The discovery of a new family of layered transition metal oxides, the cobaltites, which display strong electric thermopower and metallicity and superconductivity has triggered a large interest. In Na$_x$CoO$_2$ compounds, the cobalt-oxygen layers have an hexagonal 2D crystal structure with a tetragonal 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 either considered as a Mott-Hubbard low spin configuration for the Co ions and of the Na$^+$ ions and of the Co charges in the 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. A very distinct much weaker Pauli like magnetism is detected for $x \approx 0.35$, the parent of the superconducting hydrated compound.

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Fig. 1: 23Na NMR spectra taken in two field directions in Na0.66CoO2. 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 Na0.66CoO2 and Na0.35CoO2 (the intensities are not in scale).

Epoxy in a 7 T field, and epoxy was allowed to polymerize in the field. NMR spectra were obtained by pulse NMR spectroscopy: at fixed frequency, we measured the spin echo intensity after two 2 µs radio frequency pulses separated by 100 µs, while the field was increased by steps. A typical 23Na NMR spectrum obtained below 150 K, when Na atomic motion is totally frozen, is displayed in Fig. 1. Here, the crystal field lifts the degeneracy of the Zeeman level of the 23Na nuclear spin (I = 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 \(-\frac{1}{2} \leftrightarrow \frac{1}{2}\) transition, with

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

where \(\theta\) and \(\varphi\) are the polar coordinates with respect to the external field \(H_0\) and 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 the 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 \(H_0||c\), one can clearly distinguish three pairs of quadrupole transitions which correspond to three Na sites with distinct local environments. In our samples only the c axes of the crystallites are aligned and the a or b axes and therefore \(\varphi\) are at random. The narrow width of the transitions indicate from the above equation that \(\theta \approx 0\) and that the largest principal axis of the EFG tensor for the three resolved sites is parallel to the c axis. For \(H_0\perp c\) only one pair of transitions remains narrow which shows that \(\eta = 0\) for this site which will be labelled Na1 hereafter. The width of this quadrupole transition allows to estimate the mean deviation \(\Delta \theta \approx 5^\circ\) with respect to \(\theta = 0\), which demonstrates the high degree of alignment of the sample. The broad quadrupole transitions for \(H_0\perp c\) correspond to two Na sites labelled Na2a and Na2b with slightly distinct EFG tensors and large \(\eta\) values. The full simulation of the spectra allows to deduce \(\nu_Q \approx 1.645(5) \text{ MHz}\) and \(\eta \approx 0.00(1)\) for Na1, \(\nu_Q \approx 1.72(1) \text{ MHz}\) and \(\nu_Q \approx 1.86(1) \text{ MHz}\), \(\eta \approx 0.82(2)\) and \(\eta \approx 0.87(2)\) respectively for Na2a and Na2b. These quadrupole frequencies were found to decrease at most of 5% from 5 K to 100 K. The intensity ratio between the lines allows us to assign the Na1 NMR to Na at \((0,0,\frac{1}{4})\) which is vertically aligned with two Co, and Na2a and Na2b to Na at \((0,0,\frac{1}{4})\) aligned with the center of Co triangles in the neighboring CoO2 planes.

In the Na0.35CoO2 sample, while 59Co NMR spectra indicated that the sample is as well aligned, the 23Na quadrupolar spectrum could not be resolved in either direction which indicates the occurrence of a large distribution of EFG values. The intensity of the 23Na NMR signal has been also found about 2.0(2) larger than that expected from that of the central transition of Na0.66CoO2, which shows that for some sites the quadrupole effect is so small that satellites merge in the central line.

Simple calculations of the EFG in a point charge model indicate that the local configuration of the neighbouring Na+ charges gives a large contribution to the EFG at the Na sites for both \(x \approx 0.35\) and \(x \approx 0.7\). So the distribution of EFG seen for \(x \approx 0.35\) proves that the ordering of Na is not perfect, which might be expected, as the low T deintercalation process of Na does not lead to a thermodynamically stable phase. The well defined values of the EFG for \(x \approx 0.7\) a contrario evidence that the Na atoms are well ordered. Both Na1 and Na2 sites have a threefold c axis symmetry with respect to the CoO2 plane, which correspond to EFG tensors with axial symmetry around the c axis for the Co and O charges. So the fact that \(\eta = 0\) for Na1 proves that the Na ordering keeps a high symmetry as well. On the contrary, the resolution of two slightly different sites with large \(\eta\) for Na2 indicates a lower symmetry for these sites. They could correspond to displaced positions of Na with respect to the center of the Co triangles, as suggested by X-ray refinements. More refined information on the charge order of the Co will be obtained hereafter from the local magnetic data.

In the \(x \approx 0.7\) samples the central transitions associated with the three Na sites are not well resolved above 100 K. As the magnetic shift increases drastically at low \(T\) they are progressively fully resolved, as seen in the inset of Fig. 1. The reproducibility of these spectra was found excellent even for samples with nominal \(x\) as low as 0.5. In Fig. 2 we report the large \(T\) variation of the shift of these lines, referred to the 23Na NMR of NaCl in solution. Before discussing in detail this important information, let us compare first the properties sampled by
The linear fits give Co sites, with different n.n. through one O. One could explain then the fact that the $K_3^\alpha$ do not differ markedly and the $^{23}$Na data are compatible with a homogeneous charged state. However, we have detected the $^{59}$Co NMR signal of Co$^{3+}$ in our own samples, as done in Ref. [2]. In the presence of a distribution of Co$^{3+}$ and Co$^{4+}$, only the latter would have a sizable $\chi_{\alpha,i}$, so that for each Na nuclear spin the numerical coefficient 18 should be reduced to a smaller integer $n$ which depends on the number of Co$^{4+}$ in its local environment. For $x \approx 0.7$, a random distribution of $\approx 0.3$Co$^{4+}$ would result in a splitting of each Na site NMR in a series of lines with shifts proportional to the local $n$ value. So, the absence of magnetic splitting of the $^{23}$Na central lines at low $T$ for both sites indicates that the environment of the Na sites is perfectly ordered and corresponds then to a single value of $n$ for each site. For example the natural ordering expected for $x = 2/3$ shown in Fig. 3, in which Co on the honeycomb lattice are Co$^{3+}$ and those on the $\sqrt{3} \times \sqrt{3}$ triangular lattice are Co$^{4+}$ yields $n = 5$ for both Na1 and Na2 site, which would not be differentiated magnetically.

Although the above analysis is oversimplified, the conclusions drawn are even stronger when we take into account the angular dependence of the hyperfine couplings. Four values $A_1 \approx 3A_2$, $A_2 \approx A_3 \approx A_0$, $A_4 \approx 2A_0$ have to be considered (Fig. 3). From the angles in the structure we anticipate $A_1 \neq A_2$, so that the shift of Na1 would depend on the charge of the n.n. Co ions at the vertical of the Na. The occurence of a single Na1 line would then imply that a single configuration of Fig. 3 occurs, in which the n.n. is either Co$^{3+}$ or Co$^{4+}$. This would even imply that the charge configurations in the two neighboring CoO$_2$ layers are correlated as Na1 couples to two layers. The small extra Na line which is nearly unshifted could be due to defect Na sites which essentially would

**FIG. 3**: Model representing a Co plane with the usually assumed Co$^{3+}$-Co$^{4+}$ charge segregation for $x=0.66$. This model of ordered state is used here to illustrate that the unicity of the NMR shift of the Na1 and Na2 sites imply a perfect order of the different cobalts in plane. The oxygens represented here are those in the layer between the Co and Na planes. Three representative Na sites are shown together with hyperfine coupling paths to their neighbouring Co.
have Co\textsuperscript{3+} neighbours. Let us recall that the occurrence of a single EFG for Na\textsubscript{1} was an independent proof that the ionic configuration including that of Na\textsuperscript{+} itself is well defined around this site. On the contrary with the ordering suggested in Fig.3 the Na\textsubscript{2} site is unique and assuming $A_1 \neq 2A_3$ would only change the effective hyperfine field for this site. The occurrence of two slightly different Na\textsubscript{2} signals could correspond to a an increase of unit cell with a perfectly commensurate CDW order.

As the shifts for all sites display the same $T$ variation, the first moment (center of gravity) of the NMR spectrum $K = A\gamma_s(T)$ allows to follow $\gamma_s(T)$ beyond $T \approx 100$ K, where the lines merge together (Fig. 4). Both our SQUID data for $\gamma_s(T)$ and \textsuperscript{23}Na NMR confirm the variation usually found for $T > 100$K, that is $\gamma_s = C/(T - \theta)$, with $\theta \approx -90$ K, and $K_{\alpha_{\text{orb}}}$ $\approx$ 0. This allows us to deduce an effective hyperfine field of $H_{h.f} = 14.9$ kG/\mu_B. For $T < 100$ K the data for $K^{-1}$ in fig. 4 lie below the high $T$ Curie-Weiss law, which corresponds to an increase of $\gamma_s$. This upturn of $\gamma_s$ at low $T$ apparently tends to saturate below 3K, as can be seen in the inset of Fig. 4. Such a behaviour detected by an NMR local probe is intrinsic to the physics of the cobaltite planes. Let us point out that at the same time no anomaly is found in the linewidth nor in the signal intensity, which indicates that no magnetic transition occurs down to 1.5 K.

In the superconducting compound the intercalated water should reduce Na-Co coupling. However in our dry sample with $x \approx 0.35$ the small change of $c$ axis with respect to $x \approx 0.7$ should not change markedly the hyperfine couplings. The small $T$ independent \textsuperscript{23}Na shift measured reveals then a weak Pauli like magnetism (Fig. 2). As this doping corresponds to the overdoped case of cuprates it is not so surprising to find a situation in which the correlations are not prominent.

On the contrary, the metallic state for $x \approx 0.7$ displays a magnetism which resembles at high $T$ that of local moments with large AF interactions, and at low $T$ that of Heavy Fermions with a Kondo temperature $\lesssim 10$ K. The data leads us to anticipate that a Fermi liquid behaviour would only be reached below 1.5 K. Comparison of $\gamma_s$ at the lowest $T$ with the specific heat $C/T$ measured in comparable samples gives a large value for the Wilson ratio $R = (T\gamma_s/C)/(\pi^2k_B^2/3\mu_B^2) = 7.8$, 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. We anticipate that they result from the quasi perfect charge order which we have evidenced here for these single phase $x \approx 0.7$ samples, both from magnetic and EFG measurements. The ordering of Co\textsuperscript{3+} charges should remove electrons from the conduction channels, and yield a system which is nearer from a Mott transition than the $x \approx 0.35$ sample. In the simple usually proposed model in Fig. 3, if conductivity is driven by the motion of holes on the triangular lattice of Co\textsuperscript{4+}, it would correspond indeed to a half filled state, and frustration would play a role in the magnetic properties. Our results demonstrate that the interplay of charge ordering, magnetism and metallicity is extremely rich and is certainly at the origin of the diverse magnetic properties found for $x \geq 0.7$. The present work recalls the power of NMR techniques to address problems of local order and initiates an approach in which both EFG’s and hyperfine couplings can be combined to disentangle a complicated situation. Although we have illustrated this approach with the classical model for Co\textsuperscript{3+}-Co\textsuperscript{4+} charge order, the interplay of Co and Na ordering prevents us to ensure its validity solely from the \textsuperscript{23}Na NMR data. We anticipate that \textsuperscript{59}Co NMR data and numerical calculations of the EFG and hyperfine couplings will allow us in a near future to determine the exact type of local order occuring around the various sites. We should like to acknowledge stimulating discussions and help in experiments from J. Bobroff, D. Bono and P. Mendels.

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