On the Ordering of Na$^+$ Ions in Na$_x$CoO$_2$

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Abstract. The influence of electrostatic interactions on the ordering of sodium ions in Na$_x$CoO$_2$ is studied theoretically through Monte-Carlo simulations. For large $x$ small di- or tri-vacancy clusters are stable with respect to isolated Na vacancies. At commensurate fillings these small clusters order in triangular superstructures. These results agree with recent electron diffraction data at $x = 1/2$ and 3/4. We have performed neutron Laue diffraction experiments at higher $x$, which confirm the predictions of this simple model. The consequences on the properties of the electronic charges in the Co layers are discussed.

In the past decade, Na$_x$CoO$_2$ has emerged as a system of fundamental interest because of its high thermoelectric power, unusual magnetic properties and possibility, when hydrated, to superconduct [1]. The density $\rho$ of intercalated sodium atoms tunes directly the density of states of quasi-particles in the metallic CoO$_2$ sheets. For simple fractional fillings, electron diffraction (ED) experiments [2, 3] provide evidence for the ordering of Na$^+$ ions at room temperature. This non-trivial order is generally believed to be the consequence of intricate interactions between Na$^+$ ions, mobile electrons, and phonons. We show here that the dominant process driving this ordering is simply the Coulomb potential between Na$^+$ ions. Sodium ions can occupy sites between oxygen atoms, which form two interpenetrating triangular lattices denoted Na$_1$ and Na$_2$. Cobalt ions lie above and below Na$_1$ sites, resulting in an extra energy cost $\Delta = \Delta_c + \Delta_{sr}$ relative to an Na$_2$ site ($\Delta_c$ in the long-range Coulomb part and $\Delta_{sr}$ a short range repulsion between Na and Co ions shells). Na ions are bigger than the distance between nearest Na$_1$ and Na$_2$ sites, forbidding simultaneous occupancy of nearest-neighbor sites and that makes Coulomb energy minimization highly non-trivial. Our model Hamiltonian includes: (i) a long-range Coulomb potential, $\varepsilon/(4\pi\epsilon_0|\mathbf{r}|)$ (the dielectric constant, taken as isotropic, is fixed at $\epsilon = 6$) to account quantitatively for the variations of the chemical potential, in terms of $x$, measured in cell de
cells [4]; (ii) Na-Na ion-shell repulsion $\varepsilon = 0.04\text{eV}$ for neighbors on the same sub-lattice; and (iii) on-site energy $\Delta_{sr} = 0.01\text{eV}$. A system of two sheets of Na ions, each containing a maximum number of 1176 ions, intercalated between two CoO$_2$ layers (with periodic boundary conditions in 3 dimensions) is simulated at finite temperature and fixed chemical potential $\mu$ through a Grand-Canonical Monte-Carlo method. The hexagonal cell parameters $a=2.84\text{Å}$ and $c=10.87\text{Å}$ are fixed to those measured in the $x = 0.75$ phase, and elastic deformations are neglected. We maintain neutrality at each step by varying the charges in the Co layers assuming a uniform spreading.

The organization of Na ions is driven by the spontaneous formation of multivacancy clusters, as illustrated in Figure 1. At large distance $d$, the repulsion energy between two vacancies decreases as $1/d$. However neighboring vacancies can reduce their energy by promotion of a Na$_2$ sodium to the central Na$_1$ site. The resultant cluster has a net charge $2e^-$ spread over three sites and substantially lower energy, as the central sodium is now further from its neighbors. Formation of a tri-vacancy cluster follows a similar process and three vacancies combine with three Na$_2 \rightarrow$ Na$_1$ promotions.

Monte-Carlo results at room temperature are presented in Figure 2. The Na concentration versus chemical potential is characterized by plateaus at $x = 1/3, 1/2, 1/3, 5/6$, comparable to those appearing in electrochemical cells [4]. At $1/3$ plateau corresponds to an $(a'=2a-b, b'=2b)$ ordered structure with equal occupation of Na$_1$ and Na$_2$ sites in perfect agreement with ED spectra [2]. It can be
described as a dense lattice of divacancy clusters. The \( \frac{5}{7} \) structure is a \( \{a' = 2a + b, b' = -a + 3b\} \) triangular array of divacancies. At \( x = \frac{3}{4} \), a triangular array \( \{a' = 2a + 2b, b' = -2a + 4b\} \) of trivacancies is obtained, in agreement with ED [2, 3]. No plateau is observed at higher \( x \), but short-range ordered random mixing of di- trivacancies appears in the simulations. Nevertheless, at \( x > 0.8 \) many commensurate triangular arrays of di- trivacancies are possible and we have therefore investigated experimentally this range through neutron diffraction.

Single crystal data were collected on the SXD diffractometer at the ISIS pulsed neutron source, Rutherford Appleton Laboratory (UK) with area detectors covering a solid angle of \( 2\pi \) steradians. At \( x = 0.92 \pm 0.03 \), Figure 3 shows superstructure peaks appearing on a circle of radius \( q \approx 6.10nm^{-1} \) centered on the main Bragg points. These are compatible with a triangular array of divacancies with unit-cell vectors \( \{a' = 3a + b, b' = -a + 4b\} \).

Sodium ordering induces a periodic Coulomb potential in the Co layers. The depth of the electrostatic potential wells, \( \approx 100\text{meV} \), is substantially larger than the quasi-particle hopping frequency \( \approx 10\text{meV} \) and so will localize holes. While total energy differences are insignificant (\( \approx 0.1\text{meV} \)), the Coulomb landscape varies drastically in terms of position of vacancy clusters in successive layers along \( c \). For \( x = \frac{1}{2} \) there are only two configurations. Figure 4 (a) corresponds to divacancies in successive layers displaced by \( b \). It has a one-dimensional character with high (dark) and low (light) Coulomb-potential stripes in agreement with the low and high spin charge-ordered stripes found using neutron diffraction [5]. A large magnetic field parallel to the (\( a, b \)) plane favors alignment of holes (divacancies) in the \( c \)-direction corresponding to Figure 4 (b) with 2D character and conducting Co ions at intermediate valencies (gray circles). This could explain the abrupt change from an insulating antiferromagnet to a conducting state with reconstruction of a 2D Fermi surface when a field of 40T is applied at \( T=50K \) [6]. The potentials corresponding to the \( x = \frac{5}{7} \) and \( \frac{3}{4} \) structures are discussed in Ref. [7].

In conclusion, at \( x > \frac{1}{2} \), the ordering of sodium ions governs the electronic and magnetic properties of quasiparticles (holes) in the Co layers. Pure electrostatics with non-trivial constraints on a bipartite lattice leads to vacancy clustering. For simple fractional fillings di- and trivacancy clusters order long range.

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FIGURE 4. Na Coulomb potential in Co planes at $x = \frac{1}{2}$ with divacancies aligned along $c$ axis (a) and displaced by $b$ (b). The white (black) circles represent $\text{Co}^{n3+}$ ($\text{Co}^{n4+}$) ions. The gray circles represent conducting Co ions at intermediate valencies.