

## Unconventional charge ordering in $\text{Na}_{0.70}\text{CoO}_2$ below 300 K

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We present the results of measurements of the dc-magnetic susceptibility  $\chi(T)$  and the  $^{23}\text{Na}$ -NMR response of  $\text{Na}_{0.70}\text{CoO}_2$  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  $\text{Co}^{3.4+}$ . The  $^{23}\text{Na}$ -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 may be 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.<sup>1</sup> Indeed, recent experiments<sup>2</sup> showed that superconductivity appears in  $\text{Na}_{0.70}\text{CoO}_2\cdot\text{H}_2\text{O}$  at  $T_c \approx 5$  K. This material is obtained after the sodium deintercalation and hydration of the nominal  $\text{Na}_{0.70}\text{CoO}_2$  compound. Other recent investigations confirm that the physical properties of  $\text{Na}_x\text{CoO}_2$  are quite puzzling.<sup>3-10</sup>

$\text{Na}_x\text{CoO}_2$ , with  $x < 1$ , crystallizes in a hexagonal structure with  $P6_3/mmc$  space group symmetry,<sup>11,12</sup> a structure consisting of Na layers, intercalated between sheets formed by triangular arrangements of  $\text{CoO}_6$  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.<sup>13</sup>

We report on measurements of the dc-magnetic susceptibility and  $^{23}\text{Na}$ -NMR on polycrystalline samples of  $\text{Na}_{0.70}\text{CoO}_2$  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  $\text{Co}^{3.4+}$ . 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  $\text{Na}_{0.70}\text{CoO}_2$ , which was obtained by heating a stoichiometric mixture of  $\text{Co}_3\text{O}_4$  (Aldrich, 99.995%) and  $\text{Na}_2\text{CO}_3$  (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  $\text{Na}_x\text{CoO}_2$  with  $x = 0.7 \pm 0.04$ .<sup>14</sup> The dc-magnetic susceptibility was measured using the moving-sample technique with a commercial superconducting quan-

tum interference device 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  $(\chi - \chi_0)^{-1}$ , whereby  $\chi_0 = 1.25 \times 10^{-4}$  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  $p_{\text{eff}} = 1.1 \mu_B$  per Co ion, and a paramagnetic Curie temperature  $\theta_p$  of  $-103$  K, in fair agreement with previous results for  $\text{Na}_{0.75}\text{CoO}_2$  (see Ref. 8). The value of  $p_{\text{eff}}$  can be interpreted as evidence for the following: (i) all the Co ions are in an intermediate valent  $\text{Co}^{3.4+}$  state, or (ii) their configurations are  $\text{Co}^{4+}$  ( $S = 1/2$ ) and  $\text{Co}^{3+}$  ( $S = 0$ ) with an approximate ratio of 2:3, if it is assumed that  $g = 2$  and the orbital moments are quenched.

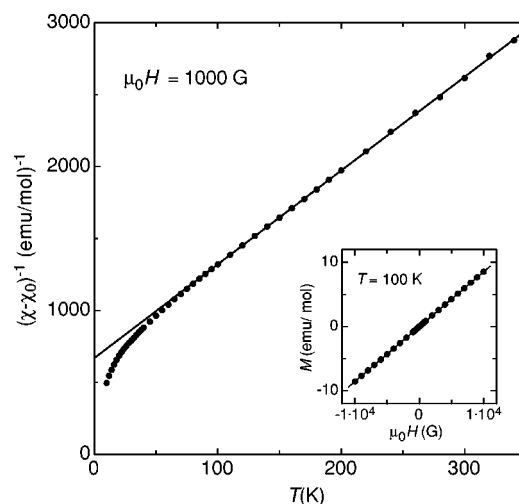


FIG. 1. The inverse magnetic susceptibility as a function of temperature for  $\text{Na}_{0.7}\text{CoO}_2$ . The solid line represents a Curie-Weiss type fit. Inset: Magnetization as a function of the external magnetic field at 100 K.

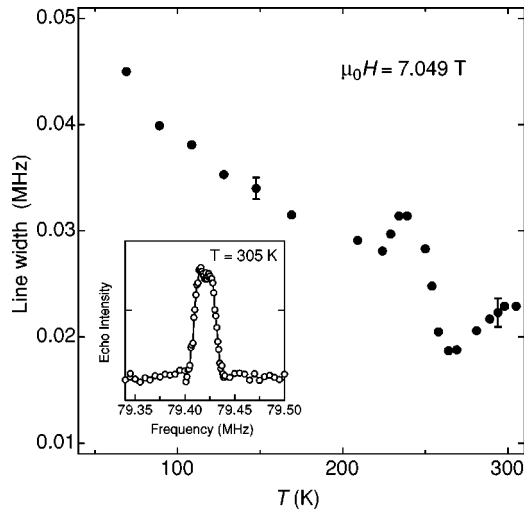


FIG. 2. Main frame: Temperature dependence of the linewidth (FWHM) of the  $^{23}\text{Na}$ -NMR central transition  $-1/2 \leftrightarrow 1/2$  for  $\text{Na}_{0.7}\text{CoO}_2$ . Inset: The central transition of the  $^{23}\text{Na}$ -NMR spectrum at  $T = 305$  K and  $\mu_0 H = 7.049$  T.

Considering the Na content, this ratio is reasonable.

The  $^{23}\text{Na}$ -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  $^{23}\text{Na}$  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.<sup>15</sup> 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  $^{23}\text{Na}$ -NMR line shape of the central line at temperatures above 295 K yields a quadrupolar frequency  $\nu_Q = e^2 q Q / (2h)$  of  $1.65 \pm 0.2$  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. The structure provides two inequivalent Na sites with respect to the Co-ion sublattice and with very different  $T$ -independent occupancies.<sup>12,16</sup> Even if we neglect the minority site, the partial occupation of the Na sites should naturally result in a distribution of different Na environments with respect to the charge distribution, i.e., a distribution of EFG's. Our experiments reveal that above room temperature, rapid Co-charge fluctuations (and some Na ionic motion) result in a single average environment.

In the main frame of Fig. 2 we display the variation of the  $^{23}\text{Na}$ -NMR linewidth (FWHM) with temperature. Below 200 K it reflects, analogous to  $\chi(T)$ , the increase of the magnetization due to the  $\text{Co}^{4+}$  ions with decreasing temperature. A prominent anomaly is observed in  $\text{FWHM}(T)$  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 aspects of the electronic structure.

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

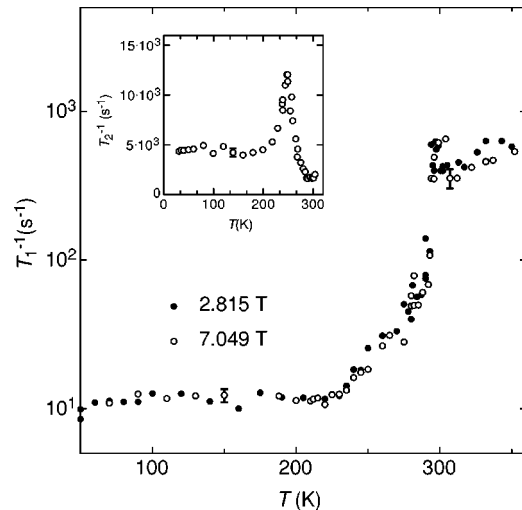


FIG. 3. Main frame: Spin-lattice relaxation rate as a function of  $T$  measured at two different external magnetic fields. Inset: Spin-spin relaxation rate as a function of  $T$ , measured in an external magnetic field of 2.815 T.

standard fits<sup>17</sup> to the nuclear magnetization recovery curves of the  $^{23}\text{Na}$  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.<sup>18</sup> 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. Note that our data cannot provide evidence for or against a peak in  $T_1^{-1}(T)$  at 250 K because of the rapidly varying slope of  $T_1^{-1}(T)$  in that temperature region.

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  $^{23}\text{Na}$ -NMR line (see Fig. 4). The line shape exhibits clear  $T$ -induced changes, but we do not observe a large increase of the width as  $T$  decreases below 295 K as usually occurs in the case of order-disorder transitions, such as, e.g., in  $\text{Ba}_2\text{In}_2\text{O}_5$  at  $1075^\circ\text{C}$ .<sup>19</sup> More importantly, the very steep decrease of  $T_1^{-1}(T)$  just below 295 K can hardly be traced back to rearrangements within the Na sublattice alone. Thus, a Na order-disorder transition seems un-

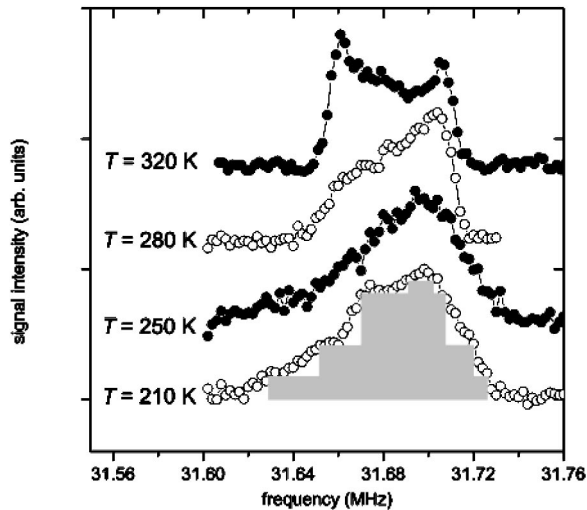


FIG. 4.  $^{23}\text{Na}$ -NMR central transitions of  $\text{Na}_{0.7}\text{CoO}_2$  measured in an external field of 2.815 T at different temperatures. The gray boxes represent rough sketches of the different contributions to the NMR line at 210 K. The line at 320 K has a single contribution.

likely to be the reason for the observed changes of the NMR spectrum at and below 295 K. Recent experiments on  $\text{Na}_{0.7}\text{CoO}_2$  searched for, but did not find, temperature-induced changes in the occupation of the two Na sites below room temperature.<sup>16</sup> Likewise, no appreciable changes in the occupation of the two Na sites below 300 K for  $\text{Na}_{0.61}\text{CoO}_2$  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 transition from the Co 3*d* 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  $\text{Co}^{4+}$  ( $S = 1/2$ ), and  $\text{Co}^{3+}$  ( $S = 0$ ) ions in a ratio of 2 to 3 is adopted. The peak in  $T_2^{-1}(T)$  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.<sup>20</sup> A complete and static charge localization cannot occur in  $\text{Na}_{0.7}\text{CoO}_2$  because this would imply an insulating phase, contrary to the experimental observations.<sup>21</sup> This partial localization should be distinguished from the 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,<sup>22</sup>

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

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 line shape 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  $^{23}\text{Na}$ -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 rearrangement 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  $\text{Co}^{4+}$  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  $^{23}\text{Na}$ -NMR spectrum between 210 and 250 K, discussed above, are rather subtle, we performed two-dimensional (2D) exchange  $^{23}\text{Na}$ -NMR experiments.<sup>23,24</sup> The results of these experiments will be discussed in detail elsewhere,<sup>16</sup> 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 counterintuitive 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,<sup>25</sup> but part of the Fermi surface is lost. In the density-wave state, the Co 3*d*-electron spin dynamics may change and account for the rapid decrease of the spin-lattice relaxation, which 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 is obtained from the results of a structural investigation<sup>16</sup> of a single crystalline sample of  $\text{Na}_{0.7}\text{CoO}_2$  by x-ray diffraction. The comparison of diffraction patterns taken at 220 and 300 K shows the presence of

an additional structural feature at 220 K. Recent density-functional calculations suggested<sup>26</sup> that charge as well as spin ordering is nearly degenerate with the paramagnetic state in  $\text{Na}_{0.5}\text{CoO}_2$ .

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  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  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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