

Na atomic order, Co charge disproportionation and magnetism in Na_xCoO_2 for large Na contents

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Abstract – We have synthesized and characterized four different stable phases of Na ordered Na_xCoO_2 , for $0.65 < x < 0.8$. Above 100 K they display similar Curie-Weiss susceptibilities as well as ferromagnetic $q=0$ spin fluctuations in the CoO_2 planes revealed by ^{23}Na NMR data. In all phases from ^{59}Co NMR data we display evidences that the Co disproportionate already above 300 K into non-magnetic Co^{3+} and magnetic $\approx \text{Co}^{3.5+}$ sites on which holes delocalize. This allows us to understand that metallic magnetism is favored for these large Na contents. Below 100 K the phases differentiate, and a magnetic order sets in only for $x \gtrsim 0.75$ at $T_N = 22$ K. We suggest that the charge order also governs the low- T energy scales and transverse couplings.

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Introduction. – The interplay between magnetism and metallicity in the copper-oxygen plane structure of the cuprates is at the origin of the great interest which has been devoted to their high-temperature superconductivity. Such an interplay has been also found recently in the lamellar cobaltates Na_xCoO_2 , which further display a high thermoelectric power together with good electronic conductivity [1]. In both systems metallicity is induced by doping the square CuO_2 or triangular CoO_2 layers by insertion of dopants in the ionic separation layers. Soon after the discovery of the cuprate superconductivity, it has been suggested that the electron gas could display intrinsic inhomogeneous charge structures, such as linear “stripes” of Cu^{2+} spins separated by doped metallic stripes [2]. However, such static structures have only been found in specific cases [3], and the magnetic properties of the Cu sites have been usually found rather homogeneous.

A distinct property of the Co ions in the large crystal field induced by their oxygen octahedral environment in the CoO_2 structure, is that the t_{2g} triplet of the Co site is much lower in energy than the e_g doublet, so that the electronic structure of the Co ions is expected to correspond to low spin configurations Co^{3+} ($S=0$) or

Co^{4+} ($S=1/2$) obtained by filling only the t_{2g} triplet states. Consequently ordered charge structures are more frequently expected than for cuprates. Indeed, using the quasi-unique site sensitivity of NMR techniques, a Na atomic order [4] and an associated Co ordered charge disproportionation (OCD) [5] has been revealed for a specific metallic $x_0 \approx 0.7$ composition, which displays a Curie-Weiss susceptibility. However, for the metallic cobaltate antiferromagnetic (AF) phases found for $x \geq 0.75$ [6,7], neutron scattering experiments have been analyzed in a uniform local moment picture [8,9]. This is unexpected for hole doping of Na_1CoO_2 which is a band insulator built from the non-magnetic Co^{3+} state [10], for which the t_{2g} multiplet is filled by the six d electrons.

Here we present the first systematic effort undertaken so far to study with local probes the variation with x of the magnetic properties and demonstrate that the OCD is generic for $x > 0.65$ including the AF phase with $T_N = 22$ K. This OCD always results in non-magnetic Co^{3+} and a second type of sites with formal valence of about 3.5 responsible for the peculiar magnetic properties. We establish that the latter display above 100 K a generic nearly ferromagnetic behaviour for four phases displaying distinct ordered Na structures, so that the OCD is an essential ingredient to explain the magnetic properties of these high x phases. Surprisingly the low- T ground-state

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Table 1: Parameters of the studied phases. The accuracy on their difference of Na content is much better than that on x itself (± 0.01). The lattice constants a, b, c corresponding to fig. 1 are given in the hexagonal or orthorhombic reference cell. When determined, the incommensurate $q(b^*)$ or commensurate modulations $q(c^*)$ are given. The Co^{3+} fraction y is obtained from ^{59}Co NMR intensity data. The 0.67 sample displays a commensurate orthorhombic superstructure ($a_{hex}\sqrt{3}, 3a_{hex}, 3c_{hex}$).

Phase	x	$a_{ort}/\sqrt{3}$ (Å)	a_{hex} or b_{ort} (Å)	c (Å)	$q(b^*)$	$q(c^*)$	A_{eff}^{iso} (kG/ μ_B)	y (%)
H67	0.67	a_{hex}	2.82920(1)	10.9387(4)	1/3	1/3	9.1(3)	26(4)
O71	0.71	2.83931(2)	2.83031(3)	10.8929(2)	0.2849(1)	0	8.0(3)	40(5)
H72	0.72	a_{hex}	2.83651(4)	10.8770(2)	0.2810(1)	0	7.3(3)	37(5)
H75	≥ 0.75	a_{hex}	2.84162(1)	10.8058(3)	–	–	7.8(3)	33(4)

magnetic properties differ markedly as, apart the AF phase, the former $x_0 \approx 0.7$ phase appears an experimental realization of a nearly ferromagnetic 2-dimensional metal without static magnetic order down to $T = 0$. The hole doped AF phases have been shown ferromagnetic in plane and AF between planes (A-type AF) [8,9]. So, the Na atomic order and the OCD of Co appear essential as well in governing the low-energy modifications of the band structure of the correlated metallic state, which drive the coupling between Co planes and the low- T magnetic and thermoelectric properties [11].

Samples. – We have synthesized our samples by standard solid-state reaction of Na_2CO_3 and Co_3O_4 powders in flowing oxygen, with nominal concentrations x increasing by increments of 2 to 3/1000 in the range $0.65 \leq x \lesssim 0.80$. X-ray powder diffraction data always exhibited the Bragg peaks corresponding to the two-layer Co structure with a hexagonal unit cell. However, we systematically detected weak additional reflections indicative of three-dimensional Na long-range ordering. It has been immediately clear that the corresponding Na order is complicated and highly dependent on Na content. This ordering was even found for a specific composition to drive an orthorhombic distortion of the average lattice as shown for $x = 0.71$ in fig. 1, on a detail of the Bragg peaks of the X-ray diffraction profile. From the Rietveld refinements of the X-ray data summarized in table 1 we could isolate four distinct phases for $0.65 \leq x \lesssim 0.80$. Each phase exhibits a specific Na ordering leading to characteristic additional diffractions: commensurate reflections, or incommensurate superstructure satellites with $q(b^*)$ as the component of the wave vector modulation.

The concentrations for which single-phase samples could be stabilized are sequenced in four distinct narrow- x non-overlapping domains outside which the synthesized samples were found as intermediate mixtures of these phases. In addition, multiphasing has been found to occur quite commonly for any x value if no particular care to homogenize the samples was taken. We could however synthesize these four phases reproducibly, forbidding any air exposure of the samples. Confirmation that nearly pure phases could be achieved on large mass samples ($\simeq 400$ mg) required for NMR measurements has been directly obtained from ^{23}Na and ^{59}Co NMR data, as shown hereafter.

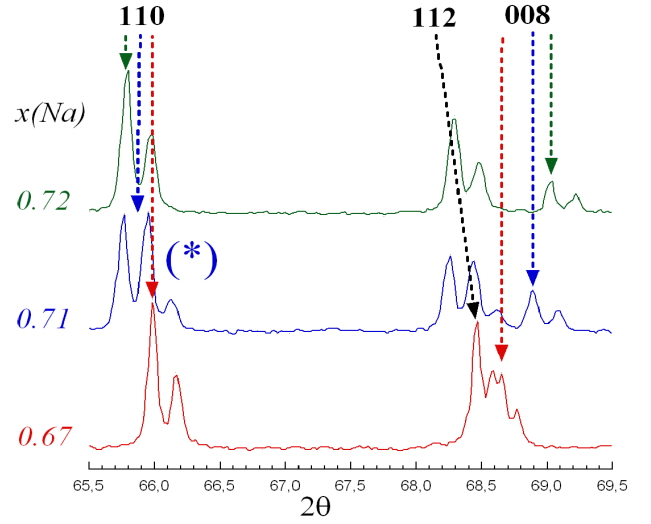


Fig. 1: Hexagonal (P63/mmc No. 196) indexation of part of the X-ray diffraction patterns. At these high-angle values the $\text{Cu } K\alpha 1$ and $K\alpha 2$ splits the reflections into two separate peaks with intensity ratio 2/1. (*) In the 0.71 case an additional structural splitting separates the hexagonal 110 (and 112) reflections into two distinct 310 and 020 orthorhombic (Cmmm No. 63) peaks.

The orderings found for these four phases always correspond to a symmetry lowering and is systematically based on an orthorhombic reference subcell (Cmmm, No. 63): $a_{ort} = a_{hex}\sqrt{3}$; $b_{ort} = a_{hex}$; $c_{ort} = c_{hex}$. Owing to the orthorhombic distortion for $x = 0.71$ the labelling H67, O71, H72 and H75 has been used hereafter and in table 1. The formerly studied $x_0 \approx 0.7$ phase [4,5] is in fact that with the lowest x value, $x = 0.67(1)$. We indeed found that any sample with larger x evolves towards this limiting composition if it is kept in insufficiently dry atmosphere.

Magnetic susceptibility and ^{23}Na NMR shifts. – The single-crystal grains of samples of these phases were oriented in the $H_0 = 7$ T NMR field within Stycast or paraffin. SQUID measurements of the macroscopic susceptibility χ_m taken in 5 T field allow us to evidence that the different phases display different magnetic properties. For instance, as evidenced in fig. 2a, the low- T magnitude of χ_m decreases progressively with increasing x . The H75

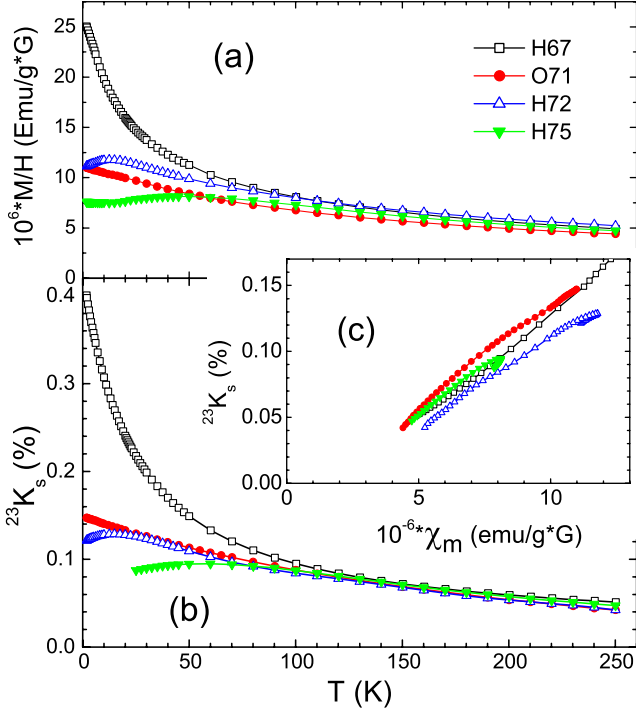


Fig. 2: (a) T -dependences of the bulk susceptibility χ_m measured with a DC SQUID in a 5 T field. (b) T -dependence of the mean ^{23}Na NMR shift. Identical behaviour above 100 K can be seen for the four phases with remarkable differences at low T . (c) The linear variations of K_s vs. χ_m underlines the phase purity of the samples. The H67 data for $T < 30$ K [4] has been omitted to better display those of the new phases.

phase is furthermore found to be the only phase in which a magnetic order is detected in low applied field. However, as minute amounts of impurities or slight admixture of phases could spoil the bulk measurements, spectroscopic measurements with local probes better determine the susceptibility of each phase.

As reported in ref. [4] on H67, the ^{23}Na NMR is an excellent probe of both Na order and of the magnetic properties. Indeed the ^{23}Na NMR displays distinct quadrupole splittings for the different Na sites of this structure. In view of the more complex structures of the new phases there was no surprise in finding a larger number of resolved Na sites, although with similar magnitudes of their quadrupole splittings. The magnetic properties of the compounds are probed at the local scale 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. 3. There one can see that the $T = 5$ K 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. The H72 batch has been found to evolve in time at room T towards O71, and a slight mixture of the two pure phases might be

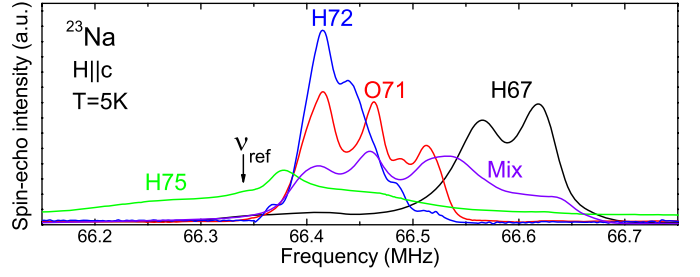


Fig. 3: ^{23}Na NMR central line spectra taken at 5 K. They are quite distinct for the four nearly pure phases, with some overlap between O71 and H72 spectra. That for a sample which is clearly a mixture of H67, O71 and H72 is shown as well. ν_{ref} is the non-magnetic ^{23}Na NMR reference.

unavoidable in the bulk samples¹. Quite generally ^{23}Na NMR allowed us to control the phase purity of the bulk of the NMR sample, as multiphase samples display superimposed spectra, as seen in fig. 3.

Let us recall, as detailed in ref. [4] that for a field $H_0 \parallel \alpha$, the NMR shift K_β^α of a Na atomic site β 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 as well 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 gravity) of the ^{23}Na NMR signal writes $K_s^\alpha = A_{\text{eff}}^\alpha \chi_s^\alpha(T)$, where A_{eff}^α is an effective hyperfine field per Co site. The T variations of K_s^α are reported in fig. 2b, and are shown to be quite identical for $T > 100$ K with a unique Curie-Weiss $(T - \Theta)^{-1}$ variation (with $\Theta \approx -80$ K). They differ markedly below 100 K, as does the SQUID data for χ_m , the low- T enhancement of $\chi_s^\alpha(T)$ observed for H67 being progressively reduced for increasing x .

The usual comparison between the SQUID and Na NMR data, displayed in the good linear K_s vs. χ_m plots of fig. 2c allows us to confirm the purity of the isolated phases. The high- T slopes of these plots yield similar values for the effective hyperfine coupling $A_{\text{eff}}^{\text{iso}}$ (table 1), which could be expected as ^{23}Na sites are coupled with many cobalts [4]. In all phases the anisotropy of $\chi_s^\alpha(T)$, given by that of K_s^α , has been found $\lesssim \pm 0.1$.

In the H75 AF phase, the saturation of $K_s(T)$, that is $\chi_s^\alpha(T)$, seen at low T in fig. 2b 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 1.4 K (and μSR to 50 mK [13]), did not evidence any frozen

¹In various published papers for x values in the range studied, e.g. [12], we could find on the susceptibility data many signs indicating that the samples were superposition of our phases.

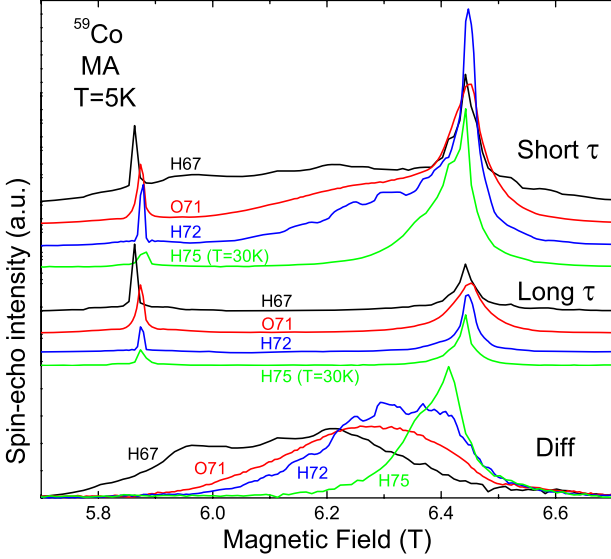


Fig. 4: Spectra taken with a large pulse spacing $\tau = 200 \mu\text{s}$ in a spin echo sequence allowed us to isolate the narrow spectra of Co1 sites with long T_2 . The broad spectra of the magnetic Co2 sites with short T_2 are obtained by subtracting the Co1 spectra from those taken with $\tau = 10 \mu\text{s}$. The average shift of the Co2 sites decreases with increasing x as does the ^{23}Na shift in figs. 2b and 3.

magnetic state in the three other phases, which are then *paramagnets in their ground state*, most probably metallic, as no electronic magnetic transition is detected.

^{59}Co NMR. – The difference between phases appears as well in the ^{59}Co NMR spectra, which also display more Co sites than for H67 [5].

Charge disproportionation. As in H67 we identified two classes of Co sites, their $(-\frac{1}{2} \rightarrow \frac{1}{2})$ transitions being easily visualized when H_0 is applied at 54.7° with respect to the c -axis, the “magic angle” for which quadrupole effects are reduced, as seen in fig. 4. A first series which we label as the Co1 “class”, is associated with non-magnetic Co^{3+} , with small spin lattice T_1^{-1} and spin spin T_2^{-1} relaxation rates, and occurs with similar NMR shifts at low T in all four phases. The more complex spectra of fast relaxing magnetic Co sites, which we label as the Co2 “class” is seen in fig. 4 to include diverse sites with much larger shifts at low T than the Co1 sites. The increase of average shift of these Co2 with decreasing x agrees perfectly with the SQUID and ^{23}Na NMR data (fig. 2).

The Co1 NMR shifts were found to vary with temperature, which is a sign that these non-magnetic sites are sensing the magnetism of the Co2 sites through transferred hyperfine couplings. Indeed, in fig. 5, we evidence that the shifts $^{59}K_1^\alpha$ of the Co1 nuclei scale linearly at low T with that of ^{23}K . The T -independent orbital contribution to $^{59}K_1^\alpha$ can be obtained by extrapolating this linear dependence to $^{23}K = 0$ (that is vanishing spin susceptibility $\chi_s(T)$). It is found isotropic and increases slightly from 1.95 to 2.05% from H67 to H75. These values are

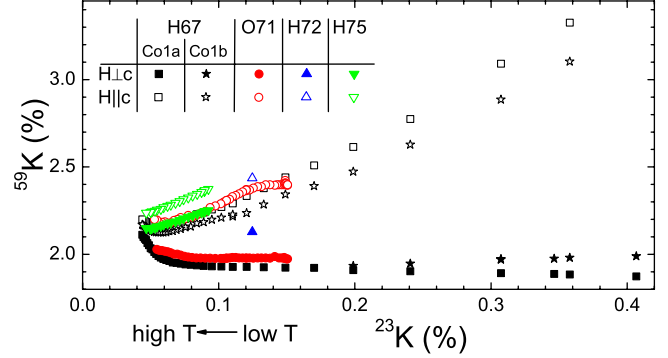


Fig. 5: At low T , the Co1 sites NMR shifts display linear variations *vs.* the ^{23}Na shifts ^{23}K . For $H_0 \parallel c$, the Co1 hyperfine coupling with the magnetic Co2 sites have similar magnitudes for all samples. For $H_0 \perp c$ it has a similar magnitude for H72 and H75 but nearly vanishes for H67 and O71. For H67 two Co1 sites are well resolved, and their shifts depart slightly below 40 K (*i.e.* $^{23}K > 0.2\%$), as reported in ref. [14]. The upturns for small ^{23}K are due to the onset of Co1-Co2 site exchange due to Na motion, as discussed in the text.

quite comparable with the purely orbital shift of 1.95% found for Co^{3+} in the band insulator Na_1CoO_2 [10]. 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 1), this overall trend being expected as all Co sites become Co^{3+} for $x = 1$. However, as we find $y < x$, the average valence of the Co2 class of sites is always $< 4+$, and the OCD detected in H67 is present in all phases, *including the AF ordered phase*.

Na motion. As seen in fig. 5 we could detect the Co1 sites up to room T in most phases, well above the onset of Na motion detected hereafter at ≈ 200 K from ^{23}Na T_1 data [15]. This implies that the OCD occurs already above room T , contrary to the proposal of ref. [14]. However, in fig. 5 significant increases of $^{59}K_1^\alpha$ with respect to the low- T linear ^{23}K dependence are observed for $T \gtrsim 150$ K, that is for $^{23}K < 0.08$. We attribute this to the onset of Co1-Co2 site exchange which becomes significant when Na motion begins to set in. Such site exchanges are usually easily detected in NMR spectra as they yield a progressive reduction of the line splitting between the two sites until they merge in a single-exchange narrowed line at very high T , when the exchange rate exceeds the line splitting. Here the increase of the Co1 NMR shift merely corresponds to the onset of Co1-Co2 site exchange. Indeed from ref. [5], $K^{ab}(\text{Co2})$ is as large as $\approx 4\%$ above 200 K, so the tiny 0.1%–0.2% increase of $K^{ab}(\text{Co1})$ corresponds to a $\approx 10\%$ decrease of the 1.5 MHz Co1-Co2 splitting, that is a very small exchange rate $\tau_{ex}^{-1} \approx 150$ kHz. This analysis is validated by the fact that weaker upturns of $K^c(\text{Co1})$ are seen for $H_0 \parallel c$ for which $K^c(\text{Co1})$ and $K^c(\text{Co2})$ happen to differ only slightly as seen in ref. [5].

Therefore this key observation that the rate of exchange τ_{ex}^{-1} of Co sites is very slow with respect to expectations for electronic processes allows us to conclude that the

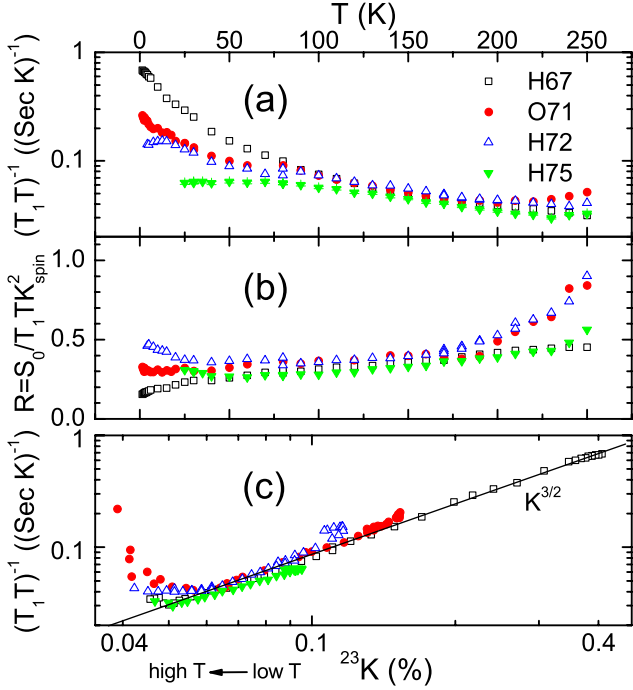


Fig. 6: T variation of $(T_1T)^{-1}$ (a) and the normalized Korringa product R (b) for the four phases. While the data are distinct below 100 K, in (c) a universal scaling between $(T_1T)^{-1}$ and ^{23}K is shown to apply. The high- T deviations due to Na motion and the slight low- T increases for H72 and O71 are discussed in the text.

Co1-Co2 site exchange is connected with Na motion. This proves that *the Co charge does correlate with the Na environment* (e.g. Na1 sites being on top of Co^{3+}).

^{23}Na spin lattice relaxation and electron spin dynamics. – 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

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

with $W = 0.9$ if only the central transition has been saturated. Since this condition is impossible to fulfill strictly experimentally, W has been left as an adjustable parameter, which was found to evolve between 0.9 and 0.7 depending on the sample and experimental conditions. The T_1^{-1} data were found slightly anisotropic, *i.e.* $\approx 30\%$ larger for $H_0 \perp c$ than for $H_0 \parallel c$, for $T < 200$ K. So, in fig. 6 we only plotted the data for $H_0 \parallel c$.

Although the low T variations of $(T_1T)^{-1}$ differ for the four phases, they do become identical above 100 K as seen in fig. 6a. There, we assign the extra high- T contribution to the occurrence of Na motion, their onset taking place at distinct $T \gtrsim 200$ K for the different phases. As can be anticipated, we could check that the magnetic behaviour is not that of a Fermi liquid, especially for the H67 sample, as $(T_1T)^{-1}$ and $^{23}K(T)$ do not combine into a constant $R = S_0/T_1T(^{23}K)^2$, where $S_0 = (\hbar/4\pi k_B)(\gamma_e/\gamma_n)^2$ is the

universal Korringa ratio. In fig. 6b R is of course sample independent between 80 and 160 K and always smaller than unity, as noticed in a $x \approx 0.7$ mixed-phase sample by Ihara *et al.* [16]. This is expected if a ferromagnetic quasi-elastic peak at $\mathbf{q} \approx 0$ dominates the spin excitations as revealed by Inelastic Neutron Scattering (INS) for the H75 phase above T_N [8]. Indeed, in such a case the $\mathbf{q} \approx 0$ response enhances 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. The identical behaviour found here above 100 K extends this result to all our Curie-Weiss phases.

To characterize further the difference of magnetic excitations in the diverse ground states we searched for relationships between $(T_1T)^{-1}$ and ^{23}K , as done in fig. 6c. Spin fluctuation theories in nearly ferromagnetic metals are expected to give $(T_1T)^{-1} = aK^n$ [17], with $n = 1$ in 3D [18], while $n = 3/2$ is expected for 2D [19,20]. For H67, we do remarkably find an accurate scaling, with $n = 1.5 \pm 0.1$, that is $(T_1T)^{-1} = aK^{3/2}$ over the entire range $1.5 \text{ K} < T < 300 \text{ K}$. This interpretation of the data implies that the Curie-Weiss temperature $\Theta = -80 \text{ K}$ found in $K(T)$ and $\chi(T)$ is not associated with AF in-plane couplings but results from the nearly ferromagnetic electronic band behaviour [17,19] as seen, for instance, in TiBe_2 [18]. Impressively this 2D *ferromagnetic* scaling extends down to low T with a unique a for all phases², including the AF phase down to T_N .

At this stage one might wonder whether the saturation of $^{23}K(T)$ observed below 100 K 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 $(T_1T)^{-1}$ 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. 3). The ^{23}Na T_1 only probes then the strength of the ferro-fluctuations, and the perfect scaling found above proves that the main incidence of AF fluctuations is to reduce the ferro ones below 100 K. Comparison with the numerical results of Hatatani *et al.* [19] allows us to point out that, for H67, the low T increase of $\chi(\mathbf{q} = 0)$ with respect to the common Curie-Weiss variation is that 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*.

Discussion. – The four phases exhibit specific Na orderings, but similar charge disproportionation, and identical ferro in-plane fluctuations above 100 K, independent of the details of the OCD. It seems to us that this analogy of properties relies heavily on the occurrence of non-magnetic Co^{3+} as it reduces the number of hopping

²For H72 and O71, the small deviations for $T \lesssim 5 \text{ K}$ are not intrinsic as data for the resolved Na lines were not found to scale perfectly. Purification of these phases is required for accurate low- T studies.

paths between magnetic sites with respect to a homogeneous structure. The associated decrease of bandwidth W and increase of hole density on the magnetic sites magnify the role of correlations U , which enhances the ferro tendency supported by LDA calculations [21] for the uniform case.

On the contrary, the ground-state magnetic properties are certainly driven by the diverse Na atomic orders evidenced here, similar to those suggested, or observed [22,23] as well for various other x values. One could expect then distinct ordered magnetic states as in the case of the $x = 0.5$ phase for which an AF order inside the Co plane sets in at $T_N = 86$ K [7,24] in the absence Co^{3+} [25]. But for the analogous ferro in-plane couplings evidenced here for large x , one would always expect A-type AF order to occur. In these AF phases, the 3D dispersion of the spin wave excitations found by INS has been analyzed with Heisenberg Co-Co AF coupling between planes either with nearest- [8,9] or next-nearest-neighbour exchange through Na orbitals [26]. For such Heisenberg transverse couplings, a hectic evolution of T_N vs. x should presumably result, depending on the actual Na order, contrary to the smooth evolution of *paramagnetism* found for $x > 0.65$ and the abrupt occurrence of AF above $x = 0.75$.

This definitely allows us then to conclude that metallic magnetism is indeed responsible as well for the low- T states for large x in these Na cobaltates. One might consider [27] that a Fermi liquid state is only reached below an energy scale given by the temperature T^* at which χ_s saturates, which increases from ≈ 1 K for H67 [4] to ≈ 60 K for H75. The band parameters associated with Na order would then be responsible for these T^* values and for the transverse couplings which drive the AF order. While some attempts have been done to take into account both correlations and OCD [28], extensions to diverse Na atomic orders are required to explain the evolution with x of the ground-state properties³.

An important experimental aspect revealed by our thorough investigation is that, contrary to the case of cuprates for which dopant-induced disorder is quite influential, and governs many aspects of the cuprates phase diagram [31], the hole doping achieved in bulk cobaltate samples by insertion of ordered Na planes corresponds to rather clean situations for many Na concentrations.

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³After the disclosure of an earlier version of these results [29], a theoretical attempt to explain them within a strong correlation approach has been done [30]. The existence of a critical doping value for the onset of in-plane ferromagnetism has been reproduced, as well as the occurrence of Co^{3+} in the presence of Na disorder, using heuristic values for the Na-Co interaction potentials.

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