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Electronic texture of the thermoelectric oxide Na0.75CoO2

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Abstract
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Electronic Texture of the Thermoelectric Oxide Na$_{0.75}$CoO$_2$


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We have obtained reproducible NMR spectra of $^{59}$Co and $^{23}$Na in Na$_{0.75}$CoO$_2$: at long time scales, there is neither a disproportionation into 75% Co$^{3+}$ and 25% Co$^{4+}$ states, nor a mixed-valence metal with a uniform Co$^{3+}$ state. Instead, the system adopts an intermediate configuration in which 30% of the lattice sites form an ordered pattern of localized Co$^{3+}$ states. Above 180 K, an anomalous mobility of specific Na$^+$ sites is found to coexist with this electronic texture, suggesting that the formation of the latter may contribute to stabilizing the Na$^+$ ordering. Control of the ion doping in these materials thus appears to be crucial for fine-tuning of their thermoelectric properties.

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From $^{59}$Co and $^{23}$Na NMR, we demonstrate the impact of the Na$^+$ vacancy ordering on the cobalt electronic states in Na$_{0.75}$CoO$_2$: at long time scales, there is neither a disproportionation into 75% Co$^{3+}$ and 25% Co$^{4+}$ states, nor a mixed-valence metal with a uniform Co$^{3+}$ state. Instead, the system adopts an intermediate configuration in which 30% of the lattice sites form an ordered pattern of localized Co$^{3+}$ states. Above 180 K, an anomalous mobility of specific Na$^+$ sites is found to coexist with this electronic texture, suggesting that the formation of the latter may contribute to stabilizing the Na$^+$ ordering. Control of the ion doping in these materials thus appears to be crucial for fine-tuning of their thermoelectric properties.

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Complexity, which underlies many physical properties of correlated electron systems [1], often results from the spatial modulation of electronic states. Besides the tendency to form ordered patterns (such as stripes in high temperature superconductors), electrostatic interactions with dopant ions are increasingly recognized as a source of electronic inhomogeneity [2,3]. Because the sodium ions in Na$_3$CoO$_2$ are mobile and can order, these battery materials are emerging as exceptional candidates for exploring such phenomena [4]. One of the most important questions regarding this system is whether the intriguing physical properties of metallic phases at $x \approx 0.6$ are related to a coupling between the electronic degrees of freedom and the spatial distribution of Na$^+$ vacancies [4–13]. On the one hand, long range sodium vacancy ordering has been reported, but the ordering pattern appears to be controversial for the most studied concentration $x = 0.75$ [13–15]. On the other hand, electronic “textures,” which may be defined as both the disproportionation of electronic (spin, charge, and possibly orbital) states and the spatial correlation between these states, are much less experimentally accessible and, not surprisingly, no electronic pattern has yet been resolved. Nevertheless, the observation of two, or more, magnetically distinct $^{59}$Co sites at the time scale ($\sim 10^{-6}$ s) of nuclear magnetic resonance (NMR) [16–21] demonstrates that some electronic disproportionation occurs in metallic Na$_3$CoO$_2$ with $x \approx 0.7$. However, because of the difficulty in accurately determining the Na content $x$, and the sensitivity of Na order to small variations in $x$ or to the synthesis method, a coherent picture of the electronic states has yet to emerge.

We have obtained reproducible NMR spectra of $^{59}$Co nuclei in high quality single crystals of Na$_{0.75}$CoO$_2$, grown in three different groups [22,23]. Our comprehensive characterization of the crystals will be published separately. For the magnetic field $H \parallel c$ (i.e., $\theta = 0^\circ$), a typical spectrum (Fig. 1) shows three distinct sites. These are labeled Co1, Co2, and Co3 in increasing order of their magnetic hyperfine shift $K = K^{\text{orb}} + K^{\text{spin}}$. The most interesting differences between these sites lie in both (i) the value of the on site orbital contribution $K^{\text{orb}}$, which is proportional to the (on site) Van Vleck susceptibility, and (ii) the value of $K^{\text{spin}}$ (“Knight shift” in metals), which for a given nuclear site $i$ is given by

\begin{equation}
K^{\text{spin}}_{\alpha\alpha,i} = A_{\alpha\alpha} \frac{\chi^{\text{spin}}(i)}{g \mu_B} + \sum_j B_{\alpha\alpha} \frac{\chi^{\text{spin}}(j)}{g \mu_B},
\end{equation}

where $A$ is the on site hyperfine coupling, $\chi^{\text{spin}}$ is the local spin susceptibility, and $j$ stands for the nearest Co neighbors to which the nucleus $i$ may be coupled via a transferred hyperfine interaction $B$. $\alpha = c, ab$ is the direction of the principal axis of $A$ and $\chi$ tensors, along which $H$ is aligned. Equation (1) makes clear that, if $B \neq 0$ and $\chi^{\text{spin}}(i) \neq \chi^{\text{spin}}(j)$, the number of NMR sites with different $K^{\text{spin}}(i)$ values may be greater than the number of different magnetic sites [i.e., of different $\chi(i)$ values]. Thus, the three $^{59}$Co NMR sites do not necessarily correspond to three distinct electronic densities.

Additional information on the cobalt sites is provided by the anisotropy and the temperature ($T$) dependence of $K$. $H|_{\alpha\beta}$ spectra are too poorly resolved to directly extract the in-plane anisotropy and the $K$ values for all sites. Nevertheless, neglecting the in-plane anisotropy, $K_{\alpha\beta}$ can be extracted from a combined knowledge of the line positions for $\theta = 54.7^\circ$ and $\theta = 0^\circ$, which define $K_{\alpha\beta} = \frac{1}{2} \times (2K_{\alpha\beta} + K_{\alpha})$ and $K_{\alpha}$, respectively. The values of $K^{\text{orb}}$ and of the effective total hyperfine field $A^{\text{hf}}$ for each site are

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The effective valence of the Co1 ion is slightly higher than that of the Co2 or Co3 sites. For the Co1a and Co1b sites, the orbital shift \( K_{orb} \) is close to the value (0.68 MHz) for Co3 sites in \( \text{Na}_2\text{CoO}_2 \), and is distinctly lower than \( v_\text{c} = 1.22 \) MHz for Co2 and 1.14 MHz for Co3. This effect arises from either in-plane (hyperfine or magnetic) anisotropy or from differences in the Co nearest neighbors at the Co1 sites. For simplicity, we report here only the properties of the more intense, less shifted, Co1a line (the maximum \( K_{orb} \) difference between Co1a and Co1b is 5 to 10 times smaller than the difference between the Co1 and the Co2 or Co3 sites).

The Co2 and Co3 sites, on the other hand, are characterized by much larger and anisotropic hyperfine fields valued at 59.2 MHz for Co2 and 64 MHz 40 K. Critical magnetic order below 22 K does not arise from a minority shell of the g holes have a small but finite probability of residing on the Co1 sites. However, the quasi-isotropic \( A^{hf} = 28 \text{ kG}/\mu_B \), as well as the different \( T_1 \) behavior (see later) for this site would suggest that most of the hyperfine field may be transferred from its magnetic near-est neighbors [i.e., the second term of Eq. (1)]. Thus, it must be concluded that there are localized sites in the cobalt planes which are permanently occupied by six \( t_{2g} \) electrons.

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For the Co1 site, the values of the orbital shift \( K_{orb} = 2.36 \% \) are almost the same as those reported for the Co3+ site in \( \text{Na}_2\text{CoO}_2 \). As argued in [19,21], the isotropic character of \( K_{orb} \) is also consistent with the filled \( t_{2g} \) shell of the Co3+ ion. Clearly, the Co1 site corresponds to nonmagnetic Co3+. This assignment may, at first sight, appear to be in contradiction with \( K_{spin}(\text{Co1}) \neq 0 \). We cannot rule out the possibility that the effective valence of the Co1 ion is slightly higher than +3; i.e., \( t_{2g} \) holes have a small but finite probability of residing on the Co1 sites. However, the quasi-isotropic \( A^{hf} = 28 \text{ kG}/\mu_B \), as well as the different \( T_1 \) behavior (see later) for this site would suggest that most of the hyperfine field may be transferred from its magnetic near-est neighbors [i.e., the second term of Eq. (1)]. Thus, it must be concluded that there are localized sites in the cobalt planes which are permanently occupied by six \( t_{2g} \) electrons.

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different Co states are spatially ordered [27]. At the same time, the specific spectral shape imposes an unprecedented set of constraints on any model of the Co and Na\(^{+}\) patterns in Na\(_{0.75}\)CoO\(_2\). However, computational uncertainties concerning the 3D stacking, which is crucial for \(^{23}\)Na and \(^{59}\)Co NMR spectra, prevent us from determining whether the in-plane pattern depicted in Fig. 4 [13], or another pattern, is correct. The problem should be solved by full DFT calculations of the Na/Co patterns and of the \(^{23}\)Na shifts, which are underway.

Surprisingly, the \(^{23}\)Na spectrum collapses into two very close lines above 180 K [see shifts in Fig. 2(b)], as if the cobalt planes were electronically homogeneous. However, the observation of distinct Co1, Co2, and Co3 sites above 180 K tells us that this is not the case. Thus, the averaging of the hyperfine fields must be due to Na\(^{+}\) ions occupying several distinct sites within the NMR time window. The Na\(^{+}\) jump frequency has to be larger than the frequency separating the NMR lines with a fine structure (\(~10\) kHz), but smaller than the typical frequency of faster probes, such as x-ray diffraction (XRD), for which Na\(^{+}\) order is already well-defined at \(~250\) K [15]. This direct observation of slow Na motion with localization around 180 K rationalizes the anomalies observed in the \(T\) dependence of magnetic [28], lattice [15], and possibly charge [29] and references therein, properties of this material.

Since the NMR time scale is basically identical for \(^{59}\)Co and \(^{23}\)Na, the observation that Co electronic differentiation coexists above 180 K with Na motional averaging is strik-
and the Na mobility in Na0.75CoO2. Since these are potential ingredients of the thermoelectric effect, controlling ion doping in these materials (either by dilute doping of ions of different mobility or via nanoscale electrochemical manipulations on Na0.75CoO2 surfaces [31]) should result in an improved thermoelectric performance. More generally, control of ionic textures in battery materials appears to be an exciting route for tailoring electronic properties.

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[27] See also I. R. Mukhamedshin et al., Phys. Rev. Lett. 93, 167601 (2004), where Co3+/4+ states were assumed.