Cascade of Bulk Magnetic Phase Transitions in Na$_x$CoO$_2$ as Studied by Muon Spin Rotation

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Using muon spin rotation, well-defined bulk $\sim$100% magnetic phases in Na$_x$CoO$_2$ are revealed. A novel magnetic phase is detected for $x = 0.85$ with the highest transition temperature ever observed for $x \approx 0.75$. This stresses the diversity of $x = 0.75$ magnetic phases and the link between magnetic and structural degrees of freedom. For the charge-ordered $x = 0.50$ compound, a cascade of transitions is observed below 85 K. From a detailed analysis of our data, we conclude that the ordered moment varies continuously with temperature and suggest that the two secondary transitions at 48 and 29 K correspond to a moderate reorientation of antiferromagnetically coupled moments.

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Beyond their long-known ionic mobility which opened the route to industrial applications, cobaltates recently received considerable attention after the discovery of high thermoelectric power in metallic Na$_{0.7}$CoO$_2$ [1] and superconductivity, maybe unconventional, in the hydrated Na$_{0.35}$CoO$_2$ compound [2]. In addition, a very rich phase diagram [3], still to be explored in detail, seems to involve many and possibly competing parameters such as doping, charge order, magnetism, frustration, and strong electronic correlations. This spans most of the topical problems in condensed matter, more specifically in the field of correlated systems. Whether one parameter has a leading role over others is a central issue for understanding the fundamentals of physics in Na cobaltates.

Cobaltates are layered compounds like the high-$T_c$ cuprates. Magnetic and conducting properties occur in the CoO$_2$ layers issued from edge sharing CoO$_6$ octahedra stacked along the c axis and separated by Na$^+$ partially filled layers. In a naive model, the increase of Na$^+$ content leads to a conversion of Co$^{3+}$ (low spin, $S = 1/2$) to Co$^{4+}$ ($S = 0$), and, hence, to a depleted antiferromagnetic (AFM) frustrated triangular lattice, and/or to electron doping occurring in a $S = 1/2$ background, which per se are interesting problems. Experimentally, both metallic and magnetic properties are found for various $x$, but at variance with high $T_c$'s, Na$^+$ and Co$^{3+}/4+$ charge orderings appear for well-defined $x$ as shown by recent electronic diffraction [4], crystallographic [5], and NMR studies [6].

Magnetic states have long been reported for $x \geq 0.75$. A commensurate spin density wave (C-SDW) was detected below 22 K with a minority volume fraction in the nominally $x = 0.75$ sample [7]. Given that the reported c-axis parameter is typical of the nonmagnetic $x = 0.70$ phase [6], the magnetic inhomogeneity might relate to a mixed phase compound. Furthermore, on the basis of a second, nominally $x = 0.90$, sample where an incommensurate (IC)SDW 25%–50% fraction order appears below 20 K, a dome-shaped continuous phase diagram was proposed, in a Hubbard approach which links magnetism to doping [8]. Bulk C-SDW was reported to occur below 20 K [9], only in one $x = 0.82(2)$ single crystal, with a muon spin rotation ($\mu$SR) signature different from the previous samples. Sorting out the actual effect of doping on magnetism of the CoO$_2$ planes clearly calls for a more refined study.

The importance of the structure is well illustrated in the peculiar $x = 0.50$ case. A well-defined commensurate superstructure has been observed [4] where Na$^+$ vacancies and Co$^{3+}/Co^{4+}$ are arranged in order to minimize both Na-Na and Na-Co Coulomb repulsion. A magnetic state was recently reported below 50 K [10] and a metal-insulator transition sets in around 30 K [3]. In addition, a susceptibility anomaly is observed around 90 K [3], the origin of which is still not known.

In this Letter, we present a study of $\sim$100% magnetic phases, detected through $\mu$SR. The structures of all investigated samples were checked by room-$T$ x-ray Rietveld refinements. For $x \geq 0.75$, we isolate two pure magnetic phases, including a novel one for $x = 0.85$. We clearly demonstrate the absence of phase separation, stress the underlying role of the structure, and, hence, the complexity of the magnetic, likely noncontinuous, phase diagram. For $x = 0.50$, we clearly establish, for the first time, that three magnetic transitions occur below 85 K.

All samples were prepared by a solid state reaction of Co$_3$O$_4$ and Na$_2$Co$_3$O$_4$. Twice the samples were annealed in air for 12 h, were quenched with intermediate grinding, and finally were annealed in flowing oxygen for 24 h at 600 °C. The $x = 0.50$ composition was reached by immersing and stirring for 4 days the starting $x = 0.70$ material in a sodium hypochlorite solution. Hexagonal parameters $a = 2.81511(3)$ Å and $c = 11.1314(2)$ Å were measured with a $Pnmm$ orthorhombic superstructure ($a\sqrt{3}, 2a, c$). Na
sites, at the vertical either of a Co site (Na1) or of the center of a Co triangle (Na2) have an equal occupancy of 0.25, in agreement with the nominal \( x \). The \( x = 0.75 \) sample displays a hexagonal \( P6_3/mmc \) lattice with \( a = 2.84175(4) \) Å and \( c = 10.8087(2) \) Å typical of the H2 phase of Ref. [5] and exhibits only a few very weak (incommensurate) additional diffraction peaks for \( 25 < \theta < 40^\circ \). Structural refinements lead to site occupancies 0.22(1) for Na1 and 0.52(1) for Na2, close to the nominal content 0.75. This material decomposes spontaneously in content 0.75. This material decomposes spontaneously in the sample number of \( a \). The structural refinements lead to site occupancies 0.22(1) for Na1 and 0.52(1) for Na2, close to the nominal content 0.75. This material decomposes spontaneously in view of the number of \( a \) sites expected (see discussion on \( x = 0.5 \)). Accordingly, \( \mu \)SR signals and their \( T \) evolution are best described by damped cosine functions (see Refs. [7,9] for details), the weight of which can be fixed at low \( T \) values.

In Fig. 2, we plot the weak transverse field (wTF) asymmetry which monitors the nonmagnetic fraction, found to be less than 10% in both samples. The sharpness of the decrease of the wTF signal allows us to extract transition temperatures, \( T_n = 20.8(5) \) and 27(1) K, for \( x = 0.75 \) and 0.85. For each sample, the frequencies (Fig. 2) scale with each other on the whole \( T \) range and decrease smoothly when \( T \) increases to vanish at \( T_n \), simply reflecting the variation of the order parameter of a unique magnetic phase probed at four different \( a \) sites.

For \( x = 0.75 \), the frequencies and \( T_n \) values are similar to that of minority \(~\!20\%\!\) phases reported in [7]. On the contrary, for \( x = 0.85 \), the frequencies are different and the transition temperature is much higher for \( x \geq 0.75 \) than any previously reported. This points at a novel magnetic phase, commensurate, as suggested above, which is worth noticing for such a nonpeculiar value of \( x \) as 0.85.

We now focus on the \( x = 0.50 \) composition. In Fig. 3, we show for various \( T \) both asymmetries versus time and their FT. Magnetic order is evident through spontaneous oscillations of the ZF \( \mu \)SR signals below 85(1) K, which corresponds to the high \( T \) kink in SQUID data (inset, Fig. 4). Unlike previous cases where the shape of the asymmetry remains similar for all \( T \) in the frozen regime, we find, for the first time, that three distinct magnetic regions exist for \( x = 0.50 \) [12]. Depending on the \( T \) range, 2 or 3 frequencies were used to fit the \( \mu \)SR data, leading to a more complex \( T \) dependence of the frequencies (Fig. 4)
The FT spectrum is mainly peaked at two frequencies, one very close to 0.0135 MHz. The former certainly corresponds to a nonmonotonic variation in the order parameter, the variation of the oscillations shape is reflected in the Fourier transforms (right panel). There, circles mark fitted frequencies.

Surprisingly, upon increasing the temperature, only the two lowest frequency signals noticeably increase from around 29 K. Correspondingly, the widths of the nuclear dipoles, is much too small to match with this site location. Possible sites, minimizing the electrostatic energy are either a Na+ vacancy or a site located 1 Å away from an O2−, forming a O−−μ− bond. The first one can be discarded since (i) nearby Na+ would repel the μ+ from this position, (ii) the Gaussian damping in the paramagnetic state, originating from Na and Co nuclear dipoles, is much too small to match with this site location only \( \Delta_{\text{calc}} = 0.28(1) \) instead of 0.17 \( \mu s^{-1} \), and (iii) in the case of partial occupancy, a much lower frequency than observed at 5 K should be found at a Na vacant site in comparison with that at the O2− site (ratio ~1:5), as already advocated in [7,9] for \( x \geq 0.75 \).

For \( x = 0.50 \), Co are known to form alternating chains in a given plane [4]. Every two chains, Na alternates above and below each Co; hence the Co valence in such a chain is expected to be uniform and weaker than for the next Co, also uniform, chain. In the following, we make the simple assumption that cobalt is either in the Co3+ or the Co4+ state [13] and consider an ideal undistorted orthorhombic structure. We arbitrarily consider μ+ bound to oxygens located above the Co plane. Inequivalent charge-magnetic configurations surrounding oxygens can be sorted by considering Co triangles next to the μ+ site together with the occupancy of nn Na+ sites (Fig. 5). Three inequivalent O2− are found, consistent with the number of frequencies observed at 5 K and above 49 K. Two have 2 nn magnetic Co4+ and have either a nn Na1 or a nn Na2, respectively, labeled (2a) and (2b) [14]. The third site (1) has a single nn Co4+ and 2 nn Co3+ with one Na1 and one Na2 filled nearby sites.

As already argued above, μ+ with 1 magnetic nn Co4+ (site 1) can be safely assigned to the highest frequency signal. A μ+ coupled to two nn Co8+ will sense pronounced changes of internal fields and may also experience quite weak fields. Our data constrain severely the orientation of the moments, since, first, \( H_{\text{int}} \) is observed to be...
The origin of these multiple transitions is not obvious at the present stage. We can clearly rule out a scenario where an IC-SDW would switch to a C-SDW since the frequencies are already well peaked at the upper transition. Whether the problem can be tackled through a purely ionic model where anisotropy and charge localization could induce the secondary transitions or whether a C-SDW order might be influenced by these parameters open new avenues to the debate on this peculiar $x = 0.5$ composition.

In summary, we clearly show the existence of bulk phase transitions in high quality powdered samples with well identified structures. This truly underlines the importance of magnetism in cobaltates, in a large range of Na doping. For $x = 0.5$, three magnetic transitions occur with an AFM order building up at 85 K and moment rearrangements at lower $T$ (48 and 29 K). For $0.75 \leq x \leq 0.85$, one can now isolate three close magnetic phases, with a C-SDW ground state, including the $x = 0.82$ of [9]. The increase of $T_c$ from 21 K for the hexagonal $x = 0.75$ to 27 K for the monoclinic $x = 0.85$ phase is quite surprising since the number of magnetic Co is expected to decrease. Whether Co-Co couplings differ because of structural changes or some charge ordering locks in a different magnetic order definitely calls for further investigations of stable structures in the range $x = 0.75$–1 as well as a clear identification of magnetic Co sites with respect to the Na order. Rather than a continuous phase diagram induced by charge doping only, the scattering of the $T_c$’s points at a tight link between structures and magnetic order. Disentangling how charge order-disorder and doping impact on the physical properties versus Na content is now a crucial issue for cobaltates which apparently combine the physics of manganites and high-$T_c$ cuprates.

[11] Loose powders or pressed disks were used. Because of a platelet shape of the grains, a $c$-axis preferential orientation could be observed parallel to the $\mu^+$ polarization.
[12] For $T > 48$ K, no magnetism was found in [10].
[13] Whatever the refinements about the charge and magnetic state of Co, we expect our discussion to hold provided only two dominant Co species exist for $x = 0.5$, one strongly magnetic and the other weakly magnetic.
[14] Because of the symmetry of the charge distribution, the $\mu^+$ locates in the midplane of the two $nn$ Co$^{4+}$ segment.