Magnetic correlations in La$_{2-x}$Sr$_x$CoO$_4$ studied by neutron scattering: possible evidence for stripe phases

M. Cwik, M. Benomar, T. Finger, Y. Sidis, D. Senff, T. Lorenz, and M. Braden

II. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, D-50937 Köln, Germany
Laboratoire Léon Brillouin, C.E.A./C.N.R.S., F-91191 Gif-sur-Yvette CEDEX, France

(Dated: February 10, 2022)

Spin correlations in La$_{2-x}$Sr$_x$CoO$_4$ ($0.3 \leq x \leq 0.6$) have been studied by neutron scattering. The commensurate antiferromagnetic order of La$_2$CoO$_4$ persists on a very short range up to a Sr content of $x=0.3$, whereas small amounts of Sr suppress commensurate antiferromagnetism in cuprates and in nickelates. La$_{2-x}$Sr$_x$CoO$_4$ with $x>0.3$ exhibits incommensurate spin ordering with the modulation closely following the amount of doping. These incommensurate phases strongly resemble the stripe phases observed in cuprates and nickelates, but incommensurate magnetic ordering appears only at larger Sr content in the cobaltates due to a reduced charge mobility.

The coupled order of charge and magnetic degrees of freedom in the stripe phases in layered cuprates and nickelates has attracted strong interest due to its possibly important role in high-temperature superconductivity. Doping holes into La$_2$NiO$_4$ or La$_2$CuO$_4$ rapidly suppresses the commensurate antiferromagnetism (AFM) of the parent compounds resulting in incommensurate ordering. In La$_{2-x}$Sr$_x$NiO$_4$ only 12% of Sr drive the system into a stripe phase. Even less charges are necessary to suppress the commensurate AFM in the cuprates. For concentrations slightly above 2%, magnetic incommensurate superstructure reflections appear, which can be interpreted in the same stripe picture as that in nickelates, although alternative explanations have been proposed.

In analogy with the cuprates and nickelates, it appears interesting to analyze the possible existence of stripe phases in La$_{2-x}$Sr$_x$CoO$_4$. The parent compound La$_2$CoO$_4$ exhibits commensurate AFM order ($T_N=275$ K) similar to La$_2$CuO$_4$ and La$_2$NiO$_4$. Furthermore, at half doping, La$_{1.5}$Sr$_{0.5}$CoO$_4$, checkerboard charge ordering occurs at high temperature, $T_{CO}=825$ K, coexisting with magnetic ordering below $T_N \approx 40$ K. The character of the magnetic ordering between these two compositions, however, has not been determined so far. We have performed neutron scattering experiments on the La$_{2-x}$Sr$_x$CoO$_4$-series which reveal an astonishingly robust commensurate AFM order at low doping and incommensurate magnetic ordering at intermediate doping in close analogy to the stripe phases in cuprates and nickelates.

La$_{2-x}$Sr$_x$CoO$_4$ and La$_{2-x}$Ca$_x$CoO$_4$ single crystals of typically 1cm$^3$ size were grown in an image furnace following reference. The stoichiometry was verified by electron-microprobe analysis, by atomic absorption spectroscopy and by single-crystal as well as by powder x-ray diffraction. The samples were further characterized by resistivity and by magnetic susceptibility measurements indicating for La$_{1.5}$Sr$_{0.5}$CoO$_4$ $T_{CO}=825(20)$ K and $T_N=50(5)$ K, respectively. Elastic and inelastic neutron scattering experiments were performed using three triple-axis spectrometers: G4.3, 4F (cold) and 1T (thermal) at the Laboratoire Léon Brillouin.

Pure La$_2$CoO$_4$ exhibits a phase transition character-
ized by a tilt of the CoO$_6$ octahedra leading to a low-temperature orthorhombic (LTO) phase. Similar to the nickelates and cuprates phase diagrams, this tilt distortion is rapidly suppressed by the Sr-doping. In the La$_{1.7}$Sr$_{0.3}$CoO$_4$ single crystal we find the characteristic LTO superstructure reflections below T$_{LTO}=227$ K, see Fig. 1. The longitudinal polarization analysis excludes any magnetic contribution at this phase transition. However, below T$_{SO}=130$ K we find additional superstructure scattering at (0,5,0.5,q$_0$) whose magnetic origin is proven through the polarization analysis. The longitudinal polarization analysis adds an additional selection rule to the general neutron-scattering law that only magnetic components perpendicular to the scattering vector Q contribute: In the spin-flip channel the magnetic polarization must be perpendicular to the neutron polarization. The experiment on La$_{1.7}$Sr$_{0.3}$CoO$_4$ was performed in the [110][001] geometry. By measuring the three spin-flip channels for P$_x$=(0.5,0.5,0)=Q, P$_y$=(0,0,1) and P$_z$=(1,-1,0)=Q, we may conclude that the ordered moment fully lies within the a,b plane, see Fig. 1. Magnetic ordering in La$_{1.7}$Sr$_{0.3}$CoO$_4$ is of the same commensurate nearest-neighbor (nn) AFM type as that in La$_2$CoO$_4$, but the magnetic scattering is very broad with a Lorentzian width of $\kappa_{ab}=0.18(2)$ Å$^{-1}$ [15], and there is no detectable correlation along the c axis. The glass-like nature of the magnetic ordering is further seen in the magnetic susceptibility which continuously increases upon cooling through T$_{SO}$ and which exhibits irreversibility effects only below 16 K [16].

To further characterize the magnetism La$_{1.7}$Sr$_{0.3}$CoO$_4$, we have also analyzed the magnetic excitations. Typical constant-energy scans across the AFM zone center are shown in Fig. 1. The small correlation length together with the steep dispersion prohibit the separation of low-energy modes, but spin-wave modes are found at higher energies confirming that the character of the magnetic correlation is commensurate AFM. The dispersion is fitted by spin-wave theory taking only a nn Co$^{2+}$-Co$^{2+}$ interaction into account. The resulting gap-less spin-wave dispersion, $\hbar\omega(q) = 4J_{AF}S\sqrt{1 - \frac{1}{4}[\cos(q_x a\pi) + \cos(q_y a\pi)]^2}$, describes the observed spin-wave energies perfectly with $J_{AF} = 5.97(8)$ meV and $S = 3/2$ indicating an intrinsic Co$^{2+}$-Co$^{2+}$ interaction of the order of $J_{AF}^{intr.}=8.5$ meV. Note that here and in the following the interaction parameters correspond to the energy per bond, and that the wave-vector q is given in reduced units of $2\pi/a$ with $a \sim 3.85\text{Å}$. The La$_{1.7}$Sr$_{0.3}$CoO$_4$ dispersion corresponds to a spin-wave velocity of 138 meVÅ from which one may roughly estimate the intrinsic La$_2$CoO$_4$ spin-wave velocity to ~200 meVÅ, lower than values of 340 meVÅ in La$_2$NiO$_4$ and of 850 meVÅ in La$_2$CuO$_4$. Energy scans at the two magnetic zone boundaries in La$_{1.7}$Sr$_{0.3}$CoO$_4$ suggest a weak splitting, see Fig. 1, which is typical for non-homogeneous magnets [17].

The smaller impact of the Sr-doping on the commensurate antiferromagnetism in La$_{2-x}$Sr$_x$CoO$_4$ is remarkable in view of the very strong effects in the nickelates and cuprates, but the impact is still larger than what is expected for a static non-magnetic impurity. The substitution of non-magnetic impurities into layered magnets has been extensively studied [17] for example in K$_2$(Co$_{1-x}$Mg$_x$)$_4$F$_4$. In accordance with percolation theory long-range AFM order persists up to the critical concentration of $x_c = 0.41$ [18], whereas the ordering in La$_{1.7}$Sr$_{0.3}$CoO$_4$ is of short range. In La$_{2-x}$Sr$_x$CoO$_4$ the magnetic impurity is coupled to the doped charge and may thus hop. The Co$^{2+}$-sites with 3d$^7$ configuration always stay in a high-spin (HS) state with S = 3/2, but at a Co$^{3+}$-site HS, S=2, intermediate-spin (IS), S=1, and low-spin (LS) states, S=0, are possible. A Co$^{3+}$ HS state

FIG. 2: (Color online) (a) Magnetic order in the checkerboard charge-ordered phase in La$_{1.5}$Sr$_{0.5}$CoO$_4$ where only Co$^{2+}$ moments contribute; b) the insertion of an additional Co$^{2+}$ row stabilizes magnetic order through the direct exchange $J_{AF}$. (c) Elastic magnetic scattering in La$_{1.5}$Sr$_{0.5}$CoO$_4$ for different temperatures (scan direction is shown in the inset): (d) peak heights of the magnetic superstructure and (e) elastic scans in La$_{2-x}$Sr$_x$CoO$_4$; (f) in-plane correlation lengths parallel and perpendicular to the modulation for La$_{2-x}$Sr$_x$CoO$_4$ and La$_{2-x}$Ca$_x$CoO$_4$ and La$_{2-x}$Sr$_x$CuO$_4$ (g) magnetic incommensurability as a function of Sr-content comparing with La$_{2-x}$Sr$_x$CuO$_4$ [3] and La$_{2-x}$Sr$_x$NiO$_4$ [2] [3].
appears unlikely in La$_{1.7}$Sr$_{0.3}$CoO$_4$, as it should at most
weakly perturbate the AFM order. Stronger effects can be expected for the IS or LS Co$^{3+}$ states where an ef-
ficient trapping of the Co$^{3+}$-site is needed to stabilize
the nn AFM order. Such charge-carrier trapping can arise from a spin-blockade mechanism as proposed for
HoBa$_2$Co$_2$O$_{5.5}$ [19]. In a Co$^{3+}$-LS versus Co$^{2+}$-HS
configuration the extra electron at the Co$^{2+}$ site may only
move by passing into the wrong spin states which render
such processes quite unfavorable.

Let us now turn to the charge and orbital ordering
in half-doped La$_{1.5}$Sr$_{0.5}$CoO$_4$, which has already been
studied by Zaliznyak et al. [11, 12]. In our crystal,
we find the same three-dimensional superstructure
reflections and perfect agreement concerning tempera-
ture dependencies, $T_N=48(2)$ K deduced from the mag-
netic reflection, and low-temperature correlation lengths,
$\xi_{ab}=68(3)$ Å, $\xi_c=13.1(4)$ Å and $\xi_{ab-charge}=19(1)$ Å.
The magnetic ordering does not occur exactly at the commen-
surate propagation vector of $(0.25,0.25,0)$ but slightly off-
set at $q=(0.25+\delta,0.25+\delta,0)$ with $\delta = 0.0057(8)$ which is
somewhat smaller than the values observed previously [11, 12]. In reference [11] it is proposed that the charge-
ordered arrangement is associated with non-magnetic LS
Co$^{3+}$ sites, whereas an Co$^{3+}$ IS spin-state is suggested
in reference [12]. Our own structural analysis [14] sup-
ports the interpretation of the LS state corroborated by a
quantitative analysis of the anisotropic magnetic suscepti-
ability [16]. The magnetic structure with non-magnetic
Co$^{3+}$ sites, depicted in Fig. 2a), perfectly describes the
elastic peaks [11] and the full spin-wave dispersion in
La$_{1.5}$Sr$_{0.5}$CoO$_4$ which we have determined [14] extending
a previous study [20]. The next-nearest neighbor (nnn)
Co$^{2+}$-Co$^{2+}$ interaction ($J_1$; linear Co$^{2+}$-O-Co$^{3+}$-O-Co$^{2+}$
path, distance $2\cdot a$) and the nn Co$^{2+}$-Co$^{2+}$ interaction
($J_2$; distance $\sqrt{2}\cdot a$) are frustrated as both interactions are
AFM. In mean-field approach the quarter-indexed struc-
ture shown in Fig. 2a) is stabilized for $J_1 > \frac{1}{2} J_2$. Set-
ing $S = \frac{1}{2}$, the magnon dispersion is well described tak-
ing into account only the nnn interaction $J_1=2.04(9)$ meV
[14], which is much lower than $J_{AF}$. However, $J_1$ couples
only half of the Co$^{2+}$ sites in a single plane (see Fig. 2).
Since in addition, $J_2$ is almost fully frustrated [21], the
degenerate in-plane order is not very stable.

Very recently, a HS Co$^{3+}$ moment was proposed for
half-doped La$_{1.5}$Ca$_{0.5}$CoO$_4$ [23] basing on the observation
of additional magnetic superstructure reflections at $Q=(0.25,0.1)$ with $l=\frac{2n+1}{2}$. We have verified that these
reflections do not appear in our La$_{1.5}$Sr$_{0.5}$CoO$_4$ sample,
they must be at least a factor of 60 smaller than the
quarter-indexed reflections associated with the Co$^{2+}$ or-
dering therein.

In Fig. 2 we resume the elastic neutron-scattering
results for the intermediate concentrations. Already
for $x=0.4$ there is no indication for the commensurate
AFM ordering; instead, superstructure reflections arise
at $(\frac{1}{2} \pm \epsilon, \frac{1}{2} \pm \epsilon, 0)$ with $2\epsilon=0.3912(12)$ which is very
close to the charge carrier content of $x=0.4$. This mag-
netic reflection, thus, perfectly agrees with the diagonal
stripe ordering occurring in the La$_{2-x}$Sr$_x$NiO$_4$-series.
In this picture the Co$^{3+}$ or Ni$^{3+}$ ions segregate into charged
stripes running along [110] separating AFM stripes, see
Fig. 2b). In consequence the magnetic modulation, $\epsilon$, is
determined by the doped charge concentration: $2\epsilon = x$.
Comparable magnetic superstructure reflections appear in all
La$_{2-x}$Sr$_x$CoO$_4$ crystals of intermediate doping,
$x=0.4, 0.45, 0.5, 0.6$, with the position following the
$2\epsilon = x$ rule. Note, that the perfect checkerboard order-
ing in the half-doped compound can be taken as a stripe
phase with $2\epsilon = 0.5$ corresponding to an alternation of
Co$^{2+}$ and Co$^{3+}$ rows along the [110]-direction. The slight
incommensurability observed in our half-doped crystal
translates into $2\epsilon=0.4886(16)$ only slightly below the
nominal hole content. The general trend in the modula-
tion suggests to consider these incommensurate phases as
stripe phases like the analogous phases in nickelates and
cuprates, but, alternatively, the incommensurate mag-
netic ordering may be interpreted as a spiral [5], which,
however, leaves the $2\epsilon = x$ relation unexplained.

We have also searched for the corresponding charge-
order peaks in La$_{1.6}$Sr$_{0.4}$CoO$_4$ by scanning diagonally
across (2.5,0.5,0), see Fig. 3. There is sizeable diffuse
scattering around $q=(0.5,0.5,0)$ in La$_{1.6}$Sr$_{0.4}$CoO$_4$, which
is absent in the same scan on a La$_{1.6}$Ca$_{0.4}$CoO$_4$ crys-
tal of similar size. Part of the signal in La$_{1.6}$Sr$_{0.4}$CoO$_4$
can be associated with the superposition of four broad
charge-order peaks at $(0.5 \pm 0.1,0.5 \pm 0.1,0)$ but a dom-
inant commensurate contribution possibly associated
with the tilt instability prohibits a quantitative analysis.
La$_{1.6}$Ca$_{0.4}$CoO$_4$ exhibits commensurate magnetic order,
and is thus a perfect reference for the background [24].

In Fig. 2(g) we compare the incommensurate modula-
tion vector for cobaltates, nickelates and cuprates. For
La$_{2-x}$Sr$_x$CuO$_4$ we take the modulation of the inelastic
correlation which however directly reflects that in static
stripe phases [9]. The cuprate modulation for vertical

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Scans across the positions where incommensurate or commensurate scattering related with charge order is expected in La$_{1.6}$Sr$_{0.4}$CoO$_4$ and in La$_{1.6}$Ca$_{0.4}$CoO$_4$.}
\end{figure}
Electronic resistivity and the spin-blockade mechanism
in the holes in these materials. In the cobaltates this effect is
already for small hole doping, whereas stripe-like phenomena
are observed already for small hole doping, whereas incommensurate order is shifted to higher doping in nickelates and cobaltates due to the reduced mobility of the holes in these materials. In the cobaltates this effect is by far strongest in agreement with their much higher electronic resistivity and the spin-blockade mechanism [3].

Similar to the most stable stripe phases appearing in cuprates and nickelates at hole-doping levels of x=1/8 and 1/3 [1][2][8], respectively, there exists a most stable composition for charge/spin order in the cobaltates as well: It is the half-doping concentration x=0.5. For this composition we find the largest in-plane correlation lengths and the strongest superstructure reflection in comparison to a fundamental reflection, see Fig. 2. As the correlation lengths for concentrations away from half doping are reduced, the integrated magnetic intensity, however, varies much less within the series. For x=0.5 the magnetic ordering is clearly seen in the magnetic susceptibility, [14][20], and the charge order causes an anomaly in the temperature dependence of the resistivity [14]. The fact that, nevertheless, the magnetic ordering is not fully commensurate (with similar deviations in different crystals [11][12]) suggests that there is an underlying intrinsic effect similar to La_{1−x}Sr_{x}NiO_{4} where the deviation from commensurability is however six times larger [22]. A reason for such a deviation might be in both cases the frustration of the nn interaction J_{2} and the degeneracy of the in-plane order mentioned above. The inclusion of additional magnetic rows lifts the degeneracy and stabilizes magnetic order due to the strong J_{AF} interaction between neighboring spins, see Fig. 2b). Also a minor polarization of some 3+ sites may lift the degeneracy. It is interesting to note, that La_{2−x}Ca_{x}CoO_{4} exhibits commensurate order around half doping with 2τ=0.5016(20) (x=0.4) and 2τ=0.5022(18) (x=0.5).

The phase diagram of La_{2−x}Sr_{x}CoO_{4}, see Fig. 4, qualitatively resembles those of La_{2−x}Sr_{x}NiO_{4} and La_{2−x}Sr_{x}CuO_{4} [3][4][6]. In all systems the nn AFM order transforms into incommensurate stripe-like order which is stabilized near a commensurate value. The magnetic transition temperatures in the cobaltates are comparable to those found in the co-doped cuprates but significantly lower than those in nickelates stripe phases, for example T_{N}~150 K in La_{1.07}Sr_{0.33}NiO_{4} [3]. There is a clear trend that the magnetic transition in La_{2−x}Sr_{x}CoO_{4} continuously decreases with the doping corroborating the interpretation that the Co^{3+} are magnetically not active.

This work was supported by the Deutsche Forschungsgemeinschaft in the Sonderforschungsbereich 608. We are thankful to D. Khomskii for various discussions.

* Electronic address: braden@ph2.uni-koeln.de
[1] J. M. Tranquada et al., Nature 375, 561 (1995).
[2] V. Sachan et al., Phys. Rev. B. 51, 12742 (1995); C. H. Chen et al., Phys. Rev. Lett. 71, 2461 (1993); J. M. Tranquada et al., Phys. Rev. B. 54, 12318 (1996).
[3] H. Yoshizawa et al., Phys. Rev. B 61, R854 (2000).
[4] S. Wakimoto et al., Phys. Rev. B 61, 3699 (2000); ibid. 60, R769 (1999).
[5] N. Hasselmann et al., Phys. Rev. B 69, 014424 (2004); O. P. Suchkov et al., Phys. Rev. Lett. 94, 097005 (2005).
[6] K. Yamada et al., Phys. Rev. B 57, 6165 (1998).
[7] M. Fujita et al., Phys. Rev. Lett. 88, 167008 (2002).
[8] S. A. Kivelson et al., Rev. Mod. Phys. 75, 1201 (2003).
[9] Y. Moritomo et al., Phys. Rev. B 55, R14725 (1997).
[10] K. Yamada et al., Phys. Rev. B 39, 2236 (1989).
[11] I. A. Zaliznyak et al., Phys. Rev. Lett. 85, 4353 (2000).
[12] I. A. Zaliznyak et al., Phys. Rev. B 64, 195117 (2001).
[13] P. Reutler et al., J. Cryst. Growth 249 , 222 (2003).
[14] M. Cwik, M. Benomar, and M. Braden unpublished.
[15] This corresponds to a correlation length of 5.5(3)Å and may suggest a mixture of ordering schemes, but the high-doping modulation extrapolated to q=(0.65,0.65,0) at x=0.3 can not explain the main signal.
[16] N. Hollmann et al., New J. of Phys. 10, 023018 (2008).
[17] Magn. Prop. of layered transition metal compounds, ed. L.J. deJongh, Kluwer Academic Publishers (1989).
[18] D. Stauffer and A. Aharony, Introduction to Percolation Theory (Taylor and Francis, London, 1994).
[19] A. Maignan et al., Phys. Rev. Lett. 93, 026401 (2004).
[20] L. M. Helme et al., Physica B 350, e273 (2004).
[21] Only the small orthorhombic distortion associated with the checkerboard charge order lifts the full frustration of J_{2} via a finite inter-layer coupling.
[22] R. Kajimoto et al., Phys. Rev. B 67, 014511 (2003).
[23] K. Horigane et al., condmat-07080939.
[24] La_{1.6}Ca_{0.4}CoO_{4} exhibits peaks at (n+1/2,m+1/2) due to commensurate charge order and due to a structural distortion.
[25] M. Haider, Dipl.-Thesis, Univ. of Cologne (2005).