Searching for Sodium Ion Ordering in Na$_x$CoO$_2$

Na$_x$CoO$_2$ shows a rich phase diagram as a function of $x$, both magnetically and electronically. High quality single crystals have been prepared by slowly removing Na ions in an electrochemical cell and performing X-ray and electron diffraction on well characterized samples. Using synchrotron X-ray diffraction on single crystals, we discovered $\sqrt{3}a$ and $\sqrt{3}a$ superlattice structures in $x = 0.71$ and $x = 0.84$ respectively, which we interpret as the ordering of Na (vacancy) clusters. We discovered a hexagonal $\sqrt{3}a \times \sqrt{3}a$ superstructure for $x = 0.84 \approx 11/13$, leading naturally to a picture of ordered di-vacancies. For $x = 0.71$, we find a hexagonal $\sqrt{3}a \times \sqrt{3}a$ superlattice which contains 12 unit cells. These results lead to a picture of coexisting local moments and itinerant carriers. The absence of ordering suggests a spin liquid state formed by Kondo coupling of local moments on a frustrated lattice. Our discovery of ordering of Na clusters at special concentrations is the first step towards modelling the electronic properties of the cobaltates.

Sodium cobaltate (Na$_x$CoO$_2$) has received a great deal of attention from the condensed matter physics and materials science communities recently because the cobalt valence can be tuned over a great range by varying the Na concentration, leading to unusual properties all the way from unconventional superconductivity when hydrated at $x = 1/3$ to a novel “Curie-Weiss metal” for $x = 0.7$ to enhanced thermopower for $x = 0.85$. While the ordering of the Na ions is thought to play an important role, up to now there is no reliable information on the Na order pattern for a given $x$. An even more serious difficulty lies in the inconsistent determination of $x$ from group to group. As a result no quantitative modeling of these materials has been possible, and the anomalous properties mentioned above remain clouded in mystery. We remedy this situation by preparing high quality single crystals by slowly removing Na ions in an electrochemical cell and performing X-ray and electron diffraction on well characterized samples. We determine that there is a special island of stability at $x = 0.71 \pm 0.01$. We also studied $x = 0.84 \pm 0.01$ which is the limit of single phase stability for high temperature melt growth. We discovered a hexagonal $\sqrt{3}a \times \sqrt{3}a$ superstructure for $x = 0.84 \approx 11/13$, leading naturally to a picture of ordered di-vacancies. For $x = 0.71$, we find a hexagonal $\sqrt{3}a \times \sqrt{3}a$ superlattice which contains 12 unit cells. Due to the unique triangular cobalt lattice structure and its stacking sequence, we find a special stability for a model of alternating layers of Na tri-vacancy and quadri-vacancy, so that $x = 0.71$ is understood to be the average of 3/4 and 2/3 doping. While our analysis builds on the vacancy clustering model suggested by Roger et al., our results differ significantly from theirs. For example, the trend of increasing cluster size with decreasing $x$ is exactly opposite to what they proposed. We believe that the new structural information provides the needed foundation for detailed modeling of these materials, and is an important first step towards the understanding of the many unusual properties of the cobaltates.

○ **Beamline**

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Phase \( \gamma \) \( \text{Na}_x\text{CoO}_2 \) is prepared by chronoamperometry technique on single crystal sample in electrochemical cell constructed as \( \text{Na}_x\text{CoO}_2/1\text{N NaClO}_4 \) in propylene carbonate/Pt. Starting from the original crystal \( \text{Na}_0.84\text{CoO}_2 \) grown with floating-zone method, constant anodic potential is applied to the sample electrode until the induced current decays to zero. The concentration \( x \) has been carefully determined by freshly cleaved surface using EPMA and verified by the reported linear lattice parameter relationship.\(^{[2, 6]}\)

The residual resistivity of \( x = 0.71 \) is low among the cobaltate family\(^{[2]}\) and our sample has been measured by M. Lee and N. P. Ong to be seven times lower than that commonly reported in the literature. Another special concentration is \( x = 0.84 \), A-type antiferromagnetic ordering around 20 K has been found between \( x \sim 0.75 \) and 0.84\(^{[4]}\) but the magnetic order disappears at \( x = 0.71 \). The resistivity shows a linear \( T \) behavior below 100 K and becomes \( T^2 \) only below \( \approx 4 \) K. The name “Curie-Weiss” metal has been given to this highly unusual combination of magnetic and transport properties.\(^{[2]}\)

We performed transmission Laue X-ray diffraction study on single crystal \( \text{Na}_x\text{CoO}_2 \) with \( x = 0.84 \) and 0.71 using synchrotron source of Taiwan NSRRC. Superlattice diffraction spots appear near the original \( P6_3/mmc \) structure indices \{100\} and \{110\} as shown in Fig. 1. Symmetric superlattice spots have been seen repeatedly in many batches of crystal, the only difference being the relative intensity of the superlattice spots. For \( x = 0.84 \) we found a hexagonal \( \sqrt{13}a \times \sqrt{13}a \) superstructure. The major character of this Laue pattern is the 12 spots ring that formed near \{100\} peaks of the original lattice. As shown in the inset of Fig. 1(a), these spots consist of 2 sets of six-fold rings rotated by \( \approx 28^\circ \), where each set is indexed using two simple hexagonal unit cells with \( a' = \sqrt{13}a \).

Figure 1(c) shows the simulated diffraction pattern along the \( c \)-axis for \( x = 0.84 \), where the agreement using two-domain simulation is high even before the intensity is corrected by the refined atomic positions and the associated structure factors. The \( \sqrt{13}a \times \sqrt{13}a \) structure corresponds precisely to the ordering of di-vacancies shown in Fig. 2. With one di-vacancy per 13 cobalt, we predict \( x = 1 - \frac{1}{13} = 0.846 \) which is within the error of the \( x = 0.84 \pm 0.01 \) as measured by EPMA.

The salient feature of the parent \( \gamma - \text{Na}_x\text{CoO}_2 \) lattice of \( P6_3/mmc \) symmetry using \( x = 0.84 \) unit cell is shown in Fig. 2. The unit cell consists of two layers of cobalt atoms located directly on top of each other and layers of Na atoms sandwiched in between. There are two Na sites in each layer, called Na1 at \((0,0,\frac{1}{2})\) and Na2 \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\), the latter being the preferred site because Na1 sits directly on top of the positively charged Co and is more costly electrostatically. Na2 sits in the center of a prismatic cage formed by six oxygens in each layer, and the two Na layers (labeled A:B) are distinguished by the different position of
these prismatic cages. In addition to the Na sites, there are sites sitting directly under oxygen which we refer to as O sites. Note that in layer A the Na2 and O sites occupy the center of the down and up pointing triangles, respectively, but their positions are interchanged when we go from layer A to layer B. This will have crucial consequences later. The di-vacancy is formed by creating three Na2 vacancies (shown in yellow) and then occupying a Na1 site. Since the di-vacancies are centered on the Na1 site, they can stack directly on top of each other, going from layer A to B. On the other hand, out of phase stacking, for example by placing the di-vacancy at the center of the green diamond shown in Fig. 2 produces ambiguity because two such sites are equivalent. This will lead to disorder. At present it is not possible to distinguish between in phase and out of phase stacking by refinement.

For $x = 0.71$, we discovered hexagonal superstructure at $\sqrt[3]{12a} \times \sqrt[3]{12a}$ which contains 12 Na2 sites per unit cell per layer. We are then led to consider tri- and quadri-vacancies in order to account for the 0.29 missing Na ions. The tri- and quadri-vacancies consist of Na1 trimers surrounded by six and seven Na2 vacancies (shown in dashed circle), respectively. Note that the trimer in the tri-vacancy is centered on the O site while the trimer in the quadri-vacancy is centered on the Na2 site. Recall that the role of O and Na2 sites are reversed between layers A and B. This has the remarkable consequence that tri- and quadri-vacancies can stack coherently, e.g. they can either (i) stack in phase, with tri-vacancy and quadri-vacancy sitting directly on top of each other, or (ii) stack out of phase, with tri-vacancy on site a in layer A and quadri-vacancy either directly below the d site or below the b,c sites. (these sites are defined in Fig 3(a).) The alternating stacking of tri- and quadri-vacancies lead to $x = 1 - \frac{1}{2} \left( \frac{1+4}{5} \right) = 0.708$. We believe the special stacking property described above means that the structure can lock-in to a particularly stable
configuration at 0.71. This may explain the exceptional stability of the 0.71 as well as the "missing" ordering phases of $\frac{3}{4}$ and $\frac{2}{3}$.

Our discovery of ordering of Na clusters at special concentrations in high quality crystals is the first step towards modeling the electronic properties of the cobaltates. For example, starting from the band insulator NaCoO$_2$, the compound with $x = 0.84$ has $\frac{2}{3}$ holes in an otherwise filled band. The strong potential of the di-vacancy may bind one hole to form a local moment, leaving the second hole itinerant to form the metallic state. This leads to a model of local moments on a triangular lattice interacting with an antiferromagnetic Heisenberg exchange $J_H$ and coupled to an equal density of conduction electrons via a Kondo coupling $J_K$.

This state of $x = 0.71$, dubbed the "Curie-Weiss metal" is in many ways the most mysterious among all the doping concentrations. The $T_N$ transition disappears and $\chi$ keeps rising with decreasing $T$. The observation of Curie-Weiss behavior in a metal again calls for the coexistence of local moments and itinerant electrons. As an example, let us assume that the quadri-vacancy binds a hole on each of the neighboring Co planes, forming an $S = \frac{1}{2}$ local moment on each plane. The local moment forms a triangular lattice with one $S = \frac{1}{2}$ per 12 cobalt. For $x = 0.71$, the concentration of itinerant carriers is $\frac{2}{12} = 0.028$ per Co, which is 2.7 times that of $x = 0.84$. We then expect a Fermi temperature of 235 K. The higher carrier density reduces the tendency towards Stoner instability, which explains the absence of a magnetic phase transition. The ultimate fate of these local moments is an interesting open question. The absence of ordering suggests a spin liquid state formed by Kondo coupling of local moments on a frustrated lattice. However, this spin liquid coexists with metallic electrons, a new possibility which deserves further investigation.

**Experimental Station**
X-ray powder diffraction end station

**References**

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