

**$^{23}\text{Na}$  NMR Evidence for Charge Order and Anomalous Magnetism in  $\text{Na}_x\text{CoO}_2$** I. R. Mukhamedshin,<sup>1,\*</sup> H. Alloul,<sup>1,†</sup> G. Collin,<sup>2</sup> and N. Blanchard<sup>1</sup><sup>1</sup>*Laboratoire de Physique des Solides, UMR 8502, Université Paris-Sud, 91405 Orsay, France*<sup>2</sup>*Laboratoire Léon Brillouin, CE Saclay, CEA-CNRS, 91191 Gif-sur-Yvette, France*

(Received 23 January 2004; published 13 October 2004)

Oriented powder samples of  $\text{Na}_x\text{CoO}_2$  are studied by  $^{23}\text{Na}$  NMR and SQUID magnetometry. In nominal  $0.50 \leq x \leq 0.70$  solid state reacted samples the dominant phase synthesized has a single composition  $x_0 \approx 0.70$ . Three Na sites are identified from their single valued quadrupole effects and magnetic shifts, which implies a very definite order of the  $\text{Na}^+$  ions and of the Co charges in the  $\text{CoO}_2$  planes. The local susceptibility of the magnetic cobalt sites displays a large enhancement below 100 K with respect to the usually found high  $T$  Curie-Weiss law. This contrasts with the Pauli-like magnetism detected for  $x \approx 0.35$ , the parent of the superconducting hydrated compound.

DOI: 10.1103/PhysRevLett.93.167601

PACS numbers: 76.60.-k, 71.27.+a, 75.20.Hr

The discovery of a new family of layered transition metal oxides, the cobaltates, which display strong electric thermopower [1], metallicity, and superconductivity [2], has triggered a large interest. In  $\text{Na}_x\text{CoO}_2$ , the  $\text{CoO}_2$  layers have a hexagonal 2D crystal structure with a trigonal distortion yielding a large crystal field and a low spin configuration for the Co ions. Those can be stabilized in  $3^+$  or  $4^+$  charged states which correspond to spin  $S = 0$  and  $S = \frac{1}{2}$ , respectively. The cobalt-oxygen subsystem can be considered either as a Mott-Hubbard  $\text{CoO}_2$  insulator doped with  $x$  electrons or as a band insulator  $\text{NaCoO}_2$  doped with  $1 - x$  holes. One expects then more magnetism for low  $x$  in contradiction with existing data, which exhibit magnetic phases [3,4] for  $x \geq 0.75$ . Important questions are therefore raised about the interplay of transport properties [5,6] with the magnetic properties. In a pioneering work, two  $^{59}\text{Co}$  NMR signals attributed to nonmagnetic  $\text{Co}^{3+}$  sites were detected [7] in a  $x = 0.5$  sample, and the question whether electrons hop on all Co sites or local  $\text{Co}^{3+}$ - $\text{Co}^{4+}$  charge segregation occurs was addressed. However, the impossibility of detecting the magnetic Co site prevented Ray *et al.* from deciding whether a charge ordered state occurs or not. In a  $x = 0.7$  sample, a singular behavior of the  $^{23}\text{Na}$  NMR spectrum at 295 K was interpreted as the onset of such a Co charge segregation [8]. Finally, recent ESR and NMR measurements indicate intrinsic *inhomogeneous* behavior in cobaltites [9]. It is then critical to understand [10] whether charge segregation depends on Na content, and whether charge order occurs in some cases. Indeed, the variety of ground states that are envisioned [11] depend on the details of the electronic structure.

In this work, a significant effort in material synthesis and characterization enabled us to provide aligned single phase powder samples. The resolution of the various Na sites by NMR in a pure  $x \sim 0.70$  phase allows us to demonstrate unambiguously the occurrence of a *charge ordered* state of the Co accompanied by an ordering of the  $\text{Na}^+$  ions. The hyperfine coupling of the  $^{23}\text{Na}$  nuclear spin with the magnetic Co sites is small enough to ensure that

all  $^{23}\text{Na}$  spins are detected, and still sizable to allow us to track the spin susceptibility  $\chi_s$  of the  $\text{CoO}_2$  planes down to 1.3 K. We could therefore, for the first time, characterize with a local probe the ground state for two key compositions. For  $x \sim 0.70$  an anomalously large  $T$  variation of  $\chi_s$  of the magnetic cobalt eventually reaches a Fermi liquid behavior below 1.5 K, while a nearly  $T$  independent Pauli  $\chi_s$  is found for  $x \sim 0.35$ .

Samples have been synthesized by mixing powders of  $\text{NaCO}_3$  and  $\text{Co}_3\text{O}_4$  with nominal Na content  $0.5 < x \leq 0.7$ , rapid heating, and solid state reaction at 860–900 °C. Both x-ray and  $^{23}\text{Na}$  NMR data indicated that the dominant synthesized phase corresponds to a single composition  $x_0$  plus an excess of cobalt oxides. The occurrence of unreacted  $\text{Co}_3\text{O}_4$  was evidenced by its  $^{59}\text{Co}$  NMR signal, its x-ray diffraction peaks ( $\theta = 31.28^\circ, 36.86^\circ, 59.34^\circ, 65.22^\circ$ ), as well as a maximum in its contribution to the SQUID susceptibility  $\chi_m$  at its Néel temperature of 30 K.  $\text{Co}_3\text{O}_4$  becomes undetectable for  $x = 0.7$ , so that the majority phase corresponds to  $x_0 \approx 0.7$ . It displays a gamma phase unit cell with  $c$  lying between 10.91 and 10.93 Å, in agreement with recent data [12]. At room  $T$ , Rietveld refinement on one  $x_0 \approx 0.7$  NMR sample gives 0.21(1) occupancy for the Na(1) site at  $(0, 0, \frac{1}{4})$  and 0.48(1) for the Na(2) site at  $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ . The Na content was reduced in such a sample by reaction with Br and acetonitrile (40N) at room  $T$  during four days. The sample appeared free from impurity phases from x rays and was indexed in the  $P6_3/mmc$  group with  $a = 2.8076(2)$  Å and  $c = 11.2086(4)$  Å corresponding to  $x \approx 0.35$  [12]. After water insertion the sample displayed superconductivity with  $T_c = 3.1$  K.

As the room  $T$  susceptibility is known to be anisotropic [5], we aligned, in a 7 T field, the powders mixed with Stycast 1266 epoxy which cured in the field. NMR spectra were obtained by pulse NMR at fixed frequency, the spin echo intensity being measured after two  $2 \mu\text{s}$  radio frequency pulses separated by 100  $\mu\text{s}$ , while the field was increased by steps. A typical  $^{23}\text{Na}$  NMR spectrum ob-

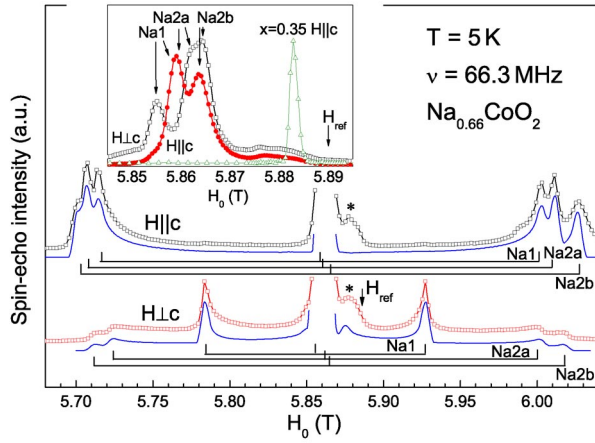


FIG. 1 (color online).  $^{23}\text{Na}$  NMR spectra taken in two field directions in  $\text{Na}_{0.66}\text{CoO}_2$ . The fully resolved quadrupole structure for the three Na sites is discussed in the text. The weak extra line (\*) with small Knight shift represents at most 5%–10% of all Na nuclei and might be assigned to defect sites in the ordered Na structure. The inset displays an enlarged view of a slow scan through the central lines for  $\text{Na}_{0.66}\text{CoO}_2$  and  $\text{Na}_{0.35}\text{CoO}_2$  (the intensities are not to scale).

tained below 150 K, when Na atomic motion is frozen [8], is displayed in Fig. 1. Here, the crystal field lifts the degeneracy of the Zeeman levels of the  $^{23}\text{Na}$  nuclear spin ( $I = \frac{3}{2}$ ). The  $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$  and  $\frac{1}{2} \leftrightarrow \frac{3}{2}$  transitions split symmetrically of  $\Delta\nu$  with respect to the central  $-\frac{1}{2} \leftrightarrow \frac{1}{2}$  transition, with

$$\Delta\nu = \nu_Q(3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\varphi)/2, \quad (1)$$

where  $\theta$  and  $\varphi$  are the polar coordinates with respect to the external field  $H_0 \parallel z$  of the principal axes  $X, Y, Z$  of the electric field gradient (EFG) tensor  $V_{ij}$  associated with the local structure. Here  $\nu_Q = 3eQV_{ZZ}/(h2I(2I - 1))$  is defined by the nuclear quadrupole moment  $Q$  and the largest principal axis component of the EFG tensor  $V_{ZZ}$ , and  $\eta = |(V_{YY} - V_{XX})/V_{ZZ}|$  is the asymmetry parameter. In the typical spectra of Fig. 1, for  $H_0 \parallel c$ , one can clearly distinguish three pairs of quadrupole transitions which correspond to three Na sites with distinct local environments. In our samples the  $c$  axes of the crystallites are aligned, but the  $a$  or  $b$  axes and therefore  $\varphi$  are at random. The narrow width of the transitions indicate from Eq. (1) that  $\theta \approx 0$  and that the largest principal axis of the EFG tensor is parallel to the  $c$  axis for the three resolved sites. For  $H_0 \perp c$ , only one pair of transitions remains narrow, then  $\eta = 0$  for this site, which will be labeled Na1 hereafter. The broad quadrupole transitions for  $H_0 \perp c$  correspond to two Na sites labeled Na2a and Na2b with slightly distinct EFG tensors and large  $\eta$  values. The full simulation of the spectra displayed in Fig. 1 agrees in nearly all details with the experimental one. It allows one to deduce  $\nu_Q \approx 1.645(5)$  MHz,  $\eta \approx 0.01(1)$  for Na1, and  $\nu_Q \approx 1.74(1)$  MHz,  $\eta \approx 0.84(2)$  and  $\nu_Q \approx$

1.86(1) MHz,  $\eta \approx 0.89(2)$ , respectively, for Na2a and Na2b. These values of  $\nu_Q$  were found to decrease by less than 5% from 5 to 100 K. The singular shape of the satellites is associated with a distribution of crystallite orientations fitted by a Lorentzian with mean deviation  $\theta \approx \pm 5^\circ$ . The nearly identical intensities (1.1/1.0/0.9) of the three  $^{23}\text{Na}$  lines allows us to assign the Na1 NMR to Na(1) vertically aligned with two Co, and Na2a and Na2b to Na(2) on top of the Co triangle centers in adjacent  $\text{CoO}_2$  planes. The fact that only three sites are observed definitely proves that the neighboring charges of the Na sites are ordered.

We performed calculations in a point charge model which applies on the fully ionized Na site, and had no difficulty to get the right order for the magnitude of the EFG values. But  $V_{ZZ}$  was found to be quite sensitive to the Na charge order chosen. For  $x = 0.66$  or  $x = 1$ , the contributions  $V_{ZZ}(\text{Co/O})$  and  $V_{ZZ}(\text{Na})$  of the  $(\text{Co}^{n+}/\text{O}^{2-})$  and the  $\text{Na}^+$  charges, respectively, were always found such that  $0.3 < |V_{ZZ}(\text{Na})/V_{ZZ}(\text{Co/O})| < 1.5$ , whatever  $3 \leq n \leq 4$ . As the  $\text{Na}^+$  contribute so largely to the EFG, our experiment proves that they are ordered in our  $x_0 \approx 0.7$  phase. Isolated Na1 and Na2 sites have a three-fold  $c$  axis symmetry with respect to the  $\text{CoO}_2$  plane, which yields EFGs with  $\eta = 0$  for the  $\text{Co}^{n+}/\text{O}^{2-}$  charges. The fact that  $\eta = 0$  for Na1 proves that the Na ordering keeps a high symmetry as well. The lower symmetry of the EFG at the Na2 sites might correspond to a displacement from its ideal location at the vertical of the center of the Co triangles, as proposed by x-ray refinements [13], or/and to a symmetry breaking charge ordering of the Na or the Co plane (i.e.,  $\text{Co}^{3+}/\text{Co}^{4+}$ ). The Na ordering remains to be identified by structural techniques as done by electron diffraction on single crystals for  $x = 0.5$ , the specific phase obtained by Na deintercalation [12]. Our data would then help us to better characterize the Co charge order, hardly detectable by diffraction techniques. An independent proof of the occurrence of such a charge order will be given hereafter from the NMR shifts which relate to local magnetic data.

As seen in the inset of Fig. 1, the central transitions of the three Na sites are resolved at low  $T$ , but merge with increasing  $T$ , as their magnetic shifts decrease drastically. These spectra were found identical whatever the nominal  $x$ , which confirms that Na enters the single  $x_0 \approx 0.7$  phase. In Fig. 2 we report the large  $T$  variation of the shifts of these lines, referred to as  $^{23}\text{Na}$  NMR of NaCl in solution. For a field orientation  $\alpha$ , the shift  $K_\beta^\alpha$  of a Na nuclear site  $\beta$  is determined by the magnetic spin susceptibilities  $\chi_{s,i}^\alpha(T)$  of the neighboring Co atoms  $i$

$$K_\beta^\alpha = K_{\beta,\text{orb}}^\alpha + \sum_i A_{\beta,i}^\alpha \chi_{s,i}^\alpha(T). \quad (2)$$

Here  $K_{\beta,\text{orb}}^\alpha$  are the usually  $T$  independent orbital contributions which will be shown to be small hereafter. The spin contribution to the shift is single valued in a uniform

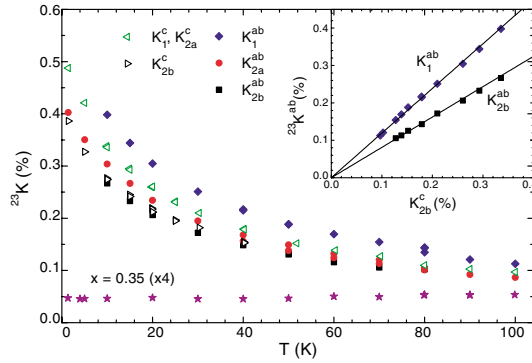


FIG. 2 (color online). Variation with  $T$  of the shifts of the three Na sites. In the inset these shifts are shown to scale perfectly. The shift of  $^{23}\text{Na}$  ( $\times 4$ ) in  $\text{Na}_{0.35}\text{CoO}_2$  is found practically  $T$  independent.

system, but in our  $x_0 \approx 0.7$  sample, charge segregation is ensured as we could detect a  $^{59}\text{Co}$  NMR signal [14], with a weakly  $T$  dependent shift, quite similar to that of Ref. [7]. So the  $^{59}\text{Co}$  nuclear spins of the nonmagnetic sites, presumably  $\text{Co}^{3+}$ , and the  $^{23}\text{Na}$  nuclear spins are only weakly coupled by transferred fields to the magnetic Co responsible for the strongly  $T$  dependent  $\chi$ . Their  $^{59}\text{Co}$  NMR signal has not been detected up to now.

In the inset of Fig. 2 the shifts of the Na lines are shown to scale linearly with each other. As the linear fits extrapolate to zero within experimental accuracy, the  $T$  independent contributions either from  $\text{Co}^{3+}$  sites or from  $K_{\beta,\text{orb}}^\alpha$  are small and do not differ markedly for the three Na sites. The linear fits give  $K_2^c = 0.80(2)K_1^c$ ,  $K_1^{ab} = 1.10(2)K_1^c$ ,  $K_{2a}^{ab} = 1.03(2)K_2^c$ , and  $K_{2b}^{ab} = 0.97(2)K_2^c$ . While Na1 has a slightly anisotropic shift, the Na2a and Na2b shifts are more isotropic, but overall the local fields detected by the three sites are quite similar.

An examination of the local structure done in Fig. 3 indicates that the  $A_{\beta,i}^\alpha$  couplings occur through a sequence of Na-O-Co orbitals, e.g., Na1 couples to its first nn Co through three O and to its second nn through one O. So, each Na site couples to many Co atoms and the unique  $T$  variation of the shifts should be assigned to a single magnetic Co. In an ionic description, for  $x_0 \approx 0.7$ , those would be  $\approx 30\%$   $\text{Co}^{4+}$ . If they were located at random, a given Na site would sense a variety of statistical configurations of nn  $\text{Co}^{4+}$ . So, the absence of splitting of the NMR of each Na site gives evidence for a well defined local order of their magnetic neighboring cobalts. To illustrate this, we consider in Fig. 3, as an example, the expected [10] ordering for  $x = 2/3$ , in which  $\text{Co}^{3+}$  are on a honeycomb lattice and  $\text{Co}^{4+}$  on a  $\sqrt{3} * \sqrt{3}$  triangular lattice. Here the only two possible magnetic configurations for the Na1 sites, located at the vertical of either a  $\text{Co}^{3+}$  or a  $\text{Co}^{4+}$ , would obviously display different NMR shifts. So a unique Na1 line implies that only one of these two occur in the crystal; i.e., Na1 is nn of a single Co species, presumably  $\text{Co}^{3+}$  to reduce coulomb repulsion.

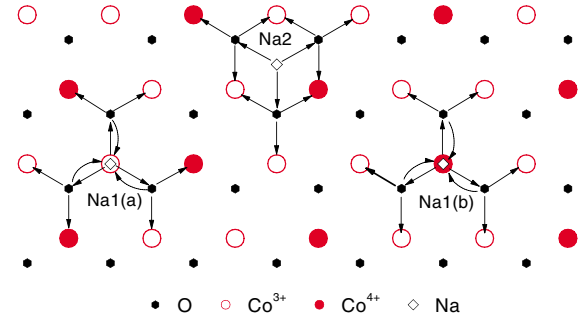


FIG. 3 (color online). The magnetic hyperfine coupling paths of the Na1 and Na2 sites to their neighboring Co through the intermediate layer oxygens are shown by arrows. Those are independent of the Co charges. The model of  $\text{Co}^{3+}$ - $\text{Co}^{4+}$  charge ordered state usually expected [10] for  $x = 2/3$  is displayed. The only possible Na1 and Na2 sites with respect to the magnetic cobalts are shown. The Na ordering is not considered in this figure which is not intended to discuss EFGs.

As Na couples to two  $\text{CoO}_2$  layers, this further implies that the Co configurations in neighboring layers are correlated. So both  $K_s$  and the EFGs allow us to demonstrate unambiguously for  $x_0 \approx 0.7$  the existence of a 3D local charge order which involves the  $\text{Na}^+$  and at least two distinct Co, one of them being magnetic.

As the shifts for all Na sites display the same  $T$  variation, with  $K_{\text{orb}}^\alpha \approx 0$ , the first moment (center of gravity) of the NMR spectrum  $K_s = A\chi_s(T)$  allows us to follow the spin susceptibility  $\chi_s(T)$  of the magnetic Co site up to room  $T$ , even when the lines merge (Fig. 4). The data for  $K_s^{-1}$  depart at low  $T$  from the Curie-Weiss law  $K_s = C/(T - \theta)$ , with  $\theta \approx -90$  K. High  $T$  fits of our macroscopic SQUID data with  $\chi_m = \chi_0 + C'/(T - \theta)$  confirm [5,12] similar values of  $\theta$  for various  $x$  values. Here  $\chi_0$  involves the  $T$  independent contributions of the diamagnetism of the ion cores and of the orbital susceptibility of the Co ions. Contrary to the spectroscopic NMR shift,  $\chi_m$  data are usually contaminated at low  $T$  by the contribution of cobalt oxides, e.g., that of  $\text{Co}_3\text{O}_4$  which displays a maximum at 30 K. In our sample with minimal  $\text{Co}_3\text{O}_4$  content,  $\chi_m - \chi_0$  displays below 100 K an increase which agrees (Fig. 4) with that found by NMR. The scaling between  $K_s$  and  $\chi_m - \chi_0$  yields an effective hyperfine field  $H_{hf} = A\mu_B N_a = 7.45 \text{ kG}/\mu_B$ . This upturn of  $K_s$  at low  $T$  tends to saturate below 3 K (inset of Fig. 4). Such a behavior of  $\chi_s$ , detected by a local probe is intrinsic to the physics of the cobaltate planes. No anomaly is found either in the linewidth or in the signal intensity; hence *no magnetic transition occurs down to 1.5 K*.

In the  $\text{Na}_{0.35}\text{CoO}_2$  aligned powder sample, the  $^{23}\text{Na}$  quadrupolar spectrum could not be resolved in any direction which might indicate a large distribution of EFG values and Na disorder. The single  $^{23}\text{Na}$  central line detected (inset of Fig. 1) exhibits a weak  $T$  independent  $^{23}\text{Na}$  shift (Fig. 2). As the  $c$  axis unit cell is only slightly larger than for  $x_0 \approx 0.7$ , the hyperfine coupling  $A$  should

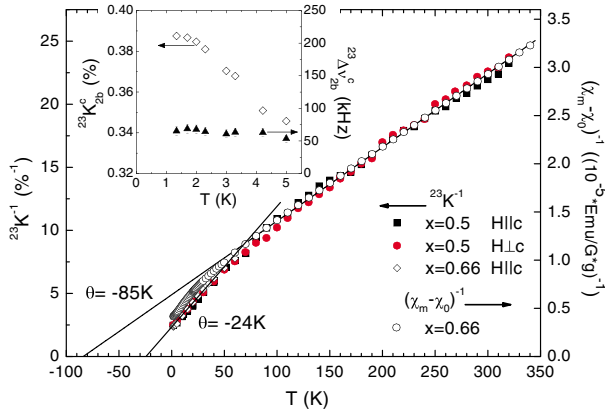


FIG. 4 (color online). The  $T$  variation of the inverse of the mean shift of the Na lines is identical for two samples with different nominal  $x$ . The large low  $T$  enhancement of the spin susceptibility is evidenced by the  $\theta$  values obtained for Curie-Weiss fits taken on either side of 100 K. A similar variation is found for the  $T$  dependent contribution to the macroscopic susceptibility. Inset: low  $T$  variation of the  $^{23}\text{Na}$  NMR shift and width.

be similar, so that  $\chi_s \approx 10$  times smaller than for  $x_0$  at room  $T$ . This weak Pauli-like magnetism does not differ from that expected from local-density approximation (LDA) calculations. In analogy with the cuprates,  $x = 0.35$  would correspond to an overdoped case, in which the correlations are not prominent. Such a weakly magnetic metallic state seems to hold up to  $x = 0.5$  for which a remarkable but not yet understood metal insulator transition occurs [12].

On the contrary, our results for  $x_0 \approx 0.7$  reveal a very intriguing metallic phase with a magnetism which resembles at high  $T$  that of local moments with large antiferromagnetic (AF) interactions, and at low  $T$  that of heavy fermions with a Kondo temperature  $\lesssim 10$  K. The data lead us to anticipate that a Fermi liquid behavior would be reached only below 1.5 K. Comparison of  $\chi_s$  at the lowest  $T$  with the specific heat  $C/T \approx 30$  mJ/(mole K<sup>2</sup>) measured in comparable samples [6] gives a large value for the Wilson ratio  $R = (T\chi_s/C) \times (\pi^2 k_B^2 / 3\mu_B^2) = 7.8$ , which reveals that a simple effective mass enhancement as obtained in heavy fermion compounds does not describe the anomalous magnetic properties of this correlated electron system. Although such a value of  $R$  would be compatible with a tendency towards ferromagnetism predicted by LDA [15], these calculations do not consider simultaneous charge ordering and AF couplings.

As a small change of  $x$  from  $\approx 0.7$  to 0.75 changes the system to an AF state [3,4], with  $T_N = 22$  K, the Co charge ordering evidenced here for the first time appears essential in driving the magnetic properties. We illustrated it with the classical  $\text{Co}^{3+}/\text{Co}^{4+}$  ionic model of Fig. 3, in which electron hopping from the  $\text{Co}^{3+}$  to the  $\text{Co}^{4+}$  sites is inhibited, yielding a half-filled Mott-

Hubbard  $\text{Co}^{4+}$  triangular lattice. Whether such a state would exhibit metallic properties due to delocalization of the  $\text{Co}^{4+}$  holes is an open question. The actual charge order might correspond as well to  $\text{Co}^{3+}/\text{Co}^{(4-z)+}$ , with  $z$  electrons delocalized on the magnetic Co sites in a strongly correlated band. So our work raises the question whether the AF state for  $x \geq 0.75$  results as well from a Co charge ordered state. Our work should stimulate efforts to produce samples with controlled electron doping of the  $\text{CoO}_2$  planes between these two phases to decide whether progressive changes occur with the occurrence of a quantum critical point (QCP). If so, we might speculate that the anomalous magnetic properties of our  $x_0 \approx 0.7$  phase result from quantum fluctuations and frustration in the proximity of such a QCP.

Another important question raised by our work concerns the role of Na ordering, which is evidenced at least for  $x = 0.5$  and  $x_0 \approx 0.7$  and results in distinct physical properties. Although, in the former case [12], it is not clear whether Co charge order does occur, this might be likely. Is the Co charge order an intrinsic property of the  $\text{CoO}_2$  planes which governs ground state properties, and drives the Na ordering as a side effect, or conversely? In the former case, disordering the Na sites would not change the physics. The answer to these questions cannot be given solely from NMR data. Our results should stimulate structural determinations of the Na order for the various phases.  $^{23}\text{Na}$  and  $^{59}\text{Co}$  NMR experiments in the lines of those presented here would then differentiate the Co charge orders. This would be an extremely important step towards understanding the physics of the various original ground states evidenced so far.

We acknowledge stimulating discussions and help in experiments from J. Bobroff, D. Bono, and P. Mendels.

\*Permanent address: Physics Department, Kazan State University, 420008 Kazan, Russia.

†Electronic address: alloul@lps.u-psud.fr

- [1] I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B **56**, R12 685 (1997).
- [2] K. Takada *et al.*, Nature (London) **422**, 53 (2003).
- [3] T. Motohashi *et al.*, Phys. Rev. B **67**, 064406 (2003).
- [4] J. Sugiyama *et al.*, cond-mat/0310516.
- [5] Y. Wang, N. S. Rogado, R. J. Cava, and N. P. Ong, Nature (London) **423**, 425 (2003).
- [6] M. Brühwiller, B. Batlogg, S. M. Kazakov, and J. Karpinski, cond-mat/0309311.
- [7] R. Ray, A. Ghoshray, K. Ghoshray, and S. Nakamura, Phys. Rev. B **59**, 9454 (1999).
- [8] J. L. Gavilano *et al.*, Phys. Rev. B **69**, 100404(R) (2004).
- [9] P. Caretta *et al.*, cond-mat/0312284.
- [10] O. I. Motrunich and P. A. Lee, cond-mat/0310387.
- [11] G. Baskaran, cond-mat/0303649; cond-mat/0310241.
- [12] M. L. Foo *et al.*, cond-mat/0312174.
- [13] J. D. Jorgensen *et al.*, Phys. Rev. B **68**, 214517 (2003).
- [14] I. R. Mukhamedshin *et al.* (to be published).
- [15] D. J. Singh, Phys. Rev. B **61**, 13 397 (2000).