Mesoscopic phase separation in Na$_x$CoO$_2$ (0.65 ≤ $x$ ≤ 0.75)

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NMR, EPR and magnetization measurements in Na$_x$CoO$_2$ for 0.65 ≤ $x$ ≤ 0.75 are presented. While the EPR signal arises from Co$^{4+}$ magnetic moments ordering at $T_c$ ≃ 26 K, $^{59}$Co NMR signal originates from cobalt nuclei in metallic regions with no long range magnetic order and characterized by a generalized susceptibility typical of strongly correlated metallic systems. This phase separation in metallic and magnetic insulating regions is argued to occur below $T^*(x)$ (220 – 270 K). Above $T^*$ an anomalous decrease in the intensity of the EPR signal is observed and associated with the delocalization of the electrons which for $T < T^*$ were localized on Co$^{4+}$ $d_{z^2}$ orbitals. It is pointed out that the in-plane antiferromagnetic coupling $J < T^*$ cannot be the driving force for the phase separation.

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I. INTRODUCTION

Na$_x$CoO$_2$ has been subject of an intense research activity in the past owing to its possible technological applicabilities as a battery electrode material. More recently it has attracted a renewed interest in view of its rich phase diagram and for the several aspects it shares in common with the superconducting cuprates. In particular, it has a layered structure formed piling up CoO$_2$ layers containing Co$^{4+}$ $S = 1/2$ ions and it becomes superconducting when the chemical pressure is modified by intercalating water molecules between Na and CoO$_2$ planes. On the other hand, while in the cuprates Cu$^{2+}$ ions form a square lattice, in Na$_x$CoO$_2$ cobalt ions form a triangular lattice which induces geometrical frustration of the antiferromagnetic interactions. Moreover, Na$_x$CoO$_2$, for $x$ around 0.7 shows an anomalous phase transition at $T_c$ ≃ 26 K, evidenced by a small peak in the specific heat. The low-temperature (T) ground state yields an extremely small macroscopic magnetization and it was argued, on the basis of $\mu$SR measurements, that it might correspond to a spin-density wave (SDW). Furthermore, slightly below room temperature, on the basis of NMR measurements alone, Gavilano et al. Ref 8 suggested that charge ordering occurs. In this T range anomalies in $^{59}$Co NMR spectra and a crossover from insulating to metallic-like behavior in the c-axes resistivity was observed for $x \approx 0.5$. Finally, a recent analysis of low-T thermal and transport properties suggested that for $x$ around 0.7 the electronic properties have to be described by a two-band model.

In the following, based on the analysis of NMR and EPR data, it will be shown that metallic and magnetic insulating domains coexist in Na$_x$CoO$_2$ for 0.65 ≤ $x$ ≤ 0.75. In particular, while EPR is sensitive to the magnetic domains with electrons localized on Co$^{4+}$ $d_{z^2}$ orbitals, NMR spectra and relaxation measurements allow to investigate the spin dynamics in the metallic regions. The phase separation is argued to occur below $T^*(x)$ (220 – 270 K), the same temperature at which Gavilano et al. Ref 8 suggested the occurrence of charge ordering. Above $T^*$ the electrons which were localized on Co$^{4+}$ $d_{z^2}$ orbitals can delocalize through an activated process.

In the next section the experimental results and technical aspects involved in the sample preparation, magnetization, EPR and NMR measurements will be given. The analysis of the EPR and NMR spectra providing evidence for a phase separation will be presented in Sect.III, together with the analysis of the generalized spin susceptibility within the metallic phase. The concluding remarks will be given in Sect. IV.
II. EXPERIMENTAL RESULTS

A. Sample Preparation

Na₂CoO₂ (x = 0.65, 0.70 and 0.75) samples were prepared following the "rapid heat-up" method\cite{12,13}. A stoichiometric mixture of 99.99% purity Co₃O₄ and Na₂CO₃ was thoroughly ground, and placed in a furnace and preheated at 750 C for 12 hours. The obtained samples were reground and annealed for 15 hours at 850 C in air, followed by slow cooling to room temperature. X-ray powder diffraction measurements confirmed all samples to be single phase of hexagonal γ-Na₂CoO₂\cite{21,22}. The lattice parameter a was estimated around 2.827 Å for all samples, while c = 10.939(3), 10.907(4) and 10.892(4) Å for x = 0.65, 0.70 and 0.75, respectively, in good agreement with the values reported in literature (see Fig.1).

B. Magnetization

Magnetization measurements were performed using a Quantum Design XPMS-XL7 SQUID magnetometer. The field cooled magnetization (M) for T ≥ Tc ≃ 26 K was observed to increase linearly with the magnetic field intensity (H). The temperature dependence of the susceptibility χ = M/H, after correcting for the core electrons diamagnetism, for x = 0.65, 0.7 and 0.75, is reported in Fig.2. One notices that χ increases on cooling and shows a small kink at Tc ≃ 26 K in all samples. The magnitude of χ was observed to increase sizeably upon decreasing x. The susceptibility measurements were repeated on the x = 0.75 sample after 4 months and no ageing effect was noticed, except for a small increase in the low-temperature susceptibility due to possible contamination from paramagnetic impurities.

C. EPR measurements

EPR spectra were recorded with an X-band spectrometer equipped with a standard microwave cavity and a variable temperature device. The room temperature derivative of the EPR powder spectra for x = 0.65, 0.7 and 0.75 is shown in Fig.3. The spectra are broad and slightly asymmetric, with a g ≃ 2, typical of Co⁴⁺ ions with a distorted octahedral coordination and a low-spin S = 1/2 configuration. One notices a remarkable decrease in the intensity of the EPR signal with increasing Na content. The intensity of the EPR signal was calibrated with respect to the one of a reference paramagnetic salt and it was found that even for x = 0.65 only about 8% of all Co sites contribute to the EPR signal. This reduced intensity at room temperature should not be associated with a poor penetration of the microwave inside the grains. In fact, at room temperature the estimated skin depth is 18 μm, close to the average grain size. Only at low temperature the shortening of the skin depth can lead to a poor irradiation. The low EPR signal originates from a reduced fraction of Co⁴⁺ sites. The intensity of the EPR signal (see Fig.4), which in principle is proportional to the contribution to the static uniform susceptibility of the irradiated Co⁴⁺ ions, shows an anomalous decrease above T* (≃ 240K for x = 0.7 and ≃ 270 K for x = 0.65) and vanishes around 500 K. At low temperature the signal intensity passes through a maximum around 125 K, then decreases and vanishes abruptly at Tc, indicating that at this temperature a transition to a phase with long range order among Co⁴⁺ moments occurs. The temperature dependence of the EPR linewidth shows a minimum around 115 K characteristic of two-dimensional (2D) antiferromagnets\cite{27,18} (see the inset to Fig.5).

D. NMR Spectra and relaxation

NMR spectra and spin-lattice relaxation measurements were carried out using standard radio-frequency (RF) pulse sequences. $^{23}$Na echo signal was maximized with a $\pi/2 - \tau - \pi$ pulse sequence while $^{59}$Co echo signal was maximized with a $\pi/2 - \tau - \pi/2$ sequence. The $^{23}$Na (see Fig.6) and $^{59}$Co NMR powder spectra were obtained from the Fourier transform of half of the echo signal and from the envelope of the echo magnitude, respectively.

$^{23}$Na NMR spectra of the central line, associated with the 1/2 − − 1/2 transition, were observed to progressively shift to higher frequency and to broaden on cooling (see Fig.7). However, the shape of the low-T spectra was not reproducible. Even after a temperature cycle in helium atmosphere, where the sample was warmed from 35 K up to 280 K and after 50 minutes cooled back to 35 K, a change in the spectrum was noticed (see Fig.8). This evidences that the modifications are not due to ageing effects but rather reflect intrinsic differences in the microscopic environment around the nuclei. In some cases a nearly symmetric line shape was observed whereas in other measurements two distinct peaks were visible\cite{14} (see Fig.9). The two peaks of $^{23}$Na central line should not be ascribed to the two
singularities expected for a quadrupolar perturbed NMR powder spectrum since, as will be shown hereafter, the temperature dependence of the spin-lattice relaxation rate measured at the two peaks is different. Also $^{59}$Co NMR spectra show analogous modifications after the sample has undergone a temperature cycle between 35 K and room temperature.

It must be mentioned that neither $^{59}$Co nor $^{23}$Na spectra show any sizeable change when the sample is cooled below $T_c$. As can be seen in Fig.7, the $^{59}$Co NMR spectrum of the central line is practically identical above and below $T_c$. This is a clear indication that the $^{59}$Co nuclei giving rise to the NMR signal, corresponding to the majority of cobalt nuclei, are in regions with no long range magnetic order. It must be mentioned that the observation of $^{59}$Co nuclei belonging to Co$^{4+}$ ions, the ones yielding the EPR signal, is prevented by the extremely fast nuclear relaxation. Hence, EPR and NMR in Na$_2$CoO$_2$ are complementary. The first probes the local susceptibility of Co$^{4+}$ rich regions which show a long range magnetic order below 26 K, the second allows to investigate the static and dynamic magnetic properties of the metallic regions with non-magnetic cobalt ions.

The paramagnetic shift $\Delta K$ of $^{23}$Na NMR central line shows the same temperature dependence of $\chi$ measured with the SQUID magnetometer. In fact, one can write

$$\Delta K = \frac{A\chi(q = 0, \omega = 0)}{g\mu_B N_A} + \delta$$

with $A$ the hyperfine coupling, $\chi(0, 0)$ the static uniform molar spin susceptibility and $\delta$ the chemical shift. Hence, the plot of $\Delta K$ vs. $\chi$ directly yields the hyperfine coupling (see Fig.8). For $x = 0.65$ $A \approx 16$ kOe, while for $x = 0.75$ a slightly smaller value $A \approx 14$ kOe was found.

Nuclear spin-lattice relaxation rate $1/T_1$ was measured by using a saturation recovery pulse sequence. The recovery of the nuclear magnetization after saturation of the central line deviates a bit from the expected behavior, namely $[1 - m(t)/m(t \to \infty)] = 0.1 \exp(-t/T_1) / 0.9 \exp(-6t/T_1)$ for $^{23}$Na and $[1 - m(t)/m(t \to \infty)] = 0.012 \exp(-t/T_1) + 0.068 \exp(-6t/T_1) + 0.206 \exp(-15t/T_1) + 0.714 \exp(-28t/T_1)$ for $^{59}$Co. The nuclear magnetization recovered at time $t$ after the saturation sequence. This discrepancy is due to the fact that the different parts of $^{59}$Co and $^{23}$Na NMR spectra have relaxation rates which differ both in magnitude and also in regards of the temperature dependence. This is evident, for instance, when the recovery of the intensity of the two shoulders of $^{23}$Na NMR spectrum in Fig.5 is recorded (see Fig.9). One notices a fast relaxing component, associated with the less intense shoulder, and a slow relaxing component due to the most intense peak. The T-dependence of the relaxation rate of the fast relaxing $^{23}$Na nuclei shows a small kink at $T_c$ (see the inset to Fig.10) and should be associated with those nuclei close to Co$^{4+}$ ions. On the other hand, the T-dependence of $1/T_1$ due to the slow relaxing nuclei shows a different trend and no peak at $T_c$. These nuclei are the ones belonging to the metallic regions. Unfortunately, it is possible to discern these two components only at low temperature and only when $^{23}$Na NMR spectra shows well defined shoulders. When this separation is not possible, since most of $^{23}$Na nuclei are characterized by a slow relaxation rate, the measured $1/T_1$ probes essentially the spin excitations of the metallic regions of the sample (see Fig.11). $1/T_1$ is observed to increase smoothly with temperature up to about 100 K where a more pronounced increase is observed, followed by an abrupt increase around $T^* \approx 220$ K for $x = 0.75$ and around $T^* \approx 270$ K for $x = 0.65$, similarly to what was observed by Gavilano et al. Ref.8. The temperature dependence of $^{59}$Co $1/T_1$ shows a similar behavior and no anomaly at $T_c$ (see Fig.11).

III. ANALYSIS AND DISCUSSION

First we will concentrate on the experimental evidences for a phase separation in metallic and in insulating magnetic domains and then we will discuss in more detail the temperature dependence of the static uniform susceptibility probed by NMR shift and magnetization measurements and of the low-frequency dynamics investigated by means of $1/T_1$ measurements.

A. Phase separation

As already mentioned in the previous section the EPR signal is characteristic of Co$^{4+}$ ions in a low-spin state, with the lowest $t_{2g}$ levels fully occupied and the highest $a^T_{1g}$ (corresponding to $d_{z^2}$) orbital half-filled. The degeneracy among the lowest twofold-degenerate $e^T$ and the $a^T_{1g}$ levels is relieved by the trigonal distortion around cobalt. Crystal field calculations show that these levels are well separated and hence $g \approx 2$ and that a reduced spin-orbit coupling can account for the small anisotropy of the $g$ tensor yielding the slightly asymmetric EPR line (see Fig.3). For $T > T^*$ the electrons localized on the $a^T_{1g}$ orbital can be promoted to the conduction band formed by the hybridization of Co$^{4+}$
$e^T$ and O $2p$ orbitals, through an activated process. This leads to an activated transport along the c-axis and to a polaronic-like motion of the electrons, as pointed out by Rivadulla et al. Ref. When the electrons are promoted to the conduction band the number of Co$^{4+}$ sites is progressively reduced, the intensity of the EPR signal diminishes with temperature (see Fig.3) and, finally, for $T > 500$ K the majority of the electrons are itinerant. Hence, one can derive the T-dependence of Co$^{4+}$ sites density directly from the EPR data.

In order to estimate the number of Co$^{4+}$ sites one has first to take into account that the EPR signal intensity depends on the T-dependent static uniform susceptibility and on the microwave screening, which is relevant at low-T. The T-dependence of the spin susceptibility was assumed to be the one of a 2D triangular antiferromagnet, with a Curie-Weiss temperature $\Theta \approx 135$ K. This value is suggested by the minimum in the T-dependence of the EPR linewidth, which usually occurs at a temperature slightly below $\Theta$. The maximum in the T-dependence of the EPR intensity around 125 K is not one of the characteristic susceptibility of a 2D triangular antiferromagnet, which should occur around $0.35\Theta \approx 47$ K (see the dotted line in Fig.2). Also the decrease of the EPR intensity below 100 K is too fast to originate from the T dependence of the susceptibility of a 2D triangular antiferromagnet. In fact, the pronounced reduction of the low-T EPR intensity results from the decrease of the skin-depth with temperature, which is proportional to the square-root of the electrical resistivity. In order to take into account this effect we have assumed for simplicity spherical grains, with an average radius of 30 $\mu$m, and that a grain is fully irradiated over a distance equal to $d$ (18 $\mu$m at room temperature). Taking into account the T-dependence of Na$_x$CoO$_2$ resistivity reported in literature we have derived the curve shown in Fig.4 for the expected integrated EPR intensity. The experimental data are observed to follow rather well the expected behavior below $T^*$, pointing out that for $T \leq T^*$ the density of Co$^{4+}$ sites is T-independent. The reduction of the EPR intensity above $T^*$, with respect to the estimated one allows to derive the temperature evolution of the fraction of electrons localized on Co$^{4+}$ $a_1^T$ orbitals (see Fig.11). If $\Delta$ is the energy difference between the $a_1^T$ level and the conduction band, the statistical population of Co$^{4+}$ ions should be given roughly by $n_{Co^{4+}}(T)/n_{Co^{4+}}(T \ll T^*) = 1/(1 + N_{eff}/\exp(-\Delta/T))$, with $N_{eff}$ an effective density of states for the itinerant electrons. Although the data in Fig.11 can be fitted rather well for a value of $\Delta \approx 0.5$ eV a more quantitative estimate would require the knowledge of the T-dependence of $\Delta$ and therefore this value should be taken just as an order of magnitude.

The observation of an EPR signal below $T^*$ suggests that, although the electrical resistivity has a metallic behavior, there is still a sizeable fraction of electrons localized on Co$^{4+}$ $a_1^T$ orbitals at low T and, hence, $T^*$ cannot signal a conventional metal to insulator transition. The absolute value of the fraction of Co$^{4+}$ sites for $T \ll T^*$, estimated from the EPR measurements, is around 8% for $x = 0.65$ and progressively decreases upon increasing the Na content. This trend is exactly the one of the magnetic entropy estimated from specific heat measurements carried out on samples of the same batch (see Fig.12). In particular, the x dependence of the intensity of the specific heat peak at $T_c$ scales with the EPR intensity upon increasing x (see the inset to Fig.12). Moreover, the magnitude of the magnetic entropy also indicates that for $x = 0.65$ a fraction around 8% of $S = 1/2$ ions contribute to the total entropy. This is a neat confirmation that the magnetic transition yielding the specific heat peak at 26 K is due to the ordering of localized Co$^{4+}$ magnetic moments. Also $\mu$SR measurements suggest that only a small fraction of the sample becomes magnetic. In fact, Sugiyama et al. Ref. observed that for $x = 0.75$ no more than 20 % of the muons injected in the sample go into (or close to) magnetically ordered regions for $T \leq T_c$. This is not by itself an indication of a SDW phase since in that case, although one might expect a reduced value of the sample magnetization, all the sample should show a long-range order.

On the other hand, $^{59}$Co NMR relaxation measurements and spectra, due to cobalt nuclei in metallic regions, show no sign of magnetic ordering. These observations clearly point towards a phase separation between antiferromagnetic insulating and metallic regions for $T < T^*$. Above $T^*$ no phase separation occurs and the electrons which for $T < T^*$ were localized on the $a_1^T$ orbital can move with a polaronic-like motion through all the sample.

The difference in the NMR spectra after temperature cycling above $T^*$ can be due to a different topological arrangement of the insulating and metallic domains. In the case of $^{23}$Na NMR spectra, the fast relaxing nuclei yielding the high frequency shoulder (see Fig.5) are the ones closer to Co$^{4+}$ ions, while the most intense peak should be associated with $^{23}$Na nuclei well inside the metallic regions. Since no effect of thermal cycles was noticed on the intensity of the EPR signal the ratio of the insulating over metallic volume should not change after the temperature cycles. Then, a different ratio in the intensity of the two components of $^{23}$Na NMR spectra should originate from a modification in the surface/volume ratio of the insulating regions. An increase in the intensity of the high frequency shoulder should be caused by an average decrease in the size of the insulating domains and vice-versa. Now, why the topology of the metallic and insulating domains should be affected by the temperature cycles? One possibility is that at high temperatures, due to their relatively high mobility, Na$^+$ ions modify their arrangement and lead to a modification in the Coulomb potential. In particular, one should expect that the metallic domains are attracted by Na$^+$ ionic potential, while the Co$^{4+}$ rich insulating domains are repulsed.

A lower boundary for the size $L$ of the magnetic domains can be estimated by taking into account that $T_c$ is $x$-independent and, therefore, is not affected by finite size effects. Then at $T_c$ the in-plane magnetic correlation length
\[\xi_{Co^{2+}}(T_c) \ll L.\] By taking for \(\xi_{Co^{2+}}(T)\) the T-dependence expected for a 2D triangular antiferromagnet and the in-plane exchange coupling \(J = 2\Theta/3 \approx 90\) K, one finds that at \(T_c\) the correlation length is less than 3 lattice steps. \(\xi_{Co^{2+}}(T_c)\) can be estimated also by taking a mean field expression for \(T_c \approx J_1 \xi_{Co^{2+}}(T_c)\), with \(J_1 \approx 10^{-2} J \approx 0.9K\) the interplanar exchange coupling among Co\(^{2+}\) magnetic moments. One finds \(\xi_{Co^{2+}}(T_c) \approx 5.4\) lattice steps. Hence, it must be concluded that \(L \gg 6\) lattice steps. Although an upper estimate for \(L\) cannot be made it must be remarked that one can conclude that the phase separation is not macroscopic, i.e. due to chemical inhomogeneities, but mesoscopic. First of all, it would be rather singular that all data reported in literature on Na\(_x\)CoO\(_2\) samples prepared in different ways indicate the same \(T_c\) and a similar magnitude of specific heat peaks\(^{20}\). Second, if the insulating magnetic domains where macroscopic the EPR signal intensity should not suffer from microwave irradiation problems. Third, the intensity of \(^{23}\)Na and \(^{59}\)Co NMR spectra should not be affected by thermal cycles if the separation was macroscopic.

Finally, it is important to observe that the phase separation is already present at \(T \gg J\). This clearly indicates that the antiferromagnetic coupling among Co\(^{2+}\) ions cannot be the driving force for this phase separation and that alternative explanations should be envisaged\(^{26}\).

### B. Spin dynamics in the metallic domains

The magnetization and NMR data allow to probe the static and dynamic magnetic properties of the metallic regions which do not undergo a phase transition. The total static uniform susceptibility measured with the SQUID is the \(\chi\) which do not undergo a phase transition. The total static uniform susceptibility measured with the SQUID is the \(\chi\) which do not undergo a phase transition. One notices (see Fig.2) that \(\chi\) can be estimated also by taking a mean field expression for \(T_c \approx J_1 \xi_{Co^{2+}}(T_c)\), with \(J_1 \approx 10^{-2} J \approx 0.9K\) the interplanar exchange coupling among Co\(^{2+}\) magnetic moments. One finds \(\xi_{Co^{2+}}(T_c) \approx 5.4\) lattice steps. Hence, it must be concluded that \(L \gg 6\) lattice steps. Although an upper estimate for \(L\) cannot be made it must be remarked that one can conclude that the phase separation is not macroscopic, i.e. due to chemical inhomogeneities, but mesoscopic. First of all, it would be rather singular that all data reported in literature on Na\(_x\)CoO\(_2\) samples prepared in different ways indicate the same \(T_c\) and a similar magnitude of specific heat peaks\(^{20}\). Second, if the insulating magnetic domains where macroscopic the EPR signal intensity should not suffer from microwave irradiation problems. Third, the intensity of \(^{23}\)Na and \(^{59}\)Co NMR spectra should not be affected by thermal cycles if the separation was macroscopic.

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is the one expected for a NFL and one can verify if, by using the form of \( \chi_{NFL}(q, \omega) \) reported above and \( \alpha = 0.7 \), the \( T \)-dependence of \( 1/T_1 \) is reproduced. From Eq. 4 by recalling that,\(^{31}\)

\[
\frac{1}{T_1} = \frac{\gamma^2}{2N} k_B T A^2 \sum_q \left[ \frac{\chi_{NFL}(q, \omega_L)}{\omega_L} \right]
\]

with \( \gamma \) the nuclear gyromagnetic ratio, under the condition that all the excitation frequencies \( \Gamma_q \) remain larger than \( \omega_L \) and in case of an external field \( H < gH_B \), one derives

\[
\frac{1}{T_1} = \frac{\gamma^2}{2N} k_B T A^2 \sum_{2D} c \frac{1 + (q \xi)^{2\alpha}}{k_B T^{\alpha+1}} .
\]

All constants involved in Eq. 3 except \( |Q| \) (entering \( \xi(T) \) expression) and \( a \), have been previously determined through the analysis of the NMR shift and of the static uniform spin susceptibility. One observes (see Fig. 14) that the \( T \)-dependence of \( 1/T_1 \) can be reproduced reasonably well for \( \alpha = 0.7 \) by taking a value of \( a \) such that \( \Gamma_Q(T = 10K) \simeq 2.2 \times 10^{12} \text{ s}^{-1} \) and \( \xi(T = 10K) \simeq 9 \) lattice steps, for \( x = 0.75 \), and \( \Gamma_Q(T = 10K) \simeq 1.3 \times 10^{12} \text{ s}^{-1} \) and for \( \xi(T = 10K) \simeq 11 \) lattice steps, for \( x = 0.65 \).

IV. CONCLUSIONS

It was shown through a series of EPR, NMR and magnetization measurements that in \( \text{Na}_x\text{CoO}_2 \) for \( 0.65 \leq x \leq 0.75 \) phase separation in metallic and in magnetic domains is present. The phase separation develops below \( T^* \Rightarrow J \) and therefore, it is unlikely that the antiferromagnetic exchange is the driving mechanism for the phase separation. Above \( T^* \) the activated delocalization of the electrons yields a marked reduction in the EPR amplitude. The spin excitations in the metallic regions are suitably described by an heuristic form of the susceptibility successfully used to describe the properties of strongly correlated metals. All the above observations are relevant in regards of the phase separation observed in the cuprates since they share many aspects in common with \( \text{Na}_x\text{CoO}_2 \). However, a deep comparison of the two systems goes beyond the aim of this work. Here we only mention that while the strong antiferromagnetic coupling in the cuprates can be relevant for the phase separation or for stripes formation\(^{32}\), in \( \text{Na}_x\text{CoO}_2 \) it is not. On the other hand, it is interesting to observe that in both systems phase separation is stabilized for those doping levels \( x \) yielding a charge distribution which is commensurate with the lattice, namely \( x \simeq 2/3 \) for the 2D triangular lattice of \( \text{Na}_x\text{CoO}_2 \) and \( x = 1/8 \) for the 2D square lattice of the cuprates\(^{32}\).

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FIG. 1: The $x$-dependence of the c-axes length is reported for the Na$_x$CoO$_2$ powder samples investigated in this work and for other samples reported in the literature.

FIG. 2: Temperature dependence of the susceptibility $\chi = M/H$, for $H = 40$ Gauss, in Na$_x$CoO$_2$ powder samples ($x = 0.65, 0.70$ and $0.75$). The dotted line shows the contribution to the susceptibility from Co$^{4+}$ magnetic moments for $x = 0.65$, as derived from EPR measurements (see the dotted line in Fig. 4). In the inset the field dependence of the magnetization at 280 K is shown for the $x = 0.65$ sample.

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FIG. 3: Derivative of the EPR signal in Na$_x$CoO$_2$ for $x = 0.65, 0.70$ and $0.75$, at $T = 293$ K. The intensity was normalized to the same reference value for all Na contents. In the inset the T-dependence of the linewidth of the EPR absorption signal for $x = 0.65$ is reported (the line is a guide to the eye).
FIG. 4: The T-dependence of the integrated EPR signal is reported for the $x = 0.65$ and $x = 0.7$ Na$_x$CoO$_2$ powder samples. The solid lines show the behavior expected on the basis of the T-dependence of the static uniform susceptibility and of the microwave skin-depth (see text). The dotted line shows the behavior of the static uniform susceptibility which should be followed if no shielding of the microwaves was present.

FIG. 5: $^{23}$Na central line NMR powder spectrum in Na$_{0.75}$CoO$_2$, for $H = 6$ Tesla. Top The spectrum at 35 K is reported before (dotted line) and after (solid line) having warmed the sample at 280 K in helium atmosphere for 50 minutes. Bottom The spectrum at 16 K is reported for two different runs performed few weeks apart.

FIG. 7: $^{59}$Co (left) and $^{23}$Na (right) central line NMR powder spectra in Na$_{0.75}$CoO$_2$, for $H = 16$ kGauss, for $T$ above and below $T_c$. The intensity of $^{23}$Na signal is reduced to about half of its actual value since the length of the $\pi/2$ RF pulse, calibrated on $^{59}$Co signal, was kept constant while sweeping the frequency.

FIG. 8: The paramagnetic shift of $^{23}$Na central line is plotted as a function of the macroscopic susceptibility, measured with a SQUID magnetometer, for the $x = 0.75$ Na$_x$CoO$_2$ sample.

FIG. 9: The recovery of $^{23}$Na central line Fourier transform intensity after a saturation RF pulse $(g(t) = 1 - m(t)/m(\infty))$. The circles show the recovery of the low frequency peak, whereas the squares show the recovery of the high frequency shoulder (see Fig. 5).

FIG. 10: T-dependence of $^{23}$Na $1/T_1$ in Na$_{0.75}$CoO$_2$ for $H = 6$ Tesla, derived from the recovery of the echo amplitude after a saturating RF pulse. In the inset these $1/T_1$ values are compared to the ones derived from the recovery of the Fourier transform high-frequency peak (closed circles) or low-frequency shoulder (open circles) (see Fig. 5 and Fig. 9).

FIG. 11: T-dependence of the fraction of Co$^{4+}$ ions in Na$_{0.65}$CoO$_2$, normalized to its value for $T \ll T^\ast$. Above $T^\ast$ a marked decrease is evident. The solid line shows the best fit for a gap between localized and itinerant states $\Delta \simeq 0.3$ eV (see text). In the inset the $x$-dependence of $T^\ast$ is reported with a schematic view of the portion of the $x$-$T$ phase diagram where phase separation (PS) is observed.

FIG. 12: $x$-dependence of the fraction of Co$^{4+}$ sites in Na$_x$CoO$_2$, normalized to its absolute value for $x = 0.65$ ($n_{Co^{4+}} (0.65 \simeq 0.08)$. The open diamonds show the values estimated from the integrated EPR intensity while the closed circles show the values derived from the estimated entropy due to localized $S = 1/2$ spins$^{24}$. In the inset the T-dependence of the ratio $C/T$, with $C$ the specific heat, is reported. The decrease in the specific heat at $T_c \simeq 26$K with increasing $x$ is evident.

FIG. 13: The inverse of the spin susceptibility measured with a SQUID magnetometer is reported against $T$ (top) and $T^{0.7}$ bottom for $x = 0.75$. The non-linearity in the former plot and the linearity in the latter one are evident.

FIG. 14: T-dependence of $^{59}$Co (top) and $^{23}$Na NMR $1/T_1T$ in Na$_{0.75}$CoO$_2$, for $H = 6$ Tesla, compared to the theoretical behavior (dotted line) expected for an exponent $\alpha = 0.7$ (see text). The theoretical curve for $^{59}$Co was derived using a hyperfine coupling constant $A = 63$ kOe.
\( \text{Na}_x \text{CoO}_2 \)

- \( x = 0.75 \)
- \( x = 0.7 \)
- \( x = 0.65 \)
Derivative of EPR Signal (Arb. Units)

\( x=0.65 \)
\( x=0.7 \)
\( x=0.75 \)

\( T=293 \text{ K} \)

\( H \text{ (Gauss)} \)
Amplitude (Arb. Units)

$\nu$ (MHz)

$T = 38 \, K > T_c$

$T = 15 \, K < T_c$
$\Delta K$

$x = 0.75$

$10^3 \chi$ (emu/mole)
$T = 23.1 \text{ K}$
From EPR

From specific heat
