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Cobalt charge states in sodium cobaltates at intermediate dopings

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ABSTRACT

A likely crucial parameter in explaining the peculiar magnetism of Na_xCoO_2 cobaltates in their paramagnetic state is their charge and spin states in the cobalt layers, responsible for the electronic properties. We examine here the situation for $0.50 \leq x \leq 0.62$, for which it is shown that an increasing amount of Co^{3+} ions appears among ∼3.5+ ions for increasing x. Together with our previous results, this defines two regions in the phase diagram, with homogeneous Co states for $x \leq 0.5$ and heterogeneous states for $x > 0.5$. The links with the sodium structural ordering and the nature of magnetism are discussed.

1. Introduction

Sodium cobaltates have recently attracted considerable attention following the discovery of hints of strong correlations [1] and of superconductivity [2]. The latter is remarkable as cobaltates feature a layered structure, reminding one of the high-temperature superconducting cuprates, with layers of edge-sharing CoO_6 octahedra separated by layers of Na ions. On changing the sodium content x, one changes the doping in the Co layers. In a naive picture, going from $x = 0$ to $x = 1$ results in a progressive replacement of Co^{4+} ions (magnetic, $S = 1/2$) with Co^{3+} ions (nonmagnetic, $S = 0$). One would thus expect reduced magnetism as x is increased, which is not what is observed experimentally. Indeed, except for the band-insulator limit $x = 1$ where we have verified the nonmagnetic 3+ state of all cobalts [3], magnetic correlations are ubiquitous, with a crossover at $x^* \sim 0.6$ from a high x weakly-ferromagnetic itinerant behavior to a low x antiferromagnetic correlation regime [4,5].

A crucial point to explain this behavior may be the actual cobalt charge and spin states in the system. Previous results by us showed that there is charge disproportionation for $0.67 \leq x \leq 0.75$ [5], while it is absent for $x \leq 0.5$ [6,7]. Here we focus on the $0.50 \leq x \leq 0.62$ intermediate doping region, which we studied extensively, especially in terms of magnetic correlations in [4]. We show there is heterogeneity of the cobalts states, with increasing amounts of Co^{3+} ions among ∼3.5+ ions for x increasing above 0.5. The latter is thus a threshold for charge disproportionation but does not coincide with the above-mentioned threshold $x^* \sim 0.6$ between correlation regimes, and is argued to be linked to the Na ordering.

2. Results and discussion

To establish the different Co states present for $0.55 \leq x \leq 0.62$, we performed ^{59}Co (spin $I = 7/2$) nuclear magnetic resonance, taking advantage of its sensitivity to the local magnetic and charge environment of Co nuclei (see [4] for experimental details). While spectra obtained at low temperature seem to indicate that the ∼3.5+ Co sites detected for $x = 0.5$ are still present (not shown), we notice the presence of a new cobalt NMR signal (left panel of Fig. 1): upon increasing x above 0.5, a set of quadrupolar satellites (marked with stars) develops on each side of the central resonance line. The corresponding Co sites have a resonance much less temperature-dependent than the ∼3.5+ sites, with isotropic NMR shift values stable around 2%, and also with a slower transverse relaxation rate. These are the fingerprints of the Co^{3+} site in the $x = 1$ and $x = 0.67$ phases [3,8], showing that such sites start appearing beyond $x = 0.5$.

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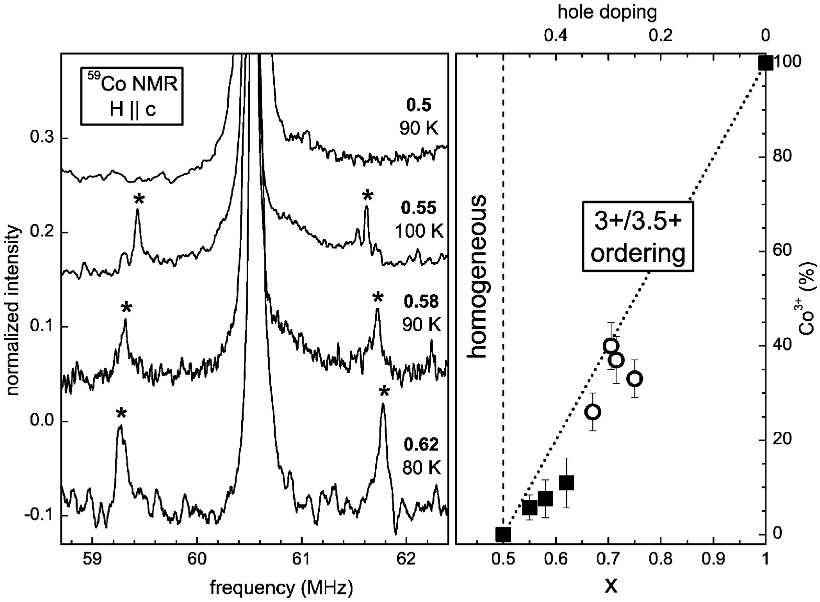

Fig. 1. Left panel: cobalt NMR spectra, with progressive apparition of a new cobalt site as x exceeds 0.5, as indicated by the quadrupolar satellites marked with a star. The $\pi/2 - \tau - \pi/2$ spin echo NMR sequence was used, with $\tau = 8 - 13\,\mu$s. Right panel: extracted fraction of Co^{3+} ions versus the doping (full squares), with the already known $x = 1$ result [3] and points from a previous study by our group (open circles) [5]. The dotted line is a visual guide.

The corresponding fractions are extracted with measurements on the central line using relaxation contrast, and with relative variation measurements on the Co^{3+} quadrupolar satellites. These fractions are presented on the right panel of Fig. 1, and agree through the condition of electroneutrality with a ~3.5+ valence for the other sites. Comparison with previous results thus shows the division of the phase diagram into two regions, with heterogeneity arising for $x > 0.5$.

Results by our group for $0.67 \leq x \leq 0.75$ [5,8] have shown the clear correlation between Co charge disproportionation and Na structural ordering. A similar argument can be made here, as the fairly well defined quadrupolar frequency of the Co^{3+} sites reflects a well-organized dopant environment. More specifically, crystallographic characterization may be compatible with a stripe-like ordering of Na ions [4], leading to a situation where Na occupancy in the vicinity of certain rows of cobalt atoms would be saturated similarly to the $x = 1$ case (Fig. 2a). These Co ions are then good candidates as 3+ $S = 0$ sites. Such a picture is well supported by the calculation of the Co^{3+} fraction resulting from such ordering [4]. The quadrupolar frequency ν_Q, varying slightly with doping from 1.10(2) to 1.25(2) MHz, is different from $\nu_Q = 0.67(2)$ MHz measured for $x = 1$ [3], but this is not a surprise as the stackings themselves

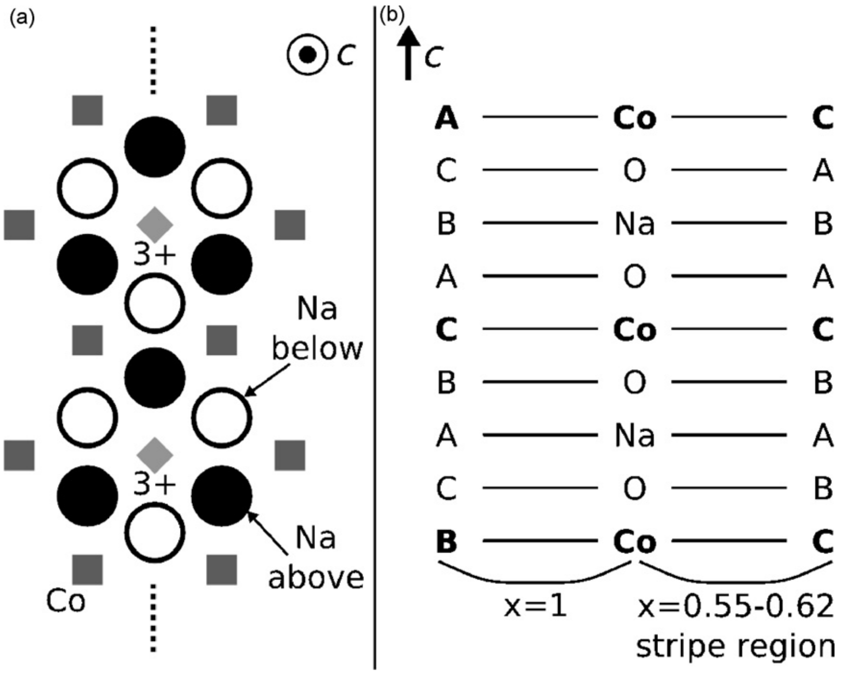

Fig. 2. (a) Suggested stripe-like local Na ordering around Co^{3+} sites for $0.55 \leq x \leq 0.62$, with Co ions marked as squares (45°-rotated in the case of Co^{3+} ions) and Na ions marked as circles (filled/open when the ion is above/below the Co layer). (b) Stacking of layers for such a structure compared to the bulk $x = 1$ case.

of the structures are different (see Fig. 2b), not even taking into account the planar stripe geometry.

The above results suggest the Co^{3+} sites to be of purely structural origin, with no connection to the threshold $x^* \sim 0.6$ between regions of magnetic correlations [4]. This is consistent with our previous study of misfit cobaltates [9], which showed that when doping is not done by sodium intercalation and is disordered, the Pauli-like and Curie-Weiss susceptibility behaviors at low and high x are preserved while no Co^{3+} can be detected. There is however a difference, for high x, in that sodium dopants maintain metallicity by concentrating holes on some cobalts. The charge disproportionation, not of intrinsic origin to the Co layers, would have the general effect of reducing the number of hopping paths, with the increased hole density on certain sites likely changing the effect of electronic correlations. Together with a number of magnetically active sites higher than in the naive 3+/4+ picture, these elements should play a role in explaining the peculiar magnetism in the paramagnetic state.

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