38] result in significant structural changes. The unit cell of Ca$_2$RuO$_4$ is shown in Fig. 1(a) along with the definition of relevant structural parameters, while the main results of the neutron data refinement are summarized in Fig. 3. The structural changes can be described in terms of the following four parameters: (i) unit cell distortion $1 - \frac{a}{c}$, where $a$ and $c$ are the in-plane lattice constants of the $Pbca$ unit cell; (ii) octahedral distortion $1 - \frac{r_{x,y}}{r_{z}}$, where $r_{x,y}$ and $r_z$ are the in-plane and apical Ru-O bond lengths of the RuO$_6$ octahedra, respectively; (iii) Ru-O-Ru bond angle; (iv) octahedral tilt angle away from the crystallographic c axis. The unit cell of the parent compound at low temperature is orthorhombic, with a $b$ lattice parameter elongated by 4.4% with respect to $a$. Large distortions away from the perfect perovskite structure ($1 - \frac{r_{x,y}}{r_{z}} = 0$, Ru-O-Ru angle $= 180^\circ$ and tilt angle $= 0^\circ$) are also present: the RuO$_6$ octahedra are significantly compressed along the local z axis ($1 - \frac{r_{x,y}}{r_{z}} < 0$) and display both a sizable rotation around the apical Ru-O bond direction and tilt away from the c axis [Fig. 1(a)]. La substitution is found to cause a reduction of the orthorhombicity of the unit cell ($1 - \frac{r_{x,y}}{r_{z}} \rightarrow 0$), in agreement with a previous study [27], and an elongation of the octahedral cage ($1 - \frac{r_{x,y}}{r_{z}} > 0$): this results in the phase diagram of Fig. 3(a), where for increasing doping levels, the system evolves from an orthorhombic cell with compressed octahedra ($x = 0, 0.05$) to a quasitetragonal cell with elongated ones ($x = 0.07, 0.12$). The rotations of the octahedral cage are also reduced [Fig. 3(b)] and the structure tends to relax towards the undistorted perovskite lattice. Further details on the structural refinement and additional room temperature results are reported in Refs. [30,39], which the reader is referred to for the corresponding CIF files.
The AFM coupling of the net magnetization of the parent compound [42], where the (100) magnetic reflection was probed, our scattering geometry limited our investigation to the magnetic diffraction peaks with a nonzero $l$ component [i.e., of the type $(h0l)$ or $(0kl)$].

The energy dependence of the (013) magnetic peak (A-centred mode) in the parent compound is reported in Fig. 4(a). The data have been corrected for self-absorption using the corresponding XANES signal [30] [also shown in Fig. 4(a)].

As already reported by Zegkinoglou et al. [42], a strong resonant enhancement of the diffracted intensity is present at both the Ru $L_3$ and $L_2$ absorption edges. This contrasts with the case of iridium oxides with the perovskite structure, where the Ir $L_2$ resonance is absent due to the strong SOC of 5$d$ electrons [43–45]. The Ru resonance originates from electric dipole $2p \rightarrow 4d$ transitions which directly probe the partially filled Ru 4$d$ states responsible for magnetism.

Each resonance displays two distinct features residing at $E = 2.8383(2)$, $2.8417(2)$ keV ($L_3$) and $E = 2.9674(2)$, $2.9721(2)$ keV ($L_2$), which arise from transitions to the crystal-field-split $t_{2g}$ and $e_g$ Ru 4$d$ orbitals, respectively [42]. The (013) signal is largely magnetic in origin as demonstrated by its temperature [Fig. 5], polarization [Fig. 6(a)] and azimuthal dependence [Fig. 7(a)]. A small contribution from ATS scattering might also be present [30], as evidenced by the weak diffracted signal observed above the Néel temperature (see blue circles in Fig. 5) and the residual intensity in the $\alpha \rightarrow \alpha'$ polarization channel [Fig. 6(a)]. The latter is also partially accounted for by the leakage from the $\alpha \rightarrow \alpha'$ channel, caused by the fact that the scattering angle of the analyzer crystal was not exactly 90°.

As well as the (013), a large energy resonance was also found for the (011) A-centred reflection [30]. Several B-centred peaks (Table I) were also investigated at various sample azimuths, but no significant diffracted intensity was detected in the parent compound. This is clearly shown in Fig. 8(a), where the (013) and (014) self-absorption corrected Ru $L_3$ resonances at low temperature are reported on the same scale. The (014) intensity is negligible and mostly resonates at the $e_g$ levels energy, thus suggesting that the signal is dominated by weak ATS scattering. This is consistent with previous neutron scattering measurements[19], which found a prevalence of the A-centred mode.

In order to verify whether the magnetic structure of the parent compound is retained upon La substitution, we probed several A-centred and B-centred magnetic reflections in the doped samples. A significant diffracted intensity was found at the same $k = (0,0,0)$ reflections. However, in stark contrast to the undoped crystal, a large resonance is present for the B-centred peaks only [Fig. 8(b)]. The B-centred resonances display similar features to the A-centred ones in the parent compound, as illustrated in Figs. 4(b) and 4(c) for the (014) reflection. In particular, a double $t_{2g} - e_g$ peak with a comparable resonant enhancement is present at both the Ru $L_3$ and $L_2$ edges. A minor exception is represented by the weaker $L_2$ (014) resonance in the $x = 0.07$ sample, which could be attributed to changes in the Ru$^{4+}$ electronic levels induced by doping (see Sec. V). It should be noticed, however, that the resonant enhancement of the (103) magnetic reflection at the two edges is similar to the one observed at lower La content [30] to be dominated by anisotropic tensor of susceptibility (ATS) scattering [41]. In contrast to the previous REXS study on the parent compound [42], where the (100) magnetic reflection was probed, our scattering geometry limited our investigation to the magnetic diffraction peaks with a nonzero $l$ component [i.e., of the type $(h0l)$ or $(0kl)$].

The globally AFM A-centred and weakly FM B-centred magnetic structure [Fig. 1(b)] give rise to two separate sets of AFM order of the two magnetic modes in Ca$_2$RuO$_4$ (100), (011), (013), (120) (101), (012), (103), (014). A-centred mode

B-centred mode

...in-plane lattice parameters of the Pbca unit cell). The horizontal angle (circles) and RuO$_6$ octahedra tilt angle away from the $c$ axis (squares) as a function of the La content. The horizontal error bars reflect the uncertainty in the doping level measured by means of EDX.

**TABLE I.** Space-group forbidden magnetic reflections arising from the main AFM order of the two magnetic modes in Ca$_2$RuO$_4$ [19,40].

<table>
<thead>
<tr>
<th>AFM reflections</th>
<th>A-centred mode</th>
<th>B-centred mode</th>
</tr>
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<tbody>
<tr>
<td>(100), (011), (013), (120)</td>
<td>(010), (101), (012), (103), (014)</td>
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self-absorption correction is also shown.

The data points correspond to the total diffracted intensity integrated on the Ru4

This is shown in the color maps of Fig. 9, where the spatial dependence of the magnetic (014) diffraction peak in the undoped sample under the beam focal spot and collecting a rocking scan to leakage from the σ polarization channel is due to leakage from the σ−π′ channel and σ′-polarized ATS scattering. The azimuthal dependence of the (014) [Fig. 7 (b)] and (103) (see Ref. [30]) reflections is also consistent with the calculations performed assuming the C-AFM structure with \( b \)-axis moments reported for pure Ca2RuO4 [19].

\[ \psi \approx 0^\circ \text{ at } T = 0.05 \text{ and } 0.07 \text{ samples, respectively} \]

\[ \psi \approx 0^\circ \text{ and } 30^\circ \text{, respectively} \]

\[ \psi \approx 0^\circ \text{ and } 0.05 \text{ at } T = 100, 120 \text{ K}, \text{ while the low-temperature } x = 0.05 \text{ and } 0.07 \text{ data sets correspond to an average of the spectra collected in the range } \psi = 0^\circ \text{–}60^\circ \text{ and at } \psi = 0^\circ \text{ and } 30^\circ , \text{ respectively} \]

The B-centred mode was found to be predominant across the whole crystal without any significant spatial dependence. This is shown in the color maps of Fig. 9, where the spatial dependence of the magnetic (014) diffraction peak in the \( x = 0.05 \) crystal is reported along with the one of the (004) Bragg peak. The measurements were performed translating the sample under the beam focal spot and collecting a rocking scan in each position. The size of the incident beam was reduced to \( 0.1 \times 0.1 \text{ mm}^2 \) through a set of slits. The (014) intensity shows limited variations throughout the measured sample area, with minor changes resulting from trivial inhomogeneities in the crystal quality across the sample [as can be seen from the comparison to the (004) map]. This excludes the presence of phase-separated domains of prevalent A or B character.

In addition to the resonant enhancement, the magnetic origin of the \( k = (0,0,0) \) space-group forbidden reflections in the doped samples is strongly supported by the fact that (i) the scattered intensity vanishes upon warming beyond \( T_N \approx 110 \text{ K} \) \( T_N \approx 70 \text{ K} \) in the \( x = 0.05 \) \( x = 0.07 \) sample and (ii) the scattered signal is predominantly \( \pi' \) polarized [Figs. 6(b) and 6(c)] regardless of the x-ray energy and \( \psi \) value chosen for the measurements [30], as expected for dipole resonant magnetic scattering [32]. As for the parent compound, the weak intensity in the \( \sigma - \sigma' \) polarization channel is due to leakage from the \( \sigma - \pi' \) channel and \( \sigma' \)-polarized ATS scattering. The azimuthal dependence of the (014) [Fig. 7(b)] and (103) (see Ref. [30]) reflections is also consistent with the calculations performed assuming the C-AFM structure with \( b \)-axis moments reported for pure Ca2RuO4 [19].

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FIG. 6. Polarization dependence of magnetic diffraction peaks in the (a) undoped, (b) \( x = 0.05 \) and (c) 0.07 sample at \( T = 7 - 8 \) K. The filled symbols refer to the scattered intensity measured over a rocking scan in the \( \sigma - \pi' \) (blue circles) and \( \sigma - \sigma' \) (red squares) channels of the polarization analyser crystal normalized to the \( \sigma - \pi' \) peak intensity, while the solid lines represent a fit to Voigt profile. The data were collected at \( E = 2.838 \) keV and \( \psi = 110^\circ, 50^\circ, 30^\circ \) for \( x = 0, 0.05, 0.07 \), respectively.

The ground-state wave function of the Ru\(^{4+}\) ion was described in terms of an admixture of \( xy, yz, \) and \( zx \) orbitals, whose respective contribution depends on the relative strength of the tetragonal crystal field \( \delta \) and SOC \( \lambda \) [20,48–53]. Within this picture, the tuning of the crystal field caused by the elongation of the RuO\(_6\) octahedra [Fig. 3(a)] is expected to result in an enhanced \( xy \) hole occupancy in the doped compounds with respect to the parent case. This is indeed what was reported for Ca\(_{2-x}\)Sr\(_x\)RuO\(_4\); here, the orbital degeneracy control achieved by Sr doping shifts the Ru \( 4d \ xy \) bands towards the Fermi level and turns the AFM exchange of the parent compound into a FM one at \( x_c = 0.5 \) [49,54]. A similar effect might be present also in the case of La doping and contribute to the stabilisation of the B-centred structure. Moreover, Hartree-Fock calculations [20,52] predicted that the increase in the \( xy \) holes population driven by tetragonal elongation should result into a \( z \) alignment of the Ru magnetic moments. Although the presence of a finite \( z \) component cannot be excluded by our measurements, a spin-flop transition to a \( c \)-axis AFM structure in the tetragonally elongated \( x = 0.07 \) sample is ruled out by the azimuthal dependence of the scattered intensity [Fig. 7(b)].

The evolution from A- to B-type magnetic order naturally explains the FM behavior seen in bulk magnetization measurements [27–29] as resulting from the weak FM component of the B-centred C-AFM mode, rather than a doping-induced local FM alignment (FM polarons) of Ru moments[28,29]. This is consistent with the interpretation given by Fukazawa et al. [27] based on their SQUID data. Given their sensitivity to the macroscopic magnetization of the sample, bulk measurements alone are not capable of unequivocally distinguishing between the two scenarios: similar results are indeed expected regardless of whether the magnetization arises from a FM ordering with a small ordered moment or an AFM structure with a weak net magnetization due to moments canting. A further confirmation comes from the measurements performed on nonstoichiometric Ca\(_2\)RuO\(_{4+\delta}\) [19]; here, a B-type C-AFM structure was also found and the bulk magnetization shows similar features to the ones of the La-doped compounds. The increase in the net moment seen for increasing levels of La directly controls the oxygen-mediated superexchange between Ru atoms[47]. This could favor the FM alignment of the net moments and might be one of the mechanisms involved in the stabilisation of the B-centred structure.

FIG. 7. Azimuthal dependence [azimuthal reference (010)] of the (013) and (014) magnetic diffraction peaks in the (a) undoped and (b) doped \( (x = 0.05, 0.07) \) samples at \( T = 7 - 8 \) K, respectively. The filled symbols refer to the scattered intensity integrated over a rocking curve at \( E = 2.838 \) keV corrected for the geometry-dependent self-absorption factor [30]. The solid lines represent the calculated azimuthal dependence (except for an arbitrary scale factor) assuming the C-AFM structure with \( b \)-axis moments reported by Braden et al. [19]. The intensity is normalized to the calculated value at \( \psi = 0^\circ \).
the doped electrons remain fully localized in the S-
importance of lattice energies in the stabilization of the
doping-induced structural changes is also expected in light of
irrespective of the Pr content. A pronounced sensitivity to the
measurements on Pr-doped Ca$_2$RuO$_4$ [39], which suggest that,
is somewhat confirmed by recent resistivity and ARPES
findings show that the concomitant structural effects are likely
in the undoped sample, for which $\psi = 80^\circ$.
content [28] is also compatible with the C-AFM scenario,
where it could arise from an increase of either the B-centred
mode volume fraction or the DMI-induced canting angle.
However, minor changes in the magnitude of the latter could
be absent for $\lambda > 77$ meV. The latter estimate is compatible
$\lambda \approx 200$ meV from a recent O K-edge RIXS
investigation[48]. Approximating to $x = 0.10$ the value of the
doping level at which the transition between the C-AFM and
PM states occurs [27], the phase diagram of Ref. [14] gives
$\lambda \approx 400$ meV. This is comparable to the value found for 5d
transition metal oxides [59] and thus seems overestimated. The
theoretical phase diagram of Ref. [14], however, neglects the
structural changes discussed in the present investigation (as
well as distortions away from the perfect cubic symmetry of
the RuO$_6$ octahedra and deviations from two-dimensionality)
and, as a result, it does not provide with an accurate description of
the physics of Ca$_{2-x}$La$_x$RuO$_4$.

VI. CONCLUDING REMARKS

In conclusion, our REXS investigation establishes the
per sistence of the C-AFM structure of the parent compound in
Ca$_{2-x}$La$_x$RuO$_4$. The AFM order was found to be present up
to $x = 0.07(1)$, while long-range order is absent in the $x = 0.12(1)$ sample. La substitution suppresses the globally AFM A-centred mode, dominant in pure Ca$_2$RuO$_4$, and favours the B-centred structure, which displays a weak net magnetization as a result of the moments canting. The latter naturally explains the net magnetization observed in previously published bulk magnetization measurements on the doped samples. Our results rule out the presence of a FM phase and also suggest that the structural changes, which accompany La doping are likely to play a pivotal role in the observed magnetic properties and should be considered alongside the electron doping effect in any meaningful description of the physics of the system.

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