59Co NMR study of the Co states in superconducting and anhydrous cobaltates

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59Co NMR spectra in oriented powders of the superconducting (HSC) Na0.35CoO2.13H2O and Na0.35CoO2 compounds reveal a single electronic Co state with identical T independent NMR shift tensor. These phases differ markedly from Na0.7CoO2, in which we resolve 3 types of Co sites. The large T variation of their spin susceptibilities χ, and the anisotropy of the orbital susceptibility χorb allow us to conclude that charge disproportionation occurs, in a non magnetic Co3+ and two magnetic sites with about 0.3 and 0.7 holes in the t2g multiplet. The data are consistent with those for the single Co site in the anhydrous and HSC phase assuming the expected Co3.65+ charge.

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The superconductivity (SC) induced by water insertion in Na0.35CoO2 has led to suggest an analogy with High Tc cuprates. Indeed, metallic and magnetic states occur in the phase diagram of these layered transition metal oxides and the SC, which occurs for a limited range of carrier contents, might be explained by the magnetic scenarios proposed for the cuprates. The triangular lattice of the cobalt planes introduces a frustration of interactions between Co spins which could be even more favorable than in the cuprates to the formation of exotic spin ground states. Furthermore, cobaltates might display a richer variety of properties due to the two possible Co electronic configurations (Co3+, S = 0 and Co4+, S = 1/2) in the high trigonal crystal field of the CoO2 plane. A segregation into these 3+ and 4+ charges has been suggested and results, at least for x0 ≈ 0.7, in a Co charge order correlated with the atomic arrangement of the Na layers. This charge ordered metallic state, presumably responsible for the thermoelectric properties, should be physically quite distinct from the insulating charge and spin stripe order due to hole localization in some cuprates.

Prior to fully addressing these comparisons, it seems essential to perform atomic probe determination of the Co states all over the phase diagram. This issue is connected with that of the role of H2O in inducing SC. While H2O insertion should not a priori modify the electronic structure, it has been recently proposed that (H2O)+ ions increase the doping of the CoO2 plane from 0.35 to 0.7, so that the electronic properties of the SC would be similar to those of the x0 ≈ 0.7 phase.

In the present work we use 59Co NMR, in oriented powders in order to probe the electronic properties of the Co sites. The analysis of the NMR shifts enables us to determine the orbital susceptibility χorb which is directly related to the charge state of the Co. We show for the first time that three types of Co states occur in the x0 phase at variance with the anticipated Co3+/Co4+ scenario. On the contrary, the x ≈ 0.35 sample is found to display a uniform Co3.65+ charge state which is not modified upon water insertion. We therefore stress the contrast between the electronic properties on the two sides of the x = 0.5 composition. The large anisotropy of χorb found for the hole doped Co sites allows us to propose a scheme to reconcile the conflicting data reported below Tc in the HSC samples, and to propose singlet SC. Our results open the way for experimental electronic characterization of the various magnetic states found for large Na content, and should stimulate realistic band structure calculations.

Two x0 ≈ 0.7 and the x ≈ 0.35 samples were already used in Ref. Their NMR signals did not evolve during the last 18 months. A new x0 sample with negligible Co3O4 content has been synthetised. A part of the x ≈ 0.35 batch was hydrated into a HSC sample (Tc ≈ 3.9 K) and the c axes of the sample crystallites were aligned in water in a 7 T applied field. The sample was then frozen and kept below 0°C.

The I=7/2 nuclear spin of 59Co both senses the magnetic properties of the Co site and couples through its nuclear quadrupole moment Q to the electric field gradient (EFG) tensor Vαβ created by its charge environment. The 59Co NMR signal detected for H||c in the HSC sample is the most typical spectrum for a single site for which c is principal axis of the EFG. It is reported in Fig. as a recording versus H of the NMR spin echo intensity obtained with a π/2 − τ − π/2 pulse sequence. It displays a set of seven equally spaced peaks symmetrically arranged around the central −1/2 ↔ 1/2 transition. The frequency splitting νQ = 3eQVZZ/(h2I(I − 1)) is a measure of the EFG component VZZ with Z||c. For H ⊥ c the in plane ab axes of the crystallites are random in our samples, which results in a powder spectrum. The lineshape reflects then the anisotropy η = (VYY − VXX)/VZZ of the in plane components of the EFG. The simulations of the spectra yield νQ=4.103(10) MHz; η=0.22(2), in perfect agreement with NQR existing data. The spectra for the anhydrous x ≈ 0.35 sample are quite similar to that of the HSC sample. The small difference relates to slight discrete changes of νQ resolved only for H||c. These can easily be attributed to EFG contributions of diverse local arrangements of Na+ ions which are negligible in the SC...
samples due to the larger Na\textsuperscript{+} - Co distances upon wa-
ter insertion. Remarkably, the spectra in the anhydrous
sample display a unique central line for all Co sites. Fur-
thermore, its anisotropic NMR shifts, which measures the
local $\chi$ are identical and nearly $T$ independent in the two
samples ($K_c=1.9\%$ and $K_{ab}=3.2\%$, see Fig. 1 and insert)
This is strong evidence that the HSC and anhy-
drous samples display a quite identical uniformly charged
state, e.g. Co\textsuperscript{3+56+}, with no resolvable difference in local
$\chi$, whatever the Na environment.

The situation is opposite for the spectra of the $x_0 \approx 0.7$
phase which display many different Co sites (Fig. 2a) with
distinct EFGs and magnetic shifts. To resolve the
latter we took spectra with $H$ tilted of $\theta = (H,c)$, such
that $3\cos^2\theta = 1$. For that "magic angle" (MA) the
quadrupole satellites of the lines with $\eta = 0$ merge with
their central lines and the quadrupole spectra for $\eta \neq 0$
are also narrowed (Fig. 2b). Besides the $^{23}$Na signal one
can easily distinguish then three Co sites, indexed with
increasing shifts Co1, Co2 and Co3. The Co2 line has
the largest broadening, to be associated hereafter with
a large anisotropy of its NMR shift. In Fig. 2a, we also
show how we contrast the signals of these sites using their
very distinct transverse spin spin relaxation time $T_2$. In-
deed, a spin echo signal dies away for $\tau \gg T_2$, and for
a short delay time ($\tau_S$) the MA spectrum displays all
sites, while for a long delay time ($\tau_L$) only the Co1 and
Na signals remain. This reveals that the signals of the
"more magnetic" Co2 and Co3 sites have $T_2 < \tau_L$. Once
the Co1 spectrum is determined with the ($\tau_L$) data, it
can be rescaled and deduced from the ($\tau_S$) spectrum to
isolate the Co2 and Co3 relaxs ("Diff" in Fig. 2).

This procedure has been quite powerful in resolving
the spectra for any $\theta$ as exemplified for $H\parallel c$ in the lower
part of Fig. 2. The ($\tau_L$) signal for Co1 is seen to dis-
play more than 7 well resolved quadrupolar lines and
a full analysis reveals that it consists of the superposi-
tion of spectra of two sites Co1a and Co1b with similar
shifts and slightly different $\nu_Q$. The spectrum of Co2 and
Co3 in Fig. 2 reveals that Co2 consists also of a set of
quadrupole lines which also correspond to two slightly
different sites Co2a and Co2b with $\nu_Q$ about twice larger
than for Co1. The highly shifted Co3 component appears
on top of the simulated Co2 spectrum. In this Letter,
the lower part of Fig. 2 is displayed to let the reader un-
derstand the method used, but the parameters listed in
Table I result from information taken on more than a
century of spectra at different $T$ and $H$. We postpone the
details on the EFG data to a full technical report and fo-
cus hereafter on the physical information extracted from
the shifts.

The large $T$ variations of of $^{59}$Co NMR shifts, which
reflect the anomalous magnetism of the CoO\textsubscript{2} planes, are detected in all cases except for the Co1 sites for $H \perp c$, as reported in Fig. 3b. For this reason this signal had
been attributed to non magnetic Co\textsuperscript{3+} in Ref. 4. We do
find here that for $H\parallel c$ the Co1 and Co2 sites exhibit a
similar increase of $K_c$ with decreasing $T$, and a larger
one for Co3, although less accurately determined. For

FIG. 1: $^{59}$Co NMR spectra in the $x \approx 0.35$ samples. Dot-
ted lines are simulations with $\nu_Q=4.1$ MHz and $\eta=0.22$ (HSC sample) and $\nu_Q = 3.55$, 4.17 and 4.45 MHz with intensity ra-
tios 47/30/23 (anhydrous sample). Insert: $T$ variation of the
$^{59}$Co NMR shifts.

FIG. 2: $^{59}$Co NMR spectra taken as the $H$ dependence of the
spin echo taken for short ($\tau_S$) or long ($\tau_L$) delay between
pulses. Upper part (a) for $H$ tilted at the "magic angle" $\theta$. Lower part for $H\parallel c$: (b) the ($\tau_L$) spectrum corresponds to the
Co1a and Co1b sites. (c) The difference reveals the short $T_2$
sites Co2a Co2b and Co3. The quadrupole satellites of the
Co1 and Co2 sites are pointed by ticks.
$H \perp c$, it is harder to resolve the powder spectrum of Co2 similar to that of Fig. 1. We better monitored the anisotropy of the Co2 and Co3 shifts by comparing $K_i$ to the isotropic $K_{iso} = \sum K_\alpha/3$ obtained from MA spectra.

The macroscopic susceptibility taken in a direction $\alpha$

$$\chi_\alpha = \chi_{dia}^{\alpha} + \chi_{orb}^{\alpha} + \chi_{s}^{\alpha} = \chi_{dia}^{\alpha} + \sum_{i,\alpha} [\chi_{i,\alpha}^{orb} + \chi_{i,\alpha}^{s}(T)]$$

involves the diamagnetism of the ion cores and the orbital and spin terms splitted in their Co(i) sites components. The NMR shifts of sites $i$ are linked to the $\chi$'s through specific hyperfine couplings $A$

$$K_{i,\alpha} = K_{iso}^{i,\alpha} + K_{i,\alpha}^{orb} = A_{i,\alpha}^{\alpha} \chi_{i,\alpha}^{s}(T) + A_{i,\alpha}^{\alpha} \chi_{i,\alpha}^{s}.$$  

The $^{59}$Co diamagnetic shift contribution is included in the reference taken 19. As the $^{23}$Na shift is purely due to the $T$ dependent spin term, it is essential to compare $^{59}K_{i,\alpha}$ to $^{23}K_{iso}$. As can be seen in Fig. 3b a linear dependence is found for all sites below 120 K when the Na motion is frozen. So these data confirm that all Co pertain to the same phase in which a single $T$ variation characterizes the local $\chi_{i,\alpha}^{s}(T)$. The slopes of the linear fits give the relative magnitude of the spin contributions $K_{iso}^{i,\alpha}/^{23}K$, while their $^{23}K=0$ intercept give the estimates of the Co orbital NMR shifts $K_{i,\alpha}^{orb}$ reported in Table 1. For comparison SQUID data for $\chi_{\alpha}^{s}(T)$ taken in $H=5$ T for our oriented sample with minimal CoO$_4$ content, also plotted in Fig. 3b versus $^{23}K$, confirm this unique $T$ dependence. These data allow us to separate $\chi_{i,\alpha}^{s}(T)$ from ($\chi_{dia}^{\alpha} + \chi_{orb}^{\alpha}$), the latter being the extrapolation to $^{23}K=0$. With tabulated values we calculate for Na$_{0.7}$CoO$_2$ $\chi_{dia}^{\alpha} = -0.35$ and then $\chi_{orb}^{\alpha} = 3.1(2)$ and $\chi_{c}^{orb} = 2.3(2)$, in $10^{-4}$ emu/mole units 20.

This anisotropy of orbital $\chi$, seen on both the macroscopic $\chi_{orb}^{\alpha}$ and the local $K_{i,\alpha}^{orb}$, being mainly of ionic origin, give us an insight on the ionic states of the Co sites. For a Co$^{3+}$ ionic state, the lower energy $t_{2g}$ triplet levels are filled and the ionic shell has a spherical symmetry, so that $\chi^{orb} = 2\mu_B^2/\Delta$ is isotropic. Here $\Delta$ is the $t_{2g} - e_g$ energy splitting. Holes introduced on the $t_{2g}$ levels yield modifications of $\chi^{orb}$ which depend of the spatial direction of the populated hole orbitals. Therefore the isotropy of $K_{i,\alpha}^{orb}$ allows us to assign Co$^{3+}$ to the Co1 site, while the anisotropic values of $K_{i,\alpha}^{2,\alpha}$ and $K_{i,\alpha}^{3,\alpha}$ imply that Co2 and Co3 have hole contents $x_i$, which will be estimated from our data. A first relation between the $x_i$, is given, for $x_0 \approx 0.7$, by the charge neutrality condition $0.5x_2 + 0.19x_3 = 0.3$, using the fractional occupancies $I_i$ of the Co sites given in Table 1. With the rough but sensible assumption that the orbital anisotropy scales with the hole content $x_i$, we obtain $x_2/x_3 \approx 0.44$ from the data for $K_{i,\alpha}^{iso} - K_{i,\alpha}^{c}$ listed in Table 1 which results in charge states Co$^{+3.3(1)}$ and Co$^{+3.7(1)}$ respectively for Co2 and Co3.

In the light of these results we may now reexamine the anisotropic $^{59}$Co shift data found hereabove in the $x \approx 0.35$ samples. As the 0.65 hole content of the $t_{2g}$ orbital in the latter samples is similar to that estimated for the Co3 site we might expect similar orbital shifts $K_c = 1.6(4)\%$, $K_{iso}^{2.5(2)} \approx 2.9(1)\%$, that is $K_{i,\alpha}^{orb} \approx 3.5(4)\%$. These values are remarkably close to the total shifts $K_c = $...
1.9%, $K_{ab} = 3.2\%$, reported in Fig. 1 in the HSC sample, in which case the spin shifts $K_{s}^{a}$ are then quite small in the HSC samples. In case of singlet SC these spin shifts are expected to decrease below $T_{c}$ and to vanish at $T=0$. Two conflicting reports indicate (i) a decrease from $K = 3.2$ to $2.7\%$ suggesting singlet SC and (ii) no variation of $K = 1.9\%$ pointing towards triplet SC. Comparing their normal state data with ours, it is clear that the authors of (i) and (ii) respectively monitored the $H \perp c$ and the $H \parallel c$ central line singularities in partially oriented samples. So their results do not contradict each other if the spin shifts are $K_{s}^{a} \approx 0.5\%$ and $K_{s}^{c} \approx 0$. In that case the data of (i) strongly supports spin singlet SC. We can further notice that $K_{s}^{a} \approx 0$ would be consistent with our observation (see Table 1) that $K_{i,c}^{orb} \approx 1.9\%$ is nearly independent of the charge state of the Co. This therefore leads us to suggest that the data are quite consistent and strongly support singlet SC. To conclude on the properties of the HSC phase, we have demonstrated here that water insertion does not modify the electronic properties for $x \approx 0.35$, which contradicts recent proposals\cite{11,12}. Therefore, the absence of SC in the anhydrous sample could result from a depression of $T_{c}$ induced by the Na$^{+}$ ion disorder. Even if such a disorder also exists in the HSC samples one can anticipate that it might be screened then by the water layers, and would less affect the CoO$_{2}$ plane carriers.

As for the $x_{0} \approx 0.70$ sample we have demonstrated that the fraction of Co$^{3+}$ is quite small, which totally discards the purely ionic Co$^{3+}$/Co$^{4+}$ picture, which would presumably yield a Mott Hubbard insulating state. Our results allow us to establish that extracting Na$^{+}$ from NaCoO$_{2}$ rather leads to delocalized states on specific Co sites, while only a few Co sites remain Co$^{3+}$. This evidence for partial hole filling on Co2 and Co3 sites is more compatible with a metallic state, such as a commensurate CDW state, although a nearly localized behaviour is still required to explain the drastic $T$ variation of the local $\chi$. We have emphasized here the different magnetic characters of the Co sites through the modifications of $K_{s}^{orb}$. The spin shifts $K_{i,\alpha}^{s}$ do also probe the local magnetism and the fact that $K_{i,iso}/23K_{iso}$ is small ($\approx 2.3$) for Co1 and increases to $10$ and $\approx 20$ for Co2 and Co3, is in perfect qualitative agreement with an increase of hole content on the $t_{2g}$ multiplet for these sites. However a nuclear spin is coupled both to its own electron orbitals giving an on-site hyperfine field (HF) and to its nearest neighbours (transferred HF). So, further analysis of the $K_{i,\alpha}^{s}$ data require a knowledge of the arrangement of the differently charged Co sites to undertake electronic structure estimates of the hyperfine couplings $A_{i,\alpha}$. Although the EFG’s and the site occupancies will help in this process, special care is presently devoted to secure first the atomic structure through x rays and neutron investigations, since it is clear that the atomic arrangement of Na is correlated to that of the Co charges.

It is often soundly suggested that the Na1 which sits on top of the Co atoms stabilize the less positively charged Co$^{3+}$, so that the role of the Na order could be essential for the physics of the $x \geq 0.5$ phases. The fact that large high $T$ Curie-Weiss dependencies occur quite generally for $x > 0.5$ might as well indicate that magnetism is an incipient property of the CoO$_{2}$ planes with sufficient hole doping on the Co. The subtle Na ordering could also play a second, more marginal 3D role, by favouring $c$ axis couplings between hole doped magnetic Co ions, which might explain the diverse low $T$ ordered magnetic states\cite{17} found for $x > 0.75$. We believe that the methods used here to determine the Co charge states can be applied for other Na ordered phases and should help to resolve these issues. In any case the results of the present work strongly suggest that magnetic models should not consider all Co sites on the same footing and will not be simple realizations of Heisenberg spin Hamiltonians. Finally, it is of course obvious at this stage that our mainly ionic approach can only be qualitative, as we are dealing with an original organization of Co charges in a strongly correlated band in which carriers avoid some sites. Further progress will have to await realistic band structure calculations taking into account the correlations, which could reproduce both charge disproportionation and anomalous magnetism.

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$10^{-4}$ emu/mole the values $\chi_{orb}^{ab} = 1.79$ and $\chi_{orb}^{c} = 1.25$ ($10^{-4}$ emu/mole), which can be estimated from the data for $K_{i,\alpha}^{orb}$ and $I_{i}$ of Table I assuming a single value for $A_{i,\alpha}^{orb}$ whatever the 3d orbital i.e. $A_{i,\alpha}^{orb} = 2 \langle r^{-3} \rangle = 13.4$ a.u, from Ref. [1] Experimental inaccuracies in the extrapolations and the rough above assumption might explain this 50% difference.