# Influence of Charge order on the Magnetic Properties of Na$_x$CoO$_2$ for $x > 0.65$

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We have synthesized and characterized the four different stable phases of Na ordered Na$_x$CoO$_2$, for $0.65 < x \lesssim 0.75$. Above 100K they display similar Curie-Weiss spin susceptibilities as well as ferromagnetic $q = 0$ spin fluctuations in the CoO$_2$ planes revealed respectively by $^{23}$Na NMR shift and spin lattice $T_1$ data. The Co disproportionate already above 300K into Co$^{3+}$ and $\approx$Co$^{3.5+}$ in all phases, which allows us to understand that magnetism is favoured. Below 100K the paramagnetic properties become quite distinct, and a 3D magnetic order sets in only for $x = 0.75$, so that charge order has a subtle incidence on the low $T$ energy scales and transverse magnetic couplings.

The lamellar cobaltates display diverse physical properties including high thermoelectric power, superconductivity, Curie-Weiss [1] and ordered antiferromagnetism (AF) [2], which are controlled for instance by the Na content inserted between the CoO$_2$ layers. Their electronic properties are expected to be constructed from the low spin states of Co$^{3+}$ ($S = 0$) and Co$^{4+}$ ($S = 1/2$) ions in the large crystal field which prevails in the edge sharing Co oxygen octahedra building the Co triangular lattice. By analogy with the cuprates, AF is expected for the hypothetical CoO$_2$ half filled Mott-Hubbard insulator and should disappear with increasing $x$. Unexpectedly, AF phases are found far from this Mott limit, for $x \geqslant 0.75$ [3], which rather corresponds to hole doping of Na$_1$CoO$_2$. This band insulator is built from the non magnetic Co$^{3+}$ state [4], for which the $t_{2g}$ multiplet is filled by the six $d$ electrons. The hole doped AF phases are ferromagnetic in plane and AF between planes (A type AF) [5, 6]. The 3D dispersion of the spin wave excitations found by Inelastic Neutron Scattering (INS) has been analyzed with Heisenberg Co-Co AF coupling between planes either with nearest [5, 6] or next nearest neighbour exchange through Na orbitals [7].

While all these approaches assume a homogeneous state for the Co sites, $^{23}$Na NMR allowed us to demonstrate that Na atomic order sets in for a specific $x_0 \approx 0.7$ phase, together with a disproportionated Co charge order [8]. In this metallic Curie Weiss phase, fixed non magnetic Co$^{3+}$ sites coexist with holes delocalized on magnetic Co sites with an average valence $\approx$Co$^{3.5+}$ [9]. Is this restricted to the Na ordering of this $x_0 \approx 0.7$ phase? This open question is all the more important as Na atomic order patterns have been suggested, or seen [10, 11] for various $x$ values. Are the singular magnetic properties driven by specific Na orders? Such a scenario appears likely as a distinct in plane AF order sets in at $T_N = 86$K for the singular $x = 0.5$ phase [3, 12], and is followed by a metal insulator transition at 50K which does not result from the Co$^{3+}$/Co$^{4+}$ charge differentiation anticipated initially [13].

In order to check the evolution from $x_0 \approx 0.7$ to the AF phases, we have synthesized and investigated with $^{23}$Na and $^{59}$Co NMR all the distinct phases from $x = 0.67$ to the first well characterized AF phase. This constitutes the first systematic effort to study the influence of $x$ and charge order on the static and dynamic susceptibilities. Our data will be shown to reveal that the CoO$_2$ planes display common magnetic properties above 100K, but that the lower $T$ properties are due to low energy modifications of the band structure of the correlated metallic state, which are apparently governed by the distinct Na orderings of the phases found.

Using $^{23}$Na and $^{59}$Co NMR spectra combined with Rietveld refinements of x ray data we have evidenced that multiphasing is quite common in Na$_x$CoO$_2$ samples. We could sort out four different stable phases for $0.65 \leqslant x \lesssim 0.75$, and synthesized reproducibly nearly pure samples, which requires a continuous control and no exposure to air. These phases all have two layer Co structures with the hexagonal (P6$_3$/mmc) unit cell as reference substructure lattice. However, as summarized in Table I the homogeneity range is sequenced in four distinct narrow $x$ domains, each with a specific Na ordering leading to characteristic additional diffraction: incommensurate satellites or superstructure commensurate reflexions. These orderings result in symmetry lowering and the reference subcell is systematically orthorhombic

TABLE I: Parameters of the studied phases. The accuracy on their difference of Na content $x$ is much better than that on $x$ itself ($\pm 0.01$); $c$ axis ($\pm 2 \cdot 10^{-4}$Å); real cell = superlattice or incommensurate modulation q(b*) determined by X ray diffraction; Co$^{3+}$ fraction $y$ obtained from $^{59}$Co NMR.

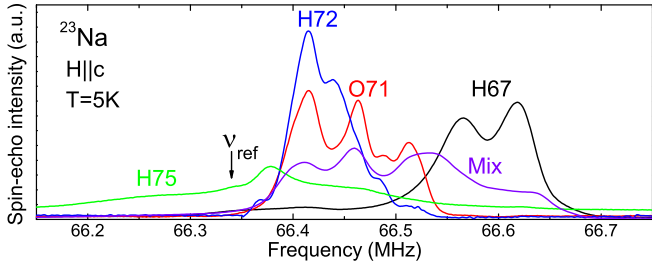| Phase | $x$ | $c$ (Å) | real cell | y (%) Co$^{3+}$ |
|---|---|---|---|---|
| H67 | $\approx .67$ | 10.938 | $a\sqrt{3}, 3a, 3c$ | 26(4) |
| O71 | $.70 \leftrightarrow .71$ | 10.900-.888 | $0.28 \leq$ q(b*)$\leq 0.29$ | 40(5) |
| H72 | $\approx .715$ | 10.879 | q(b*)$\approx 0.281$ | 37(5) |
| H75 | $\geq .75$ | 10.807 | not determined | 33(4) |

FIG. 1: (color online) $^{23}$Na NMR central line spectra taken at 5K. They are quite distinct for the four nearly pure phases, with some overlap between O71 and H72 spectra. That for a sample which is clearly a mixture of H67, O71 and H72 is shown as well. $\nu_{ref}$. is the non magnetic $^{23}$Na NMR reference.

(Ccmm, n°63): $a_{ort} = a_{hex}\sqrt{3}$; $b_{ort} = a_{hex}$; $c_{ort} = c_{hex}$. Among these phases a single one, $x = 0.71$, exhibits a significant distortion with respect to the hexagonal substructure, with $a_{ort}/\sqrt{3} \approx 2.84$Å, $b_{ort} \approx 2.83$Å, hence the labelling H67, O71, H72 and H75 used hereafter and in Table I. The formerly studied $x_0 \approx 0.7$ phase [8, 9] has in fact the lowest $x$ value $x = 0.67(1)$ reached for any material when it evolves in insufficiently dry atmosphere.

The single crystal grains of these samples were oriented in the $H_0 = 7$ Tesla NMR field within Stycast or paraffin. As reported in Ref.8 on H67, the $^{23}$Na NMR displays quadrupole splittings which allow us to distinguish the different Na sites in the structure. In view of the more complex structures of the new phases there was no surprise in finding more resolved sites, with splittings quite similar in magnitude. The magnetic properties of the compounds are probed through the NMR shifts of the different Na sites resolved in the $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$ transition of the $^{23}$Na spectra presented in Fig.1. There one can see that the 5K spectra are quite distinct for the four phases. For H75 a large broadening occurs in the AF state below $T_N = 22$K, while the spectrum of H67 is much more shifted than those of O71 and H72, which are distinct but display some overlap. As the H72 batch has been found to evolve fast at room $T$ towards O71, a slight mixture of the two pure phases might be unavoidable in these samples. Quite generally $^{23}$Na NMR allowed us to control phase purity, as multiphase samples display superimposed spectra, as seen in Fig.1.

Let us recall, as detailed in Ref.8 that for a field $H_0 \parallel \alpha$, the NMR shift $K_\beta^\alpha$ of a Na atomic site $\beta$ probes the spin susceptibility $\chi_{s,i}^\alpha(T)$ of the neighbouring Co sites $i$ through transferred hyperfine couplings $A_{\beta,i}^\alpha$ with $K_\beta^\alpha = \sum_i A_{\beta,i}^\alpha \chi_{s,i}^\alpha(T)$. The main result found for H67, and verified here for the other phases, is that the $K_\beta^\alpha(T)$ variations scale with each other for all Na sites. This $T$ dependence is associated with the average $\chi_s^\alpha(T)$ of the magnetic Co sites of the structure. So, overlooking the diversity of Na sites, the first moment (or center of
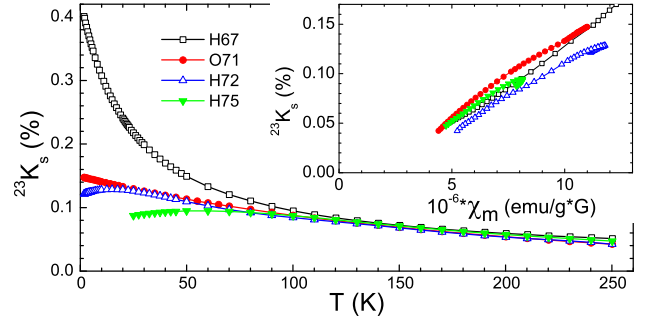


FIG. 2: (color online) $T$ dependence of the mean $^{23}$Na NMR shift. Identical behaviour above 100K can be seen for the four phases with remarkable differences at low $T$. Inset: the linear variations of $K_s$ versus SQUID data for $\chi_m$ underlines the purity of the samples. The H67 data for $T <$30K [8] has been omitted to better display those of the new phases.

gravity) of the $^{23}$Na NMR signal writes $K_s^\alpha = A_{eff}^\alpha \chi_s^\alpha(T)$ where $A_{eff}^\alpha$ is an effective hyperfine field per Co site. The $T$ variations of $K_s^\alpha$ are reported in Fig.2, and are shown to be quite identical for $T > 100$K with a unique Curie-Weiss $(T + \Theta)^{-1}$ variation (with $\Theta \approx$80K). They surprisingly differ markedly below 100K, the low $T$ enhancement of $\chi_s^\alpha(T)$ observed for H67 being progressively reduced for increasing $x$.

In the H75 AF phase, the saturation of $K_s(T)$, that is $\chi_s^\alpha(T)$, seen at low $T$ in Fig.2 should be associated with the onset of AF correlations. In a uniform Heisenberg model, one would then assign the progressive increase of $\chi_s^\alpha(T)$ at low $T$ with decreasing $x$ to a decrease of $T_N$ and of out of plane AF coupling strength. However this primary interpretation fails as NMR data taken down to 1.4K (and $\mu$SR to 50mK [14]), did not evidence any frozen magnetic state in the three other phases, which are then *paramagnets in their ground state*, most probably metallic, as no electronic transition is detected.

SQUID measurements of the macroscopic susceptibility $\chi_m$ taken in 5 T also revealed the different magnetic properties of the 4 phases. The slopes of the $K_s$ versus $\chi_m$ plots reported in Fig.2 yield similar values for the hyperfine coupling ($A_{hf}^c =$ 9.1(3), 8.0(3), 7.3(3) and 7.8(3)KGauss/$\mu_B$ from H67 to H75 respectively), which could be expected as $^{23}$Na sites are coupled with many Co [8]. In all phases the anisotropy of $\chi_s^\alpha(T)$, given by that of $K_s^\alpha$, does not exceed $\pm 0.1$.

The difference between phases was also clearly seen in the $^{59}$Co NMR spectra, which also display many Co sites as for H67 [9]. We identified two classes of Co sites, their $(-\frac{1}{2} \rightarrow \frac{1}{2})$ transitions being better visualized in Fig.3 when $H_0$ is at the "magic angle" for which quadrupole effects are reduced (54.7° from the $c$ axis). A first series, the Co1 "class", are non magnetic Co$^{3+}$ with small spin lattice $T_1^{-1}$ and spin spin $T_2^{-1}$ relaxation rates and similarly small NMR shifts $\approx 2\%$ in the four phases, as
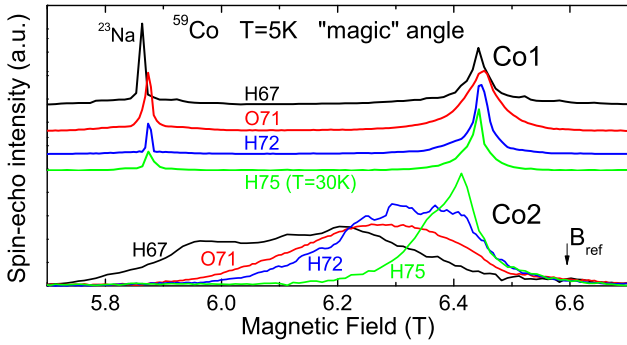
FIG. 3: (color online) Spectra taken with a large pulse spacing $\tau = 200 \ \mu s$ in a spin echo sequence allowed us to isolate the narrow spectra of Co1 sites with long $T_2$. The broad spectra of the magnetic $Co_m$ with short $T_2$ are obtained by subtracting the Co1 spectra from those taken with $\tau = 10 \ \mu s$. The $Co_m$ shifts decrease with $x$ as the $^{23}$Na shift does in Fig.1 and 2.

compared to the magnetic sites to be discussed below. Their shift is dominated by the $T$ independent isotropic orbital susceptibility of the $Co^{3+}$ ion (1.95% in insulating $Na_1CoO_2$ [4]). The complex spectra of the fast relaxing magnetic $Co_m$ "class", which involved Co2 and Co3 sites in H67 [9], are also shown in Fig.3. They include diverse unresolved sites with an average NMR shift increasing markedly with decreasing $x$ in perfect agreement with expectations from $^{23}$Na NMR data.

The fraction $y$ of $Co^{3+}$ sites, estimated from the Co1 relative NMR intensity (corrected for $T_2$ decay), increases slightly, but not regularly with $x$ (Table I), this overall trend being expected as all Co sites become $Co^{3+}$ for $x = 1$. However as $y < 1 - x$, the average valence of the $Co_m$ sites is always much smaller than $Co^{4+}$, and the charge disproportionation detected in H67 is present in all phases, *including the AF ordered phase*.

Our data involves various evidences that this charge distinction occurs already above room $T$, contrary to the proposal of Ref.15, as i) we could detect the Co1 sites up to room $T$, and the $Co_m$ up to 220K, at least in H67, ii) the perfect scaling of $^{23}K$ with $\chi_m$ in Fig.2 applies up to room $T$, well above the onset of Na motion at ≈200K detected hereafter from $^{23}$Na $T_1$ data. These findings, and more refined observations [16] prove as well that the Co charge disproportionation is correlated with the Na environment (e.g. Na1 sites being on top of $Co^{3+}$).

To search for differences in the dynamic electronic susceptibilities of these phases we have taken extensive $^{23}$Na $T_1$ data. As $^{23}$Na has a spin $I = 3/2$, its nuclear magnetization recovery should be given by

$$M(t) \propto M_0(1 - W \exp(-6t/T_1) - (1 - W)\exp(-t/T_1)),$$

with $W = 0.9$ if only the central transition has been saturated. This condition being impossible to fulfill strictly experimentally, $W$ has been left as an adjustable parameter, which was found to evolve between 0.9 and 0.7
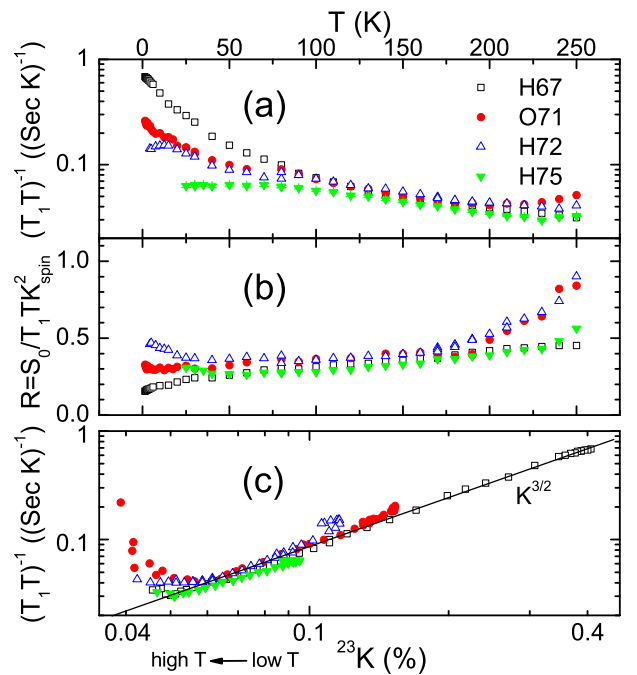


FIG. 4: (color online) $T$ variation of $(T_1T)^{-1}$ (a) and the normalized Korringa product $R$ (b) for the four phases. While the data are distinct below 100K, in (c) a universal scaling between $(T_1T)^{-1}$ and $^{23}K$ is shown to apply. The high $T$ deviations due to Na motion and the slight low $T$ increases for H72 and O71 are discussed in the text.

depending on the sample and experimental conditions. The $T_1^{-1}$ data were found slightly anisotropic, i.e. ≈30% larger for $H_0 \perp c$ than for $H_0 \parallel c$, for $T < 200K$. So, in Fig.4 we only plotted the data for $H_0 \parallel c$.

As might be expected, all phases display nearly the same $(T_1T)^{-1}$ above 100K, $^{23}K(T)$ being identical as well (Fig.1). These two quantities can be correlated in the Korringa ratio $R = S_0/T_1T(^{23}K)^2$, which measures the deviation with respect to the Fermi liquid value $S_0 = (\hbar/4\pi k_B)(\gamma_e/\gamma_n)^2$. In Fig.4b $R$ is indeed found sample independent between 80 and 160K. An extra high $T$ contribution to $T_1^{-1}$ is assigned to fluctuations induced by Na motion, their onset taking place at distinct $T$ for the different phases. Below 160K, $R$ is always smaller than unity, as has been noticed in a $x \approx 0.7$ mixed phase sample by Ihara *et al.* [17]. As recalled there, $R < 1$ is an evidence that the excitation spectrum is dominated by ferromagnetic $\mathbf{q} \approx 0$ fluctuations that enhance markedly $\chi_s(\mathbf{q} = 0)$, that is $^{23}K_s$, while $(T_1T)^{-1}$ is less enhanced as it probes $\chi''(\mathbf{q}, \omega)$ at all $\mathbf{q}$ values. This corroborates the observation by INS [5] of a quasielastic peak at $\mathbf{q} \approx 0$ above $T_N$ in the H75 phase. The identical behaviour found here above 100K for all samples extends this result to all our Curie-Weiss paramagnetic phases.

Below 100K the data for $(T_1T)^{-1}$ and $R$ reported in Fig.4 differ markedly for the various phases, which reflects the distinct ground states revealed by the shift data

in Fig.2. To sort out whether the fluctuation spectrum is modified at low $T$ we searched for relationships between $(T_1 T)^{-1}$ and $^{23}K$, as done in Fig.4c. Spin fluctuation theories in nearly ferromagnetic metals are known to give $(T_1 T)^{-1} = aK^n$ [18], with $n = 1$ in 3D [19], while $n = 3/2$ is expected for 2D [20]. For H67, we do remarkably find an accurate scaling with $n = 1.5 \pm 0.1$ over the entire range 1.5K$< T <$300K. Of course, $^{23}K$ and $(T_1 T)^{-1}$ being identical above 80K for all phases, apart the Na motion contribution, this scaling applies as well. Ferromagnetic 2D fluctuations are indeed characteristic of all phases at high $T$. But, the very impressive experimental result in Fig.4 is that the $(T_1 T)^{-1} = aK^{3/2}$ scaling law is seen to extend down to low $T$ with a unique $a$ coefficient for all phases [21], whatever the behaviour of $\chi_s(\mathbf{q} = 0)$, including the AF phase down to $T_N$.

At this stage one might wonder whether the saturation of $^{23}K(T)$ observed below 100K in H75 is related to AF plane to plane couplings. Such AF fluctuations that enhance $\chi''(\mathbf{q} = \mathbf{q}_{AF})$ should result in an increase of $(T_1 T)^{-1}$ and $R$ with a divergence at $T_N$. But they are not probed by the $^{23}$Na nuclei, as the local fields induced by two adjacent Co layers cancel in the A type AF structure, as confirmed by the weak $^{23}$Na NMR shift in the Néel state (Fig.1). The $^{23}$Na $T_1$ only probes then the strength of the ferro fluctuations, and the perfect scaling found between $(T_1 T)^{-1}$ and $^{23}K^{3/2}$ is then a proof that the main incidence of AF fluctuations is to reduce the ferromagnetic ones below 100K. For H67, the comparison with the numerical results of Hatatani *et al.* [20] allows us to point out that the low $T$ increase of $\chi(\mathbf{q} = 0)$ with respect to the common Curie-Weiss variation is exactly the situation expected by these authors in the immediate vicinity of a ferromagnetic instability. Therefore the H67 phase *appears as an ideal 2D nearly ferromagnetic metal without 3D ordering settling in at low $T$.*

The four phases differentiated in this thorough investigation exhibit specific Na orderings, but similar Co charge disproportionation, and quasi identical ferromagnetic in plane fluctuations above 100K which appear independent of the detailed distribution of Co charges. However, it seems to us that the occurrence of non magnetic $Co^{3+}$ is essential as it reduces the number of hopping paths between magnetic sites with respect to a homogeneous structure. The associated decrease of bandwidth $W$ and increase of hole density on the remaining magnetic sites magnify the importance of correlations $U$, which might enhance the ferromagnetic tendency supported by LDA [22] for the homogeneous case.

As for the ground state properties, one would expect AF to be driven by specific Na orderings in some phases, which would presumably give a hectic evolution versus $x$, contrary to the smooth one found for $x <$0.75, and to the abrupt occurrence of AF for any $x >$0.75. In any case metallic magnetism is the key point in these phases, which prohibits the use of local moment Heisenberg mod-

els. One might consider [23] that a Fermi liquid state is only reached below an energy scale given by the temperature $T^*$ at which $\chi_s$ saturates, which increases from $\approx$ 1K for H67 [8] to $\approx$ 60K for H75. The band parameters associated with Na and Co charge orders would then be responsible for these $T^*$ values and for the transverse couplings which drive spin density wave order. While some attempts have been done to consider both correlations and charge order [24], extensions to diverse local orders are certainly required to fully explain the evolution with $x$ of the ground state properties of these materials.

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