Muon-spin rotation study of magnetism in Na$_x$CoO$_2$ single crystals with 0.78 $\leq$ $x$ $\leq$ 0.97

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Abstract – By muon spin rotation we investigated the magnetic properties of a series of highly Na-doped Na$_x$CoO$_2$ single crystals with 0.78(1) $\leq$ $x$ $\leq$ 0.97(1). Our data provide evidence for an intrinsically inhomogeneous magnetic state which can be described in terms of hole-doping (Na vacancy)-induced magnetic clusters that percolate at 1 – $x$ $\geq$ 0.04 until they yield a bulk magnetic state near $x$ = 0.78. Evidence for a strong (likely geometrical) frustration of the magnetic order is obtained from the anomalous doping dependence of the spin fluctuation rate (above the ordering temperature) which is strongly enhanced at $x$ = 0.78 as compared to $x$ = 0.97.

The discovery of superconductivity with $T_c$ $\leq$ 5K in the hydrated layered cobaltate Na$_{0.35}$CoO$_2$·1.3H$_2$O [1] has renewed the interest in the physical properties of the parent compound Na$_x$CoO$_2$. Its rich phase diagram includes several phases with extraordinary electromagnetic and thermoelectric properties [2–4]. One attractive feature is the triangular coordination of Co which may favor geometrical frustration and unconventional ground states [5,6]. Another curious aspect concerns the finding that the anomalous electromagnetic properties are not confined to the Mott-insulator regime at low $x$, but also occur in the vicinity of the anticipated band-insulator at $x$ = 1. Examples are the occurrence of magnetic order at $x$ $\geq$ 0.75 [7–11], signatures of strong spin-charge coupling [12] and giant thermoelectric effects [4]. The nature of the underlying magnetic state is still debated. While initial data were interpreted in terms of an incommensurate spin-density-wave (SDW) [7], recent neutron- and muon-spin-rotation ($\mu$SR) studies on single crystals [8–11] yield commensurate A-type antiferromagnetic (AF) order and a weakly anisotropic magnetic exchange coupling constant that contrasts with the large Fermi-surface anisotropy. Besides, an interpretation in terms of localized Co moments in the low-spin-state is also questionable since the long range magnetic order would occur in a strongly diluted state with only 1 – $x$ magnetic Co$^{4+}$ ions ($^3t^2_2$, $S = 1/2$) and $x$ non-magnetic Co$^{3+}$ ions ($^6t^2_2$, $S = 0$).

Here we present muon spin rotation ($\mu$SR) and dc magnetization measurements which provide new insight into the evolution of the magnetic properties of highly Na-doped Na$_x$CoO$_2$ single crystals with 0.78(1) $\leq$ $x$ $\leq$ 0.97(1). Our data provide evidence for hole-doping (or Na vacancy)-induced magnetic clusters which remain isolated at 1 – $x$ $\leq$ 0.04 but percolate at 1 – $x$ $>$ 0.04 until a homogeneous magnetic state is achieved near 1 – $x$ $\approx$ 0.25. We also find that this long-range ordered magnetic state exhibits signatures of strong (likely geometrical) frustration.

The Na$_x$CoO$_2$ crystals have been cleaved from ingots that were grown with an optical floating-zone furnace [13]. The average Na:Co ratio of our crystals has been carefully determined by inductively coupled plasma spectroscopy (ICPS) and by neutron activation analysis with an accuracy of about 1%. The crystals were also characterized by electrical transport, dc magnetometry, and single-crystal X-ray diffraction. The latter suggest that the $x$ = 0.78 crystals are single phase (likely $\alpha'$), while the ones at
Fig. 1: The $\mu$SR data for Na$_{0.97}$CoO$_2$. (a) Displays the zero-field spectra at representative temperatures. The solid lines show fits as obtained with the function $P(t)/P(0) = 0.4 \cdot \exp(-\lambda_1 t)^\beta + 0.6 \cdot KG \cdot \exp(-\lambda_2 t)$, where $KG$ represents the so-called Kubo-Toyabe function which accounts for the nuclear magnetic moments. (b) and (c) show longitudinal-field spectra at 30 K and 15 K, and (d) the transverse field (TF) relaxation rate of the fast relaxing component. Inset: X-ray diffraction data (Cu$K\alpha$ with wavelength, $\lambda = 1.54\text{Å}$) for crystals from two different growth batches with $x = 0.97(1)$ indicating the presence of a pure $\alpha$-phase or mixed $\alpha$ and $\alpha'$ phases, respectively. Arrows mark the position of the $\alpha'$-phase (002) peak and the $\alpha$-phase (003) peaks.

$x = 0.87$, 0.92 and 0.97 contain mixed $\alpha$- and $\alpha'$-phases, similar as was previously reported [3,4]. For the latter, the intensity of the $\alpha'$-phase peaks was found to exhibit a strong variation, even for crystals with a similar bulk Na content (according ICPS and neutron activation analysis). Accordingly, we suspect as outlined below that the X-ray data my be strongly affected by Na deficient surface layers. Finally, the $\mu$SR measurements were performed with the GPS setup at the $\pi m3$ beamline of the Paul-Scherrer-Institut (PSI) in Villigen, Switzerland, which provides 100% spin-polarized muons. Details concerning the technique can be found in [14]. Here we only note that the zero-field $\mu$SR technique provides information about the local scale distribution of the internal magnetic fields of magnetic materials. In particular, it yields a reliable estimate of the bulk volume fractions of the magnetic phases, even for the case of weak and strongly disordered magnets.

First we discuss the $\mu$SR data of the Na$_{0.97}$CoO$_2$ crystal with $1 - x = 0.03(1)$ holes per Co (fig. 1). The zero-field (ZF) spectra between 5 and 300 K are shown in fig. 1(a). The low-$T$ spectra evidently consist of two distinct parts. Nearly 40% of the signal depolarizes rapidly while the remaining 60% exhibits a much slower relaxation. This suggests that the sample is in a spatially inhomogeneous magnetic state with about 40% of the volume containing sizeable magnetic moments and around 60% remaining non-magnetic. It is also evident that the correlations in the magnetic regions persist to temperatures in excess of 200 K. The absence of oscillations in the fast relaxing signal implies a broad distribution of the magnetic fields that originates either from static but spatially disordered moments or else from dynamical fluctuations. It is well known that a large longitudinal field (LF) enables one to distinguish between these two cases [14]. It gives rise to a strong reduction of the amplitude of the magnetic signal (so-called “decoupling effect”) in the static case but not in the dynamic one. Accordingly, the data at LF = 1 kOe in figs. 1(b) and (c) establish that a transition from a
X-ray diffraction data which signal the presence of two phases [17]. The former interpretation was motivated by deficient and thus magnetic phase [16] or even of impurity of chemical inhomogeneity due to inclusions of a Na-deficient region that are frequently observed in X-ray [16,17] and neutron diffraction [3]. We noticed however, that the X-ray signature of the $\alpha'$-phase in highly Na-doped crystals appears to be time dependent, even on the scale of weeks. On the contrary, we confirmed that the $\mu$SR data do not exhibit any noticeable changes, not even after one year. Accordingly, we suspect that the apparent instability of the crystal surface at ambient conditions towards the formation of Na$_2$CO$_3$ and a subsequent development of a Na-deficient surface layer may play an important role here. We note that this is especially relevant for polycrystalline samples on which the majority of experiments has been performed [3,7,11,17]. In this context, we emphasize that our crystals are mm sized and that $\mu$SR is a truly bulk sensitive technique since the muon implantation depth is of the order of 100 $\mu$m.

Our combined $\mu$SR and dc magnetisation measurements are indeed consistent with the point of view that the relevant length scale of the magnetic phase separation at $x = 0.97$ is on the order of nanometers. In the first place they are suggestive of an antiferromagnetic spin coupling within the magnetic clusters. Specifically, the dc magnetisation data in fig. 2 yield a fairly small value of the total Curie-moment which is otherwise difficult to reconcile with the large magnetic volume fraction and the sizeable magnetic Co moment that emerges from the $\mu$SR data. The solid lines in fig. 2 show fits to the high-temperature magnetisation data for $T > 50$ K with the function, $\chi_{\text{mol}} = \frac{C}{T + \Theta} + \chi^0$. The Curie-Weiss term with $C = (1 - x)N_A\mu^2_{eff}/3k_B$, Avogadro number, $N_A$, effective moment, $\mu_{eff}$, and Boltzmann constant, $k_B$, accounts for the paramagnetic component. The $T$-independent term, $\chi^0$, accounts, besides Van-Vleck paramagnetism and core diamagnetism, for the strong correlation effects within the clusters. The parameters obtained at $x = 0.97$ for the field directions parallel ($\parallel$) and perpendicular ($\perp$) to the $c$-axis are $\Theta_{\parallel,\perp} = -61$ and $-45$ K, $\lambda_0^{\parallel,\perp} = 1.0 \times 10^{-4}$ and $0.78 \times 10^{-4}$ cm$^3$/mol and $C_{\parallel,\perp} = 8.4 \times 10^{-3}$ and $5.5 \times 10^{-3}$ cm$^3$/mol, respectively. For 3% doping this translates into a moment per doped hole of $\mu_{eff} = 1.5$ and 1.2 in units of Bohr magneton, $\mu_B$, respectively. With a spin only Landé factor of $g = 2$ we thus derive a total spin of $S_{\parallel,\perp} = 0.4$ and 0.28 per cluster. Such a small magnetic moment per cluster needs to be reconciled with the sizeable moment per magnetic Co ion of about 0.1–0.3 $\mu_B$ that has been inferred from $\mu$SR and neutron experiments [8–11]. While this value was obtained for AF samples with $x \approx 0.82$, our $\mu$SR data indicate that the Co moments at $x = 0.97$ are of similar magnitude. The local field at the muon site, $B_\mu$, as deduced from the TF-$\mu$SR depolarization rate of...
\[ \lambda^F_T \sim 23 \mu s^{-1} \] at \( x = 0.97 \) (assuming randomly oriented moments) of \( \langle B \rangle = \frac{\lambda^F_T}{\nu} \approx 270 \text{G} \) (\( \gamma \approx 851.4 \text{MHz/T} \) is the muon gyromagnetic ratio) compares indeed well to the one obtained from the highest precession frequency of the antiferromagnetic samples of \( \nu = 3.3 \text{MHz} \) (see fig. 3) with \( B = \frac{2\nu}{\nu} \approx 240 \text{G} \). It is now interesting to note that the non-magnetic regions experience noticeable magnetic stray fields which apparently originate from the magnetic clusters, since they also undergo a freezing transition around 20 K. This is evident from the ZF- and LF-\( \mu \)SR data in figs. 1(b) and 1(c) which show that the slowly relaxing component exhibits a decoupling effect for LF = 50 Oe at 15 K that is absent at 30 K. The large magnitude of the decoupling effect at 15 K suggests that stray fields essentially persist throughout the entire non-magnetic volume of the sample. This result needs to be compared with the estimates based on dipolar field calculations which indicate that the stray fields around antiferromagnetically ordered clusters are extremely short ranged, i.e. they are noticeable only over a few nanometers. Accordingly, our combined \( \mu \)SR and dc magnetisation data are indeed suggestive of a nanoscopic coexistence of the magnetic and the non-magnetic regions.

This conclusion is supported by our finding that with increasing hole doping, \( 1-x \), the magnetic clusters percolate and form extended magnetic patches until a homogeneous magnetic state is achieved near \( x = 0.78 \). This is shown in fig. 3 which displays the ZF-\( \mu \)SR time spectra for \( x = 0.92, 0.87 \) and 0.78. Figure 3(d) shows the distribution in frequency space as obtained with a maximum-entropy analysis. It is evident that all the 5 K spectra contain an oscillatory component due to magnetic order at least in parts of the volume. We used the function \( P(t) = P(0) \sum_i A_i \cos(2\pi \nu_i t) \exp(-\lambda_i t) \) to obtain the parameters for the precession frequency, \( \nu \), the relaxation rate, \( \lambda \), and the relative amplitudes, \( A_i \), as shown in fig. 4 together with previous data for \( x = 0.82(1) \) [8]. Starting from a threshold of \( x^{tr} \approx 0.04 \), the amplitude of the oscillatory signal increases rapidly with hole doping, and approaches 100% around \( x = 0.78 \). The full oscillatory amplitude of the 5 K spectrum at \( x = 0.78 \) also confirms that the magnetic field at the muon site, \( \vec{B}_\mu \), is almost perpendicular to the muon spin direction (which is tilted by 60 degree against the c-axis). Accordingly, the \( \mu \)SR amplitudes should indeed be proportional to the corresponding magnetic volume fractions [8]. The c-axis orientation of \( \vec{B}_\mu \) furthermore suggests that the muons reside at interstitial sites near the oxygen ions rather than on vacant Na sites where \( \vec{B}_\mu \) would have a larger component parallel to the CoO\(_2\) layers and be much smaller in magnitude as was previously noted [8,11]. While we do not attempt here a detailed assignment of the muon sites, we notice that the signal at \( \nu = 1.2 \text{MHz} \) likely arises from the muons that are stopped near the boundaries of the magnetic patches, since it has a large relaxation rate of about \( 3 \mu s^{-1} \), it

Fig. 3: Zero-field \( \mu \)SR spectra for Na\(_x\)CoO\(_2\) crystals with \( x = \) 0.92, 0.87 and 0.78 which exhibit a rapidly increasing fraction of the oscillatory signal below \( T_N \).

Fig. 4: Doping dependence of the fit parameters of the magnetic component in the ZF-\( \mu \)SR spectra at 5 K. (a) Amplitude of the precession frequencies. The half down (up) filled symbols show the amplitudes of the splitted frequencies at \( x = 0.78 \) with 2.2 (2.6) MHz and 3.1 (3.3) MHz, respectively. Solid (open) circles show the sum of the oscillatory (total magnetic) amplitudes. The dotted line is a guide to the eye (b) Doping dependence of the corresponding relaxation rates as shown by the same symbols.
dominates at $x = 0.92$ and 0.87 and is absent at $x = 0.78$. Correspondingly, we suggest that the signals near 2.5 and 3.0 MHz, which become very narrow and further split at $x = 0.78$, arise from muons that reside within the order patches. Whether the distinction between these muon sites arises from different structural (for example due to the Na neighbors) or magnetic environments requires further investigation.

Next, we discuss the remarkable trend that the $\mu$SR spin fluctuation rate, $\tau_\mu$, at $T > T_N$ is strongly enhanced for $x = 0.78$ as compared to $x = 0.97$. At $x = 0.97$ slow spin fluctuations with $10^{-6} \text{s} > \tau_\mu > 10^{-10} \text{s}$ persist to at least 200 K while at $x = 0.78$ the spin fluctuations become too fast to be detected within the $\mu$SR time window of $\tau_\mu < 10^{-10} \text{s}$ immediately above $T_N = 22 \text{ K}$. This is evident from fig. 3(c) where already the 25 K spectrum exhibits a Gaussian shape and a small relaxation rate that is entirely due to the nuclear moments. This trend is supported by the magnetization data for $x = 0.78$ (fig. 2) which exhibit a broad maximum around 60 K that is characteristic for low-dimensional and/or geometrically frustrated systems with strong (quantum) fluctuations. We emphasize that this behavior once more is not compatible with a purely chemical phase separation where the spin fluctuations should be enhanced due to finite-size effects for the isolated nanoscopic magnetic clusters at $x = 0.97$. Our data therefore highlight that the ordered magnetic state at $x = 0.78$ is not a conventional kind of A-type antiferromagnet that should not be subject to such strong frustration effect, not even for a triangular lattice.

Finally, we note that the main features of our data, like the presence of hole-doping–induced nanoscopic magnetic clusters that percolate and form a homogeneous magnetic state near $1 - x \approx 0.75$ with signatures of strong geometrical frustration, can be accounted for in the context of the so-called spin state transition (SST) model [12,19,20]. The SST may be induced by the doped holes and the related Na vacancies which lower the crystal field symmetry of the neighboring Co$^{3+}$ ions and thus give rise to a splitting of the $e_g$ levels that reduces the energy difference to the highest occupied $t_{2g}$ level. Accordingly, at low doping each hole induces a magnetic cluster with a central low spin (LS, $S = 1/2$) Co$^{4+}$ ion that is surrounded by six intermediate spin (IS, $S = 1$) Co$^{3+}$ ions. A corresponding doping-induced SST is indeed well established for the perovskite La$_{1-x}$Sr$_x$CoO$_3$, whose Co ions are in a corresponding valence state and crystallographic coordination [21]. In comparison, the possible SST in Na$_2$CoO$_2$ has some unique aspects like the small total moment of the magnetic clusters of only $\mu_{eff} \sim 1.5 \mu_B$ and a long-range ordered magnetic state at $1 - x = 0.25$ [12,19], where the IS Co$^{3+}$ moments reside on a 2-d Kagomé lattice which is geometrically frustrated and thus subject to strong quantum fluctuations. Explicit calculations have shown that while the dominant interactions within the clusters are AF, a weak residual FM in-plane interaction between the clusters gives rise to an A-type AF state [19,20]. Furthermore, the SST model accounts for the rapid disappearance of magnetism at $1 - x > 0.25$ where the symmetry reduction associated with the doped holes becomes insufficient to induce a SST.

Certainly, our present data do not suffice to establish such a SST scenario in highly Na-doped Na$_x$CoO$_2$. Nevertheless, our results emphasize two important aspects which should obtain increased attention in future experimental and theoretical studies. These are the presence of doping-induced nanoscopic magnetic clusters with a small total spin value and the strong (likely geometrical) frustration of the magnetic correlations in long-range ordered state in the vicinity of $1 - x = 0.25$.

In summary, by $\mu$SR and dc magnetisation measurements we have explored the magnetic properties of a series of highly Na doped Na$_x$CoO$_2$ single crystals with $0.78(1) \leq x \leq 0.97(1)$. Our data provide evidence for an intrinsically inhomogeneous magnetic state with hole-doping (Na vacancy)-induced magnetic clusters that percolate at $1 - x \geq 0.04$ until they yield a bulk magnetic state near $x \approx 0.78$. From the anomalous doping dependence of the spin fluctuation rate (above the ordering temperature), which is strongly enhanced at $x = 0.78$ as compared to $x = 0.97$, we obtained evidence that the bulk magnetic state is subject to strong (likely geometrical) frustration.

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