Unconventional Charge Ordering in Na$_{0.70}$CoO$_2$ below 300 K

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We present the results of measurements of the dc-magnetic susceptibility $\chi(T)$ and the $^{23}$Na-NMR response of Na$_{0.70}$CoO$_2$ at temperatures between 50 and 340 K. The $\chi(T)$ data suggest that for $T > 75$ K, the Co ions adopt an effective configuration of Co$^{3+}$. $^{23}$Na-NMR response reveals pronounced anomalies near 250 and 295 K, but no evidence for magnetic phase transitions is found in $\chi(T)$. Our data suggest the onset of a dramatic change in the Co 3d-electron spin dynamics at 295 K. This process is completed at 230 K. Our results maybe interpreted as evidence for either a tendency to electron localization or an unconventional charge-density wave phenomenon within the Co 3d electron system near room temperature.

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The discovery of high-$T_c$ superconducting cuprates has initiated an enhanced interest in transition-metal oxides with layered structures, among them layered alkali-metal cobalt oxides. In analogy with the high-$T_c$ cuprates it was argued that cobalt-oxide layers may result in unusual physical properties of these compounds, including unconventional superconductivity[1]. Indeed, recent experiments[2] suggest that the hydration of nominal Na$_{0.70}$CoO$_2$ induces superconductivity below a critical temperature $T_c \approx 5$ K. Other recent investigations confirm that the physical properties of Na$_x$CoO$_2$ are quite puzzling[3, 4, 5, 6, 7, 8, 9, 10].

Na$_x$CoO$_2$, with $x < 1$, crystallizes in a hexagonal structure with $P6_3/mmc$ space group symmetry[11, 12], a structure consisting of Na layers, intercalated between sheets formed by triangular arrangements of CoO$_6$ octahedra. Tunnels with an effective radius of 0.81 Å connect the Na positions and allow the Na ions (ionic radius 0.97 Å) to move, providing some degree of ionic conductance above room temperature[13].

We report on measurements of the dc-magnetic susceptibility and $^{23}$Na-NMR on polycrystalline samples of Na$_{0.70}$CoO$_2$ at temperatures between 50 and 300 K and in external magnetic fields of 2.815 and 7.049 T. Above 295 K the Co ions are intermediate valent with an average configuration Co$^{3+}$. Drastic changes in the Co 3d electron system occur below 295 K. This may be interpreted as either an enhanced tendency to electron localization with decreasing $T$ or the formation of an unconventional charge-density-wave state.

Our sample consisted of randomly oriented powder of nominal Na$_{0.70}$CoO$_2$, which was obtained by heating a stoichiometric mixture of Co$_3$O$_4$ (Aldrich, 99.995%) and Na$_2$CoO$_4$ (Aldrich, 99.995%) in air for 15 h at 850 °C. To ensure the oxygen content the powder was annealed for 2 h at an oxygen pressure of 500 bar at 500 °C. X-ray powder diffraction showed that the resulting material was of single phase with lattice parameters $a = 2.826(1)$ and $c = 10.897(4)$ Å. Neutron powder diffraction experiments performed on samples prepared in a similar way yielded a composition of Na$_x$CoO$_2$ with $x = 0.7 \pm 0.04$[14]. The dc-magnetic susceptibility was measured using the moving-sample technique with a commercial SQUID magnetometer and for the NMR measurements we used standard spin-echo techniques.

In Fig. 1 we display the temperature dependence of the inverse magnetic susceptibility $(\chi - \chi_0)$, whereby $\chi_0 = 1.25 \cdot 10^{-4}$ emu/mol, obtained by fitting the experimental data by a curve which includes a Curie-Weiss law and a temperature-independent contribution ($\chi_0$), at temperatures above 100 K. Between 75 and 340 K, the Curie-Weiss type behavior is emphasized by the solid line. The inset of Fig. 1 shows the magnetization $M$ as a function of the applied field $H$ at 100 K. It reflects the paramagnetic response of the magnetic moments that are responsible for the behavior of $\chi(T)$. The solid straight line in Fig. 1 is compatible with an effective paramagnetic moment $p_{eff} = 1.1 \mu_B$ per Co ion, and a paramagnetic Curie temperature $\theta_p$ of -103 K, in fair agreement...
with previous results for Na$_{0.75}$CoO$_2$ (see Ref. 8). The value of $p_{eff}$ can be interpreted as evidence for i) all the Co ions are in an intermediate valent Co$^{3,4+}$ state, or ii) their configurations are Co$^{4+}$ ($S = 1/2$) and Co$^{3+}$ ($S = 0$) with an approximate ratio of 2:3, if it is assumed that $g = 2$ and the orbital moments are quenched. Considering the Na content, this ratio is reasonable.

The $^{23}$Na-NMR spectra were measured in fixed external magnetic fields of 2.815 and 7.049 T. In the inset of Fig. 2 we display an example of a signal measured in a field of 7.049 T and at $T = 305$ K, which is attributed to the $^{23}$Na nuclear-Zeeman central transition $-1/2 \leftrightarrow 1/2$. The shape of this line (see also Fig. 4) is as expected for a randomly oriented powder, broadened by second-order quadrupolar effects[15]. This is corroborated by the fact that at high temperatures the NMR linewidth scales linearly with the inverse of the applied magnetic field. Analyzing the $^{23}$Na NMR lineshape of the central line at temperatures above 295 K yields a quadrupolar frequency $\nu_Q = e^2 qQ/(2h)$ of 1.65 ± 0.2 MHz. Here $eQ$ is the largest component of the electric field gradient EFG at the Na nuclear site and $eQ$ is the quadrupolar moment of the Na nucleus. Note that above room temperature the EFG’s are the same at all Na sites.

In the main frame of Fig. 2 we display the variation of the $^{23}$Na-NMR linewidth (FWHM) with temperature. Below 200 K it reflects, analogous to $\chi(T)$, the increase of the magnetization due to the Co$^{4+}$ ions with decreasing temperature. A prominent anomaly is observed in FWHM($T$) near 250 K. Since we find no corresponding anomaly in $\chi(T)$, this feature cannot involve magnetic degrees of freedom and, as we argue below, it most probably is related to structural aspects.

In Fig. 3 we present the temperature dependence of the spin-lattice relaxation rate $T_1^{-1}(T)$, measured in fields of 2.815 and 7.049 T. The values of $T_1^{-1}$ were extracted from standard fits[16] to the nuclear magnetization recovery curves of the $^{23}$Na central nuclear Zeeman transition, after the application of a long comb of rf pulses. Below 230 K, $T_1^{-1}$ is approximately $T$-independent, as in the case of spin-lattice relaxation driven by flips of paramagnetic moments[17]. With increasing temperature we observe, near 230 K, the onset of an increase of the relaxation rate $T_1^{-1}$. This onset is accompanied by a significant anomaly in the $T$-dependence of the spin-spin relaxation rate $T_2^{-1}$, which is shown in the inset of Fig. 3. Together, these two relaxation-rate features provide evidence for a crossover phenomenon or a phase transition. Close to 250 K, the value of $T_2^{-1}$ is of the order of the NMR linewidth (Fig. 2) which, therefore, is dominated by $T_2$ effects.

With increasing $T$, the slope $dT_1^{-1}/dT$ increases and an almost discontinuous enhancement of $T_1^{-1}$, by a factor of 20, occurs at 295 K. In view of the smooth evolution of $\chi(T)$, this rapid change in $T_1^{-1}(T)$ manifests a phase transition which obviously does not involve magnetic degrees of freedom. No anomaly in the spin-spin relaxation rate is observed at 295 K. The order of magnitude difference of $T_1^{-1}$ below and above 295 K seems too large to be caused by a structural phase transition. In an effort to interpret the observed relaxation features, we focus on possible changes within the Na and Co subsystems, respectively.

First we consider the $T$–induced changes of the quadrupolar features of the $^{23}$Na-NMR line (see Fig. 4).
The lineshape exhibits clear $T$-induced changes, but no evidence for “motional narrowing”, which is expected if an order-disorder transition occurred at 295 K, such as, e.g., in Ba$_2$In$_2$O$_3$ at 1075 °C[18]. Thus, a Na order-disorder transition seems unlikely to be the reason for the observed changes of the NMR spectrum at and below 295 K. Recent experiments on Na$_{0.7}$CoO$_2$ searched for, but did not find, temperature-induced changes in the occupation of the 2 Na sites below room temperature[19]. Likewise, no appreciable changes in the occupation of the 2 Na sites below 300 K for Na$_{0.61}$CoO$_2$ were reported in ref. 12. Hence the transition at 295 K is most likely due to a $T$-induced variation in the Co subsystem.

Considering the results for $\chi(T)$, the homogeneity of the EFG and the very high and temperature independent spin-lattice relaxation rate above room temperature, we conclude that the Co ions are in an intermediate valent state of 3.4+ above 295 K. The electron transitions from the Co 3d orbitals to conduction band states is, compared to the NMR frequencies, very fast. The rapid decrease of the spin-lattice relaxation rate observed below 295 K and the corresponding changes in the NMR spectrum may be interpreted as evidence for a partial electron localization, i.e., the characteristic frequency $\tau_c^{-1}$ (with $\tau_c$ the correlation time) of the valence fluctuations decreases to values well below the NMR Larmor frequencies as the temperature is reduced. At lower temperatures a “quasi” mixed-valent phase with Co$^{4+}$ ($S = 1/2$), and Co$^{3+}$ ($S = 0$) ions in a ratio of 2 to 3 is adopted. The peak in $T_c^{-1}(T)$ seems to indicate that $\tau_c$ reaches a value of the order of $10^{-4}$ s, i.e., of the order of $T_2$, near 250 K[20]. A complete and static charge localization cannot occur in Na$_{0.7}$CoO$_2$ because this would imply an insulating phase, contrary to the experimental observations[21]. This partial localization should be distinguished from case of a “slowing down” of the spin flips of localized moments, which is unlikely to occur. If below 200 K, $\tau_c^{-1}$ is well below the NMR frequencies (“slow-motion regime”) and if we assume that the spin-lattice relaxation is driven by the independent flips of “slow” and localized spins then, neglecting spin diffusion[22],

$$T_1^{-1} = A \cdot \tau_c / (1 + \omega^2 \tau_c^2) \approx A / (\omega^2 \tau_c),$$

(1)

where $A$ is a constant. Since, as seen in Fig. 3, $T_1^{-1}(T)$ is field and frequency independent it would follow that $\tau_c \propto H^{-2}$, whereas for these high temperatures ($\mu_B H \ll k_B T$) a field-independent $\tau_c$ is expected. More likely is the scenario described above, where the ionic moments form and decay by the motion of electrons, and these changes drive the nuclear relaxation.

In trying to interpret the features at 250 K, we first focus on the NMR spectrum at 210 K, whose lineshape is not drastically different from the one at 250 K, but exhibits some distinct shoulders. Although these features are not very prominent, they are perfectly reproducible and their relative positions scale with 1/$H$ (data not shown) as expected for quadrupolar features of the $^{23}$Na-NMR central line. We identify four contributions, represented by the gray rectangles in Fig. 4, which we attribute to four inequivalent Na sites in the Co-ion environment. The quadrupolar frequencies of the four Na sites are of the order of 2.6, 2, 1.5 and less than 0.7 Mhz, respectively. These subtle changes of the NMR spectrum may be due to either a slight re-arrangement of the static or, on the time scale of the NMR experiments, very slowly varying positions of the Na ions. Alternatively, very slow Co charge fluctuations cannot be excluded. Temporally varying Na environments are mainly determined by the actual configuration of nearest neighbor Co$^{4+}$ ions. At low temperatures, this configuration is stable over a sufficiently long time period, such that they appear as static in the NMR measurements and provide the shoulders in the line at 210 K. At higher temperatures, however, this feature may be lost.

Since the changes of the $^{23}$Na-NMR spectrum between 210 and 250 K, discussed above, are rather subtle, we performed 2D exchange $^{23}$Na-NMR experiments[23, 24]. The results of these experiments will be discussed in detail elsewhere[19], but we mention here that our experiments detected (data not shown) small changes of the Larmor frequencies of Na nuclei, in the temperature range between 240 - 260 K and on a time scale $\tau_{mix}$, typically smaller than $10^{-4}$ s, but $\tau_{mix}^{-1} \ll \nu_L$, the NMR Larmor frequency. At first sight, this observation may be interpreted as evidence for a restricted and slow motion.
of Na ions near 240 K, which decreases again at higher temperatures. This seems rather counter-intuitive and therefore probably indicates that the frequency changes are due to changes in the Na environments, i.e., in the Co-oxide layer. Our 2D NMR experiments cannot distinguish between genuine Na ionic motion and temporal changes of the Na environments.

Another scenario consistent with our experimental results is the formation of an unconventional charge density wave in the Co subsystem at 295 K. The system remains metallic at low temperatures[25], but part of the Fermi surface is lost. In the density-wave state, the Co 3d-electron spin dynamics may change and account for the rapid decrease of the spin-lattice relaxation, that we observe below 295 K. The charge density wave may also lead to a slight rearrangement of the Na ions around 250 K.

Support for our claims are obtained from the results of a structural investigation[19] of a single crystalline sample of Na$_7$CoO$_2$ by X-ray diffraction. The comparison of diffraction patterns taken at 220 and 300 K show the presence of an additional structural feature at 220 K. Recent density functional calculations suggested[26] that charge as well as spin ordering is nearly degenerate with the paramagnetic state in Na$_{0.5}$CoO$_2$.

In conclusion, from the results of our dc-susceptibility and NMR measurements, we infer that below 295 K the Co 3d$-$electron system within the CoO layers is affected by at least one phase transition. Two scenarios seem possible: (a) a partial charge ordering phenomenon involving Co$^{3+}$ and Co$^{4+}$ upon decreasing temperature, completed only near 230 K; and (b) an unconventional charge density wave within the Co subsystem develops. The system remains metallic at all temperatures.

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