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Muon-spin rotation study of magnetism in Na_xCoO_2 single crystals with $0.78 \leqslant x \leqslant 0.97$

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Abstract – By muon spin rotation we investigated the magnetic properties of a series of highly Na-doped Na_xCoO_2 single crystals with $0.78(1) \leqslant x \leqslant 0.97(1)$. 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 $1-x \gtrsim 0.04$ 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 $T_c \leqslant 5\,\mathrm{K}$ in the hydrated layered cobaltate $Na_{0.35}CoO_2 \cdot 1.3\,H_2O$ [1] has renewed the interest in the physical properties of the parent compound Na_xCoO_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 $x \geqslant 0.75$ [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 (μSR) 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 ($^5t_{2g}$, $S = 1/2$) and x non-magnetic Co^{3+} ions ($^6t_{2g}$, $S = 0$).

Here we present muon spin rotation (μSR) and dc magnetization measurements which provide new insight into the evolution of the magnetic properties of highly Na-doped Na_xCoO_2 single crystals with $0.78(1) \leqslant x \leqslant 0.97(1)$. Our data provide evidence for hole-doping (or Na vacancy)-induced magnetic clusters which remain isolated at $1-x \lesssim 0.04$ 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_xCoO_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 α'), while the ones at

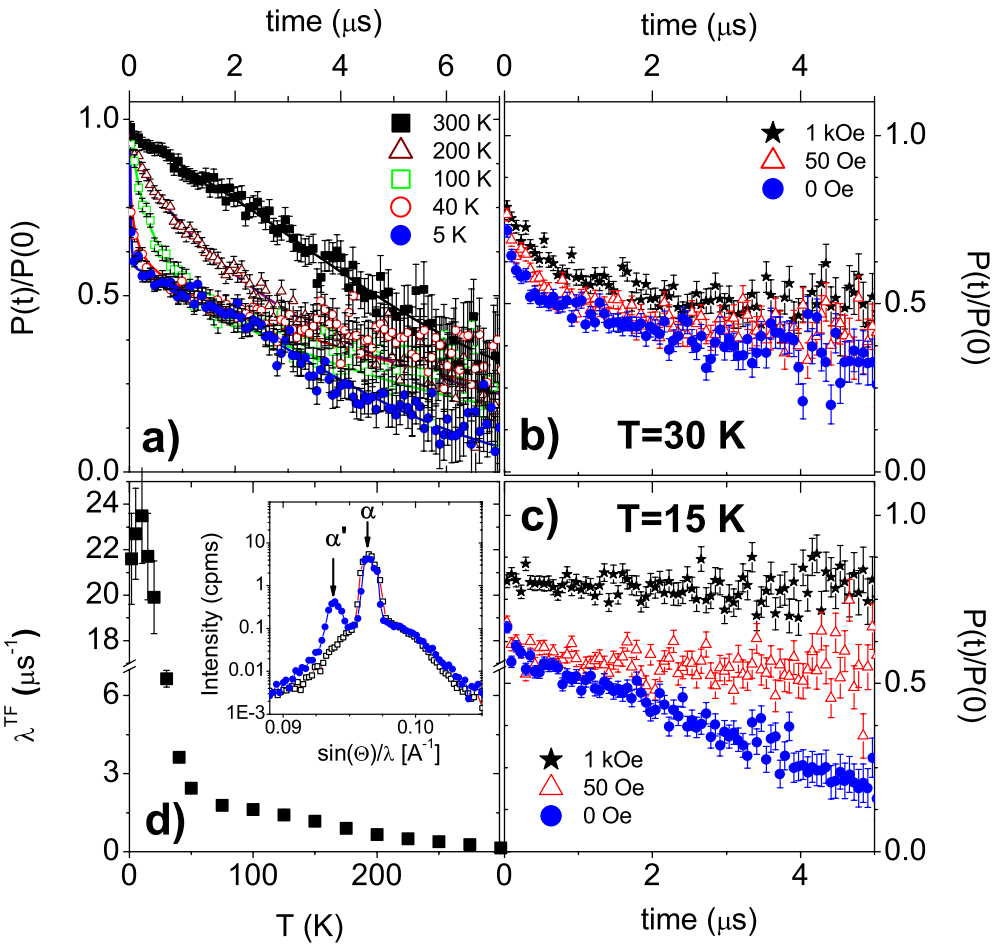

Fig. 1: The μSR data for $Na_{0.97}CoO_2$. (a) Displays the zero-field spectra at representative temperatures. The solid lines show fits as obtained with the function $P(t)/P(0) = 0.4 \cdot \exp(-\lambda_1 t)^\beta + 0.6 \cdot KG \cdot \exp(-\lambda_2 t)$, where KG represents the so-called Kubo-Toyabe 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, $\lambda = 1.54$ Å) for crystals from two different growth batches with $x = 0.97(1)$ indicating the presence of a pure α-phase or mixed α and α' phases, respectively. Arrows mark the position of the α'-phase (002) peak and the α-phase (003) peaks.

$x = 0.87$, 0.92 and 0.97 contain mixed α- and α'-phases, similar as was previously reported [3,4]. For the latter, the intensity of the α'-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 μSR measurements were performed with the GPS setup at the πm3 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 μSR 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 μSR 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

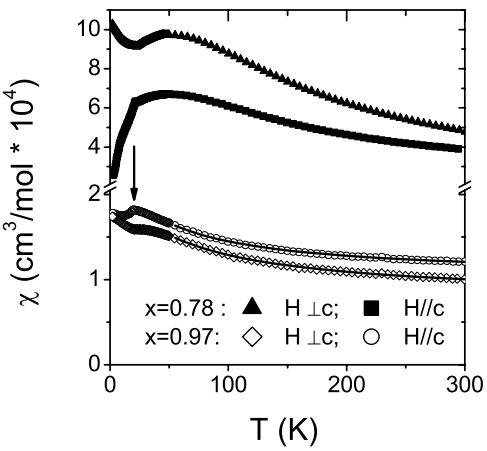

Fig. 2: T-dependent magnetic susceptibility of Na_xCoO_2 with $x = 0.97$ and 0.78. Solid lines show Curie-Weiss fits for $x = 0.97$ as specified in the text. The arrow marks the freezing transition at $T_f = 20.7$ K.

static to a dynamic state takes place between 15 and 30 K. The signatures of the corresponding spin freezing transition are also apparent in the transverse field (TF) relaxation rate, λ^{TF}, in fig. 1(d). The slow increase of λ^{TF} between 300 and 50 K is consistent with a gradual decrease of the spin fluctuation rate, while the following rise and the saturation below 20 K are characteristic of a freezing transition at $T_f \approx 20$ K. Furthermore, the transition width and the large value of λ_0^{TF} are characteristic for a glassy state [15]. This freezing transition is also evident in the dc magnetic susceptibility in fig. 2 due to a deviation from the Curie law below 50 K and a cusp around $T_f = 20$ K, as marked by the arrow.

The inhomogeneous magnetic state for samples with $x \approx 1$ was previously noticed but it was discussed in terms of chemical inhomogeniety due to inclusions of a Na-deficient and thus magnetic phase [16] or even of impurity phases [17]. The former interpretation was motivated by X-ray diffraction data which signal the presence of two Na_xCoO_2 phases with different Na content [3,4,16,17]. However, in the following we argue that such a purely chemical scenario is not sufficient to explain our data. Instead, we present evidence that the formation of intrinsic, doping induced magnetic nanoclusters seems to play an important role. For example, we investigated crystals from two growth batches with $x = 0.97(1)$ out of which one also exhibited the X-ray signatures of a secondary Na-deficient α'-phase, while the other according to X-rays was an almost pure α-phase (see inset of fig. 1(d)). Despite this substantial difference, our μSR data yield virtually identical bulk magnetic properties for both crystals (fig. 1 shows our μSR data of the pure α-phase crystals). The only distinction concerns a minor difference in the magnetic volume fraction that is well consistent with the 1% uncertainty in the Na content. These observations suggest that one needs to distinguish between a nanoscale phase separation as probed by μSR and a macroscopic one as evidenced for example with X-rays. While a strong correlation between the Na vacancies and the doped holes which determine the electronic and magnetic properties of the CoO_2 layers is evident [18], it remains unknown how the nanoscale magnetic clusters are related to the macroscopic Na-deficient regions that are frequently observed in X-ray [16,17] and neutron diffraction [3]. We noticed however, that the X-ray signature of the α'-phase in highly Na-doped crystals appears to be time dependent, even on the scale of weeks. On the contrary, we confirmed that the μSR 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_2CO_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 μSR is a truly bulk sensitive technique since the muon implantation depth is of the order of 100 μm.

Our combined μSR 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 μSR data. The solid lines in fig. 2 show fits to the high-temperature magnetisation data for $T > 50$ K with the function, $\chi_{mol} = \frac{C}{T-\Theta} + \chi^0$. The Curie-Weiss term with $C = (1-x)N_A\mu_{eff}^2/3k_B$, Avogadro number, N_A, effective moment, μ_{eff}, and Boltzman constant, k_B, accounts for the paramagnetic component. The T-independent term, χ^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 ($\|$) and perpendicular ($\perp$) to the c-axis are $\Theta_{\|,\perp} = -61$ and -45 K, $\chi^0_{\|,\perp} = 1 \cdot 10^{-4}$ and $0.78 \cdot 10^{-4}$ cm^3/mol and $C_{\|,\perp} = 8.4 \cdot 10^{-3}$ and $5.5 \cdot 10^{-3}$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, μ_B, respectively. With a spin only Landé factor of $g = 2$ we thus derive a total spin of $S_{\|,\perp} = 0.4$ 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 μ_B that has been inferred from μSR and neutron experiments [8–11]. While this value was obtained for AF samples with $x \approx 0.82$, our μSR data indicate that the Co moments at $x = 0.97$ are of similar magnitude. The local field at the muon site, B_μ, as deduced from the TF-μSR depolarization rate of

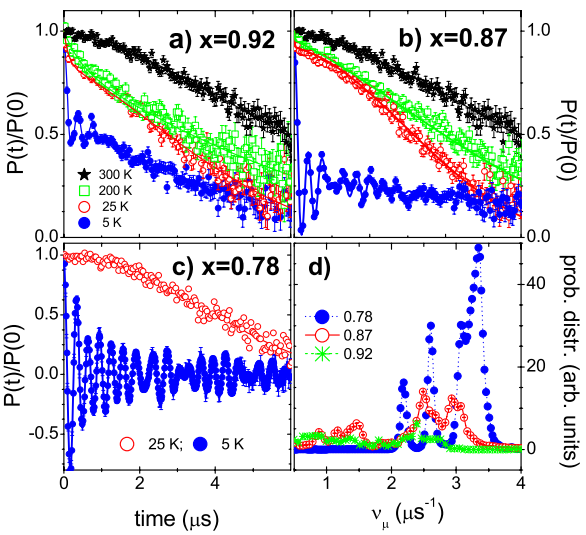

Fig. 3: Zero-field μSR spectra for Na_xCoO_2 crystals with $x = 0.92$, 0.87 and 0.78 which exhibit a rapidly increasing fraction of the oscillatory signal below T_N.

$\lambda_o^{TF} \sim 23\,\mu s^{-1}$ at $x = 0.97$ (assuming randomly oriented moments) of $\langle B_\mu \rangle = \frac{\lambda_o^{TF}}{\gamma_\mu} \approx 270\,\mathrm{G}$ ($\gamma_\mu = 851.4\,\mathrm{MHz/T}$ is the muon gyromagnetic ratio) compares indeed well to the one obtained from the highest precession frequency of the antiferromagnetic samples of $\nu_\mu = 3.3\,\mathrm{MHz}$ (see fig. 3) with $B_\mu = \frac{2\pi\nu_\mu}{\gamma_\mu} \approx 240\,\mathrm{G}$. 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-μSR data in figs. 1(b) and (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 μSR 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-μSR 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

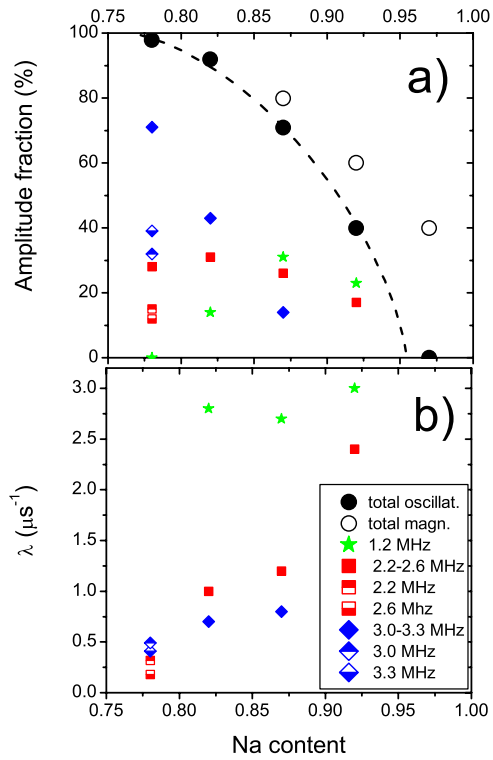

Fig. 4: Doping dependence of the fit parameters of the magnetic component in the ZF-μSR spectra at 5 K. (a) Amplitude of the precession frequencies. The half down (up) filled symbols show the amplitudes of the splitted frequencies at $x = 0.78$ with 2.2 (2.6) MHz and 3.1 (3.3) MHz, respectively. Solid (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.

the function $P(t) = P(0) \sum_i A_i \cos(2\pi\nu_\mu^i t) \exp(-\lambda^i t)$ to obtain the parameters for the precession frequency, ν_μ, the relaxation rate, λ, and the relative amplitudes, A, 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 μSR 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 $\nu_\mu = 1.2\,\mathrm{MHz}$ 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

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 μSR spin fluctuation rate, τ_μ, 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 $10^{-6}\,\mathrm{s} > \tau_\mu > 10^{-10}\,\mathrm{s}$ persist to at least 200 K while at $x = 0.78$ the spin fluctuations become too fast to be detected within the μSR time window of $\tau_\mu < 10^{-10}$ s immediately above $T_N = 22$ 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 $La_{1-x}Sr_xCoO_3$, whose Co ions are in a corresponding valence state and crystallographic coordination [21]. In comparison, the possible SST in Na_xCo_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_xCoO_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 μSR and dc magnetisation measurements we have explored the magnetic properties of a series of highly Na doped Na_xCoO_2 single crystals with $0.78(1) \leqslant x \leqslant 0.97(1)$. Our data provide evidence for an intrinsically inhomogeneous magnetic state with hole-doping (Na vacancy)-induced magnetic clusters that percolate at $1 - x \gtrsim 0.04$ 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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