Magnetic Correlations in $La_{2-x}Sr_xCoO_4$ Studied by Neutron Scattering: Possible Evidence for Stripe Phases

M. Cwik,[1] M. Benomar,[1] T. Finger,[1] Y. Sidis,[2] D. Senff,[1] M. Reuther,[1] T. Lorenz,[1] and M. Braden[1,*]

[1]*II. Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, D-50937 Köln, Germany*

[2]*Laboratoire Léon Brillouin, C.E.A./C.N.R.S., F-91191 Gif-sur-Yvette CEDEX, France*

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Spin correlations in $La_{2-x}Sr_xCoO_4$ ($0.3 \leq x \leq 0.6$) have been studied by neutron scattering. The commensurate antiferromagnetic order of La_2CoO_4 persists in 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. $La_{2-x}Sr_xCoO_4$ 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.

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The coupled order of charge and magnetic degrees of freedom in the stripe phases in layered cuprates [1] and in nickelates [2] has attracted strong interest due to its possibly important role in high-temperature superconductivity. Doping holes into La_2NiO_4 or La_2CuO_4 rapidly suppresses the commensurate antiferromagnetism (AFM) of the parent compounds resulting in incommensurate ordering. In $La_{2-x}Sr_xNiO_4$ only 12% of Sr drive the system into a stripe phase [2,3]. The stripe phase in the nickelates is most robust close to 1/3 doping [3] where the spin-wave velocity is comparable to that in pure La_2NiO_4 [4,5]. Even less charges are necessary to suppress the commensurate AFM in the cuprates: already for $x \geq 0.02$ an incommensurate superstructure appears, which can be interpreted in the same stripe picture as that in nickelates [6], although alternative explanations have been proposed [7]. For larger Sr concentration, $x > 0.055$ this ordering is lost and samples become metallic and superconducting. Nevertheless, the inelastic magnetic correlations in $La_{2-x}Sr_xCuO_4$ are incommensurate and can be interpreted in terms of dynamic stripes, since the incommensurability matches the expected stripe modulation [8]. Upon codoping $La_{2-x}Sr_xCuO_4$ with a rare-earth ion [1] and in $La_{2-x}Ba_xCuO_4$ [9,10], however, static stripe ordering has been clearly established.

In analogy with the cuprates and nickelates, it appears interesting to analyze the possible existence of stripe phases in $La_{2-x}Sr_xCoO_4$ [11]. The parent compound La_2CoO_4 exhibits commensurate AFM order ($T_N = 275$ K) similar to La_2CuO_4 and La_2NiO_4 [12]. Furthermore, at half-doping, $La_{1.5}Sr_{0.5}CoO_4$, checkerboard charge ordering occurs at high temperature, coexisting with magnetic ordering below $T_{mag} \sim 40$ K [13,14]. We have performed neutron scattering experiments on the $La_{2-x}Sr_xCoO_4$ series which reveal an astonishingly robust commensurate AFM order at low doping and incommensurate magnetism at intermediate doping.

$La_{2-x}Sr_xCoO_4$ and $La_{2-x}Ca_xCoO_4$ single crystals of typically 1 cm^3 size were grown in an image furnace following Ref. [15]. The stoichiometry was verified by electron-microprobe analysis, by atomic absorption spectroscopy, and by single-crystal as well as by powder x-ray diffraction [16]. The samples were further characterized by resistivity and by magnetic susceptibility measurements indicating for $La_{1.5}Sr_{0.5}CoO_4$ the onset of charge ordering at $T_{CO} = 825(20)$ K and magnetic ordering below $T_{mag} = 50(5)$ 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_2CoO_4 exhibits a phase transition characterized by a tilt of the CoO_6 octahedrons [12] 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, for example, (0.5,0.5,4) see Fig. 1. Note that wave vectors $\mathbf{q}$ are given in reduced units of $\frac{2\pi}{a}$ with $a \sim 3.85$ Å. The polarization analysis excludes any magnetic contribution at this structural transition. However, below $T_{mag} = 130$ K we find additional superstructure scattering at $(0.5, 0.5, q_l)$ 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 $\mathbf{Q}$ 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] scattering plane. By measuring the three spin-flip channels for $\mathbf{P} \parallel \mathbf{x} = (0.5, 0.5, 0) = \mathbf{Q}$, $\mathbf{P} \parallel \mathbf{y} = (0, 0, 1) \perp \mathbf{Q}$, and $\mathbf{P} \parallel \mathbf{z} = (1, -1, 0) \perp \mathbf{Q}$, we may conclude that the ordered moment fully lies within the a, b plane, see Fig. 1(a). Magnetic ordering in $La_{1.7}Sr_{0.3}CoO_4$ is of the same commensurate nearest-

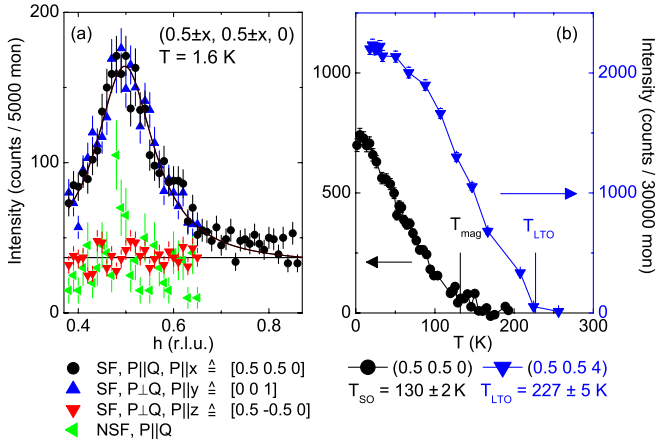

FIG. 1 (color online). Magnetic and structural scattering in $La_{1.7}Sr_{0.3}CoO_4$. (a) Spin-Flip (SF) and Non-Spin-Flip scattering (NSF) along $(\frac{1}{2} \pm x, \frac{1}{2} \pm x, 0)$ for neutron polarization **P** perpendicular or parallel **Q** at $T = 1.6$ K. (b) Temperature dependence of the magnetic $(\frac{1}{2}, \frac{1}{2}, 0)$ (multiplied by 10) and structural superstructure $(\frac{1}{2}, \frac{1}{2}, 4)$ peak intensities.

neighbor (nn) AFM type as that in La_2CoO_4, but the magnetic scattering is very broad with a Lorentzian width of $\kappa_{ab} = 0.18(2)$ Å^{-1} [17], and there is no detectable correlation along the c axis. The glasslike nature of the magnetic ordering is further seen in the magnetic susceptibility which continuously increases upon cooling through T_{mag} and which exhibits irreversibility effects only below 16 K [18]. To further characterize the commensurate AFM ordering in $La_{1.7}Sr_{0.3}CoO_4$, we have analyzed the dispersion of the magnetic excitations, which is well described by spin-wave theory taking only a nn Co^{2+}-Co^{2+} interaction into account [19].

The smaller impact of the Sr doping on the commensurate antiferromagnetism in $La_{2-x}Sr_xCoO_4$ 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 nonmagnetic impurity. The substitution of nonmagnetic impurities into layered magnets has been intensively studied [20], for example in $K_2(Co_{1-x}Mg_x)F_4$. In accordance with percolation theory long-range AFM order persists up to the critical concentration of $x_c = 0.41$ [21], whereas the ordering in $La_{1.7}Sr_{0.3}CoO_4$ is of short range. In $La_{2-x}Sr_xCoO_4$ 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 appears unlikely in $La_{1.7}Sr_{0.3}CoO_4$, as it should at most weakly perturb the AFM order. Stronger effects can be expected for the IS or LS Co^{3+} states where an efficient 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 $HoBaCo_2O_{5.5}$ [22]. 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 unfavorably.

Let us now turn to the charge and magnetic ordering in half-doped $La_{1.5}Sr_{0.5}CoO_4$, which has already been studied by Zaliznyak *et al.* [13,14] and which is illustrated in Fig. 2(a). In our crystal, we find the same quasi-two-dimensional superstructure reflections and perfect agreement concerning temperature dependencies, $T_{\mathrm{mag}} = 48(2)$ K deduced from the magnetic reflection, and low-temperature correlation lengths, $\xi_{ab} = 68(3)$ Å, $\xi_c = 13.1(4)$ Å, and $\xi_{ab\text{-charge}} = 19(1)$ Å. The magnetic ordering does not occur exactly at the commensurate propagation vector of (0.25,0.25,1) but slightly offset at $\mathbf{q} = (0.25 + \delta, 0.25 + \delta, 1)$ with $\delta = 0.0057(8)$ which is somewhat smaller than the values observed previously

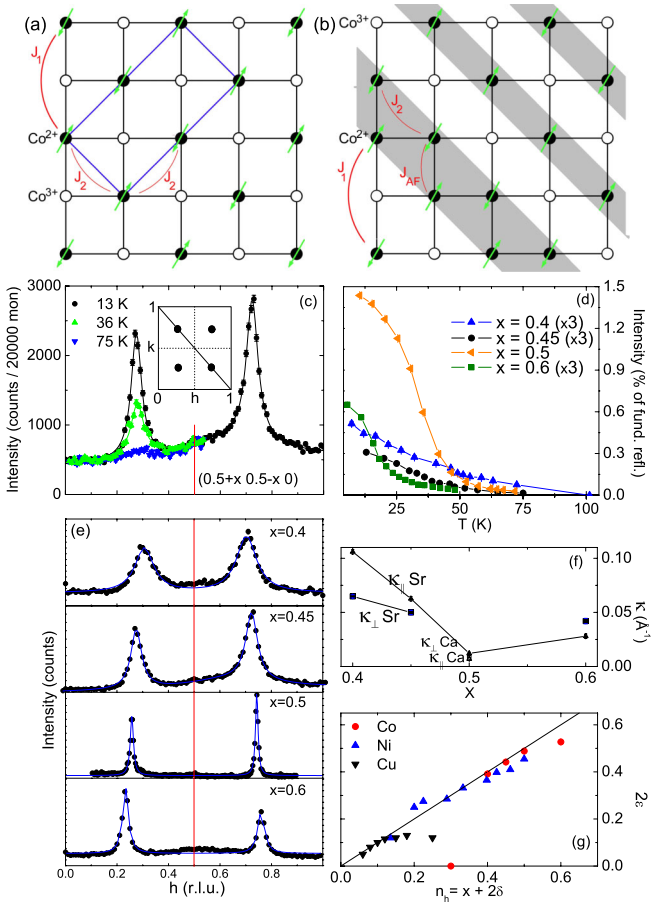

FIG. 2 (color online). (a) Magnetic order in the checkerboard charge-ordered phase in $La_{1.5}Sr_{0.5}CoO_4$ with only Co^{2+} contributing (filled circles); (b) the insertion of an additional Co^{2+} row stabilizes magnetic order through the nn exchange J_{AF}. (c) Elastic magnetic scattering in $La_{1.55}Sr_{0.45}CoO_4$ (the scan direction in the $(hk0)$ plane is shown in the inset); (d) peak heights of the magnetic superstructure and (e) elastic scans in $La_{2-x}Sr_xCoO_4$; (f) in-plane inverse correlation lengths parallel and perpendicular to the modulation for $La_{2-x}Sr_xCoO_4$ and $La_{1.5}Ca_{0.5}CoO_4$; (g) magnetic incommensurability as a function of Sr content compared with those in $La_{2-x}Sr_xCuO_4$ [8] and in $La_{2-x}Sr_xNiO_4$ [2,3].

[13,14]. The charge and magnetic order is presumably associated with orbital order, but the nature of the latter remains controversial. In Ref. [13], the Co^{3+} sites are proposed to be nonmagnetic, and an analysis of the superstructure is interpreted by a Co^{3+} IS spin-state [14] whereas a HS state was deduced from magnetic susceptibility data [11]. Our own structural analysis [16] supports the interpretation of the LS state corroborated by a quantitative analysis of the anisotropic magnetic susceptibility [18]. The magnetic structure with nonmagnetic Co^{3+} sites, depicted in Fig. 2(a), perfectly describes the elastic peaks [13] as well as the full spin-wave dispersion in $La_{1.5}Sr_{0.5}CoO_4$, which we have determined [23] extending a previous study [24,25].

In Figs. 2(c)–2(g) we summarize 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 $x = 0.4$. The corresponding peaks are also observed at $(\frac{1}{2} \pm \epsilon, \frac{1}{2} \pm \epsilon, 3)$ using a different scattering plane. These reflections perfectly agree with the diagonal stripe ordering occurring in the $La_{2-x}Sr_xNiO_4$ series. In this picture the Co^{3+} or Ni^{3+} ions segregate into charged stripes running along [110] separating AFM stripes, see Fig. 2(b). In consequence, the magnetic modulation ϵ is determined by the doped charge concentration: $2\epsilon = x$. Comparable magnetic superstructure reflections appear in all $La_{2-x}Sr_xCoO_4$ crystals of intermediate doping, $x = 0.4$, 0.45, 0.5, and 0.6, with the position following the $2\epsilon = x$ rule. Note that the perfect checkerboard ordering 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 modulation suggests to consider these incommensurate phases as stripe phases similar to nickelates and cuprates, but other interpretations cannot be excluded. Alternatively, the incommensurate magnetic ordering may be interpreted as an incommensurate ordering with spiral or helicoidal character [7], which, however, leaves the $2\epsilon = x$ relation unexplained.

In Fig. 2(g) we compare the incommensurate modulation vector for cobaltates, nickelates, and cuprates. For $La_{2-x}Sr_xCuO_4$ we take the modulation of the inelastic correlation which, however, directly reflects that in static stripe phases [8]. The cuprate modulation for vertical stripes is multiplied by a factor of 2 because the hole occupation in the cuprate stripes amounts only to one-half. The three systems combined follow the ideal linear relation, but in each of them a saturation of the stripe distance sets in at large x [3]. In the cuprates the incommensurability already starts to saturate around $x \sim 0.14$, whereas it saturates only around $x \sim 0.5$ in $RE_{2-x}Sr_xNiO_4$ [3,27]. In cuprates stripelike phenomena are observed already for small hole doping, whereas incommensurate ordering 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 strongest in agreement with their much higher electronic resistivity and the spin-blockade mechanism [11,22].

The phase diagram of $La_{2-x}Sr_xCoO_4$, see Fig. 3, qualitatively resembles those of $La_{2-x}Sr_xNiO_4$ and $La_{2-x}Sr_xCuO_4$ [3,6,8]. In all systems the nn AFM order transforms into modulated order which is stabilized near a commensurate value. The magnetic transition temperatures in the cobaltates are comparable to those found in the codoped cuprates but significantly lower than those in the nickelates stripe phases, for example $T_N \sim 150$ K in $La_{1.67}Sr_{0.33}NiO_4$ [3]. There is a clear trend that the magnetic transition in $La_{2-x}Sr_xCoO_4$ continuously decreases with the doping corroborating the interpretation that the Co^{3+} are magnetically not active.

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. 4. There is sizable diffuse scattering around $\mathbf{q} = (0.5, 0.5, 0)$ in $La_{1.6}Sr_{0.4}CoO_4$, which is absent in the same scan on a $La_{1.6}Ca_{0.4}CoO_4$ crystal 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 dominant 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 [28].

Similar to the most stable stripe phases appearing in cuprates and nickelates at hole-doping levels of $x = 1/8$ and $1/3$ [1,3,10], respectively, there exists a most stable composition for charge and 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

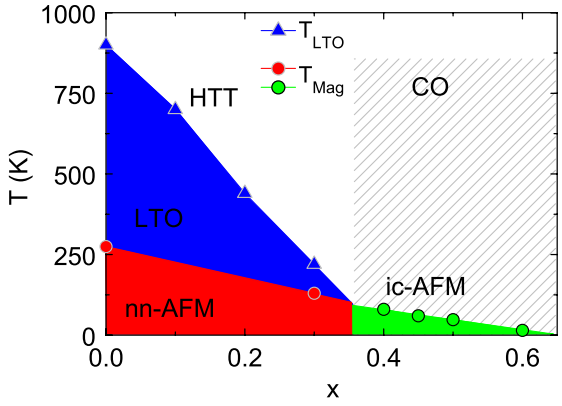

FIG. 3 (color online). Phase diagram of $La_{2-x}Sr_xCoO_4$. Structural transition temperatures between the tetragonal (HTT) and LTO phases were determined by powder x-ray diffraction [30], T_N of pure La_2CoO_4 was taken from [12]. Magnetic transition temperatures at finite Sr content were determined extrapolating a linear fit to the superstructure intensities.

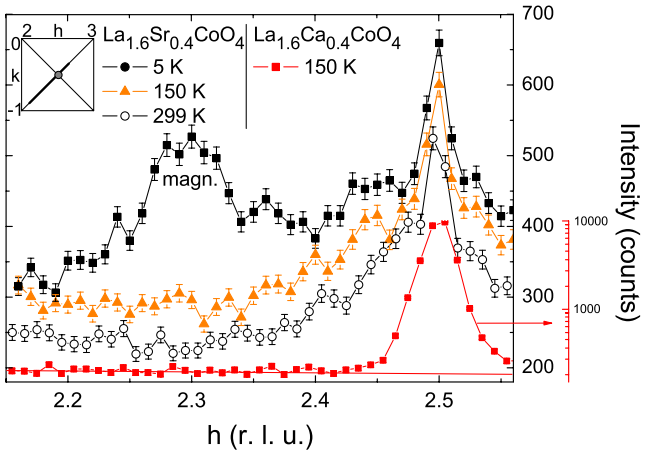

FIG. 4 (color online). Scans across the positions where incommensurate or commensurate scattering related with charge order is expected in $La_{1.6}Sr_{0.4}CoO_4$ and in $La_{1.6}Ca_{0.4}CoO_4$.

lengths and the largest peak heights in comparison to a fundamental reflection, see Fig. 2. Because the correlation lengths for concentrations away from half-doping are reduced, the integrated magnetic intensity varies much less within the series. For $x = 0.5$ the magnetic ordering is clearly seen in the magnetic susceptibility, [16,24], and the charge order causes an anomaly in the temperature dependence of the resistivity [16]. The fact that, nevertheless, the magnetic ordering is not fully commensurate (with similar deviations in different crystals [13,14]) suggests that there is an underlying intrinsic effect similar to $La_{1.5}Sr_{0.5}NiO_4$ where the deviation from commensurability is, however, 6 times larger [27].

Considering the perfect checkerboard ordering, the next-nearest-neighbor Co^{2+}-Co^{2+} interaction (J_1; linear Co^{2+}-O-Co^{3+}-O-Co^{2+} path, distance $2a$ and the nn Co^{2+}-Co^{2+} interaction (J_2; distance $\sqrt{2}a$ are frustrated as both interactions are AFM. In a mean-field approach the quarter-indexed structure shown in Fig. 2(a) is stabilized for $J_1 > \frac{1}{2}J_2$. However, J_1 couples only half of the Co^{2+} sites in a single plane [see Fig. 2(a)]. Since in addition, J_2 is almost fully frustrated [29], the degenerate in-plane order is not very stable. This instability might be the reason for the magnetic ordering to occur slightly away from the commensurate value expected for $x = 0.5$. 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. 2(b).

In conclusion we have studied the magnetic correlations as a function of doping in the $La_{2-x}Sr_xCoO_4$ series. Because of an efficient trapping of the charge carriers the commensurate AFM ordering is much more stable than in the isostructural cuprates and nickelates persisting up to $x = 0.3$, but at higher doping incommensurate magnetic order develops similar to stripe phases.

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*braden@ph2.uni-koeln.de

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