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**Oxygen nonstoichiometry and the origin of Na ion ordering in P2-Na_xCoO_2**

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The impact of oxygen deficiency on physical properties of Na_{2-x}CoO_2 has been investigated. From the combined thermogravimetric, magnetic susceptibility, and synchrotron x-ray Laue diffraction studies, it is demonstrated that Na_{2/3}CoO_2 shows no superlattice ordering due to Na ions; however Na_{2/3}CoO_{1.98}, which has the same Co valence as that of Na_{0.71}CoO_2, shows nearly identical magnetic and transport properties and the same simple hexagonal superlattice ordering of \sqrt{12}a. It is proposed that the Na ion ordering found in Na_{2/3}CoO_{1.98} is identical to the ideal Na_{0.71}CoO_2 of large \sqrt{12}a \times \sqrt{12}a \times 3c superlattice but with additional Na vacancies which are bound to the oxygen defects at room temperature. We conclude that oxygen vacancies play a key role in stabilizing the superlattice structure and must be accounted for in its modeling.

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**I. INTRODUCTION**

P2-Na_xCoO_2 (also called γ phase) is composed of alternating layers of Na and CoO_2 with a hexagonal in-plane network that can be described by space group P6_3/mmc. 1 Na vacancy ordering has been an important subject both experimentally and theoretically following the discovery of rich ordering has been solved satisfactorily for room temperature. The Na superlattice as a result of Na ion transport environment at 700 °C and quenched. 14 The proposed microscopic structure is very different from the trivacancy and quadrivacancy layer model we proposed for Na_{0.71}CoO_2.

We have demonstrated that the particularly stable phases found near 0.71, 0.50, 0.33, and 0.25 also show sharp drop of the Na atom diffusion coefficients at room temperature. 6 However, it is quite surprising that the commonly predicted stable phases near \(x=3/4\) and 2/3 do not exist, as revealed by our single-crystal electrochemical depthlateral studies at room temperature. The Na superlattice as a result of Na ion ordering has been solved satisfactorily for \(x \approx 0.833\), 0.820, 0.77, and 0.71 so far, based on Na multivacancy model of divacancy, trivacancy (T), and quadrivacancy (Q) cluster ordering. 5,9 For example, \(x=0.71\) is composed of alternating Na layers with trivacancy and quadrivacancy clusters ordered in a large simple hexagonal superlattice of size \(\sqrt{12}a\). 5,8 The implication of such Na vacancy ordering has helped understand the origin of small cross sections of the Fermi surface hole pockets observed by Shubnikov de Haas oscillation and the intriguing coexistence of metallic conductivity with Curie-Weiss behavior. This led us to propose that the Na vacancy ordering creates one special partial localization environment for the doped holes, i.e., part of the charge is localized near the vacancy center and the rest are itinerant throughout the vacancy-free region. Similar conclusion has been drawn based on \(^{59}\)Co and \(^{23}\)Na NMR in a sample of nominal stoichiometry Na_{0.75}CoO_2 as well, i.e., neither charge disproportion nor uniform average valence but an intermediate configuration should be used to describe this unique type of charge distribution. 10

While Na vacancy is unavoidable for Na_{x}CoO_2 samples prepared under ambient pressure, even under pure oxygen environment, the most probable Na content for samples prepared using solid-state reaction is usually in the range of 0.75–0.85. 11 Different vacancy ordering patterns for \(x=2/3\) have been proposed based on density-functional theory calculations. 12,13 However, single-crystal diffraction studies on Na_{x}CoO_2 have not revealed any signature of Na ion ordering for \(x=2/3\). 6 On the other hand, Platova et al. have proposed based on NMR and x-ray diffraction results, that a simple hexagonal superlattice of \(\sqrt{12}a\) exists in Na_{2/3}CoO_2 where powder sample were carefully prepared under oxygen environment at 700 °C and quenched. 14 The proposed microscopic structure is very different from the trivacancy and quadrivacancy layer model we proposed for Na_{0.71}CoO_2. It is very surprising that the physical properties of their samples are very similar to ours despite the difference in Na concentration and their proposed superlattice size is identical to that found in Na_{0.71}CoO_2 based synchrotron x-ray Laue and electron-diffraction studies on single-crystal sample with electrochemically fine-tuned \(x\). 5,8 We have pointed out previously that the controversy could have resulted from differences in oxygen content, i.e., the identical \(\sqrt{12}a\) simple hexagonal superlattice is a result of identical average Co valence between Na_{0.71}CoO_2 and Na_{2/3}CoO_{1.98}. 5,8 Herein, we provide conclusive evidence to resolve the controversy regarding the \(\sqrt{12}a\) superlattice ordering observed in \(x=2/3\). It turns out that oxygen content plays an important factor that cannot be ignored when discussing all related physical properties in the Na_{x}CoO_{2-x} system. The nature of immobile and randomly distributed oxygen vacancy at room temperature renders the Na ion ordering more complicated, especially when the ordering along the c axis (staging) is considered as well. 8,9
II. EXPERIMENT

Single-crystal samples have been prepared from floating-zone method growth, following an additional electrochemical deintercalation technique as reported previously. Oxygen environment with pressure higher than 8 atm has been kept in the optical floating-zone growth chamber to reduce Na loss due to evaporation and the generation of Co₃O₄ impurity phase, in particular, to prevent the occurrence of oxygen deficiency. High-quality single-crystal Na₉CoO₂ of $x \sim 0.84$ could be obtained reproducibly starting from polycrystalline feed rod prepared from Na₂CO₃ and Co₃O₄ of Na₂:Co = 0.85:1 ratio. Samples with Na content of 0.71 and 2/3 were prepared from electrochemical deintercalation as reported previously, where the as-grown crystal sample of Na₀.₈₄CoO₂ was used as working electrode, Pt as counter-electrode, and Ag/AgCl with sieved liquid junction as reference electrode. The applied voltages relative to Ag/AgCl reference electrode were 0.05 V and 0.20 V for the preparation of $x = 0.71$ and 2/3, respectively. Electron probe microanalysis (EPMA) has been performed on freshly cleaved inner surfaces to verify the chemical composition of each element. Perkin-Elmer thermogravimetric (TG)/differential thermal analysis (DTA) was used for thermal gravimetric analysis. Synchronous x-ray Laue diffraction for superstructure investigation was performed at the NSRRC, Taiwan and magnetic-susceptibility measurement was done using Quantum Design superconducting quantum interference device vibrating-sample magnetometer (SQUID-VSM).

III. RESULTS AND DISCUSSIONS

Na₀.₇₁CoO₂ sample can be prepared through electrochemical deintercalation method precisely, as indicated by the diverging diffusion coefficient derived previously. However, the target Na concentration for Na₂/₃CoO₂ is very hard to obtain precisely, partly because of its metastable nature. We have prepared sample with $x = 0.67 \pm 0.01$ and verified by both the x-ray lattice parameter analysis of linear c(x) extrapolation reported previously and EPMA to confirm this crucial concentration for this study. Additional oxygen control has been performed using TGA scan under various gas flows, including oxygen and air, up to 950 K. The as-prepared single-crystal samples of nearly oxygen deficiency-free samples for $x=0.71$ and $x = 2/3$ have been ground into powder and go through additional annealing under TGA as shown in Fig. 1. We find that a significant weight loss occurs for $x=2/3$ only near 700 K and this weight loss is recoverable under oxygen. On the other hand, $x=0.71$ sample is stable at the same temperature range, whether the flowing gas is oxygen or air. The reversible weight loss for $x=2/3$ sample near 700 K is about 0.30 wt %, which corresponds to an oxygen loss of 0.02. Interestingly, the Co valence of Na₀.₇₁CoO₂ and Na₂/₃CoO₁.₉₈ are identical, and this thermal analysis suggests that the most stable average Co valence is near +3.29. To prepare oxygen-deficient Na₀.₇₁CoO₁.₉₈ single-crystal sample for further study, we annealed the as-prepared Na₂/₃CoO₂ single-crystal sample at 700 K for 12 h and quenched, similar to the method used by Platova et al. on their powder sample. We believe that the powder sample studied by Platova et al. has an oxygen-deficiency level about 0.02 as described above.

It is instructive to compare the Laue diffraction patterns of Na₀.₇₁CoO₂, Na₂/₃CoO₂, and Na₂/₃CoO₁.₉₈ as shown in Fig. 2. The Laue pattern of Na₀.₇₁CoO₂ shows perfect superlattice of $\sqrt{12}a$ as reported previously. The superstructure of Na₀.₇₁CoO₂ has been modeled to be composed of alternating layers of sodium trivacancy (T) and quadrivacancy (Q) clusters ordered in simple hexagonal shape. Additional structure refinement suggests that these alternating layers of TQTQTQ stacking has a 3c periodicity described by a right-hand screw symmetry advanced Na trimers along the c axis. While Na₂/₃CoO₂ shows no superlattice formation, as indicated in Fig. 2(b), Na₂/₃CoO₁.₉₈ reveals a superstructure nearly identical to that of Na₀.₇₁CoO₂ in the reciprocal space. We note however, that detailed comparison of Laue patterns in Fig. 2 shows some systematic missing of superlattice diffraction planes for Na₂/₃CoO₁.₉₈ as comparing with that of Na₀.₇₁CoO₂, which suggests that even though these two samples possess identical superlattice size of $\sqrt{12}a$, subtle difference must exists as suggested by the NMR studies. These results seem to suggest that similar Na ion ordering can be achieved as long as the average Co valence is close to +3.29.

Experimentally Na₀.₇₁CoO₂ has been shown to be the most stable phase as indicated by its significant sharp drop of the diffusion coefficient and the convincingly refined crystal structure of Na trivacancy and quadrivacancy cluster stacking of $\sqrt{12}a \times \sqrt{12}a \times 3c$ superlattice ordering. The observed identical superlattice size suggests that Na₂/₃CoO₁.₉₈ can very well be a defect-type variation in the ideal Na₀.₇₁CoO₂. To provide a more quantitative description to the current finding, let us take as an empirical fact that Na₀.₇₁CoO₂ with the trivacancy and quadrivacancy ordering is most stable. The Na₂/₃CoO₁.₉₈ with oxygen vacancy means that for every 48 Co atoms, one oxygen is missing, i.e., one out of four $\sqrt{12}a \times \sqrt{12}a$ supercell contains an oxygen vacancy. In order not to pay too much Coulomb energy for the O²⁻ vacancy, two additional Na vacancies will appear. Then
on average the two trivacancy layers become quadrivacancy

FIG. 2. (Color online) The Laue patterns for (a) Na$_{0.71}$CoO$_2$, (b) Na$_{2/3}$CoO$_2$, and (c) Na$_{2/3}$CoO$_1.98$ taken along [001] direction at room temperature. The strong diffraction peaks are indexed as [100] and [010] of the primitive cell with size $a$ constructed by Co ions, and the six superlattice peaks in hexagonal shape surrounding each primitive index correspond to a real lattice of size $\sqrt{12}a$.

... within the proposal of Platova et al. for Na$_{2/3}$CoO$_2$ why oxygen vacancies are needed to stabilize the superlattice structure. In any case, based on our findings it is clear that the role of oxygen deficiencies need to be accounted for in the modeling of the $x=2/3$ material.

Magnetic-susceptibility measurement results are summarized in Fig. 3. The displayed data are powder average of the single-crystal measurement, i.e., $2/3\chi_{\text{dia}} + 1/3\chi_{\text{core}}$ without considering the minor correction of in-plane anisotropy. There is no magnetic anomaly found down to 2 K for all three samples. The Curie-Weiss behavior for a system with metallic property has long been a puzzle, and it transforms from Curie-Weiss to Pauli-type behavior only when $x$ is reduced to the level of nearly half-filled Na layer. Based on our proposed Na vacancy cluster model published previously, Na trivacancy and quadrivacancy cluster superlattice ordering could be responsible for the Curie-Weiss metal behavior, i.e., part of the doped holes are localized near the Na vacancy cluster center while the rest are itinerant. Both localized and itinerant electrons should contribute to the magnetic susceptibility. We propose that the total magnetic susceptibility should include contributions from temperature-independent core diamagnetic $\chi_{\text{core}}$, van Vleck paramagnetic $\chi_{\text{VV}}$, Pauli paramagnetic $\chi_{\text{Pauli}}$, and the spin susceptibility from localized spins which are tentatively described by a Curie-Weiss-type behavior of $C/(T-\theta)$. The Curie-Weiss behavior for all three samples has been fitted following an equation of $\chi = C/(T-\theta)$ with parameters shown in Table I.

FIG. 3. (Color online) Magnetic-susceptibility data for Na$_{0.71}$CoO$_2$, Na$_{2/3}$CoO$_2$, and Na$_{2/3}$CoO$_1.98$ in applied field of 1 T. The inset demonstrates the reliability of Curie-Weiss law fitting through difference between measured data and fitted equation of $\chi + C/(T-\theta)$ with parameters shown in Table I.
though more holes are introduced compared with Na$_{2/3}$CoO$_{1.98}$. Clearly, formation of long-range Na multivacancy cluster ordering such as that demonstrated by the ideal Na$_{0.71}$CoO$_2$, is prohibited in Na$_{2/3}$CoO$_2$, unless oxygen vacancy is introduced.

The coexistence of local moments and itinerant electrons is a complicated many-body problem which is not fully understood. The data fitting using Curie-Weiss law plus Pauli is only a crude beginning. For instance, the $C$ coefficient found for Na$_{0.71}$CoO$_2$ corresponds to a $S=\frac{1}{2}$ local moment per doped hole, which is clearly inconsistent with metallic behavior. We also acknowledge that another point of view has been proposed in the literature, i.e., the Curie-Weiss behavior signifies an almost ferromagnetic metal, as described, for instance, by the self-consistent renormalized (SCR) spin-fluctuation theory. However, in the standard SCR theory, the spin susceptibility saturates at low temperatures leading to Fermi-liquid behavior whereas in the present system $\chi$ continues to rise down to 4 K (as seen in Fig. 3). Such a low Fermi-liquid scale is not expected without fine tuning. Furthermore, the resistivity exhibits a linear $T$ dependence below 100 K and crossover to $T^1$ below 4 K while the specific heat exhibits $T \ln T$ dependence. At the moment, neither the itinerant spin-fluctuation model nor the partial local moment picture is capable of explaining these anomalies. We leave this complicated and interesting issue open for future discussions. The main point of the present analysis is simply that the magnetic properties of Na$_{0.71}$CoO$_2$ and Na$_{2/3}$CoO$_{1.98}$ are very similar while that of Na$_{2/3}$CoO$_2$ has distinctly different $C$ and $\theta$.

We have also performed four-probe resistivity measurements on the Na$_{0.71}$CoO$_2$, Na$_{2/3}$CoO$_2$, and Na$_{2/3}$CoO$_{1.98}$ crystals as shown in Fig. 4. For Na$_{0.71}$CoO$_2$, the resistivity shows metallic behavior and drops with decreasing temperature. There is a crossover at about 100 K, below which the resistivity becomes practically linear in $T$. Similar behavior has also been observed in Na$_{2/3}$CoO$_2$ and Na$_{2/3}$CoO$_{1.98}$. However, such deviation from the $T$-linear dependence at low temperature is evident and more significant in Na$_{2/3}$CoO$_2$. In addition, we note that the resistivity value is more than twice as large in Na$_{2/3}$CoO$_2$ at low temperature, which suggests a shorter carrier lifetime due to a more disordered phase in Na$_{2/3}$CoO$_2$. These observations are in accord with the absence of Na superstructure ordering as mentioned earlier and also imply an intimate correlation between the Na ordering and the Co layer electronic structure.

Longitudinal magnetoresistance (LMR) and transverse magnetoresistance (TMR) were measured for the three samples, where LMR and TMR were obtained under a magnetic field up to 14 T applied parallel and perpendicular to the CoO$_2$ plane, respectively. The orbital magnetoresistance (OMR) was determined by subtracting TMR with LMR in order to exclude the spin-related contribution to the TMR. A comparison of LMR and OMR for the three samples is shown in Fig. 5. The OMR is positive for all three samples with quadratic magnetic field dependence as expected from orbital contribution, which is simply proportional to the square of carrier mobility. Na$_{2/3}$CoO$_2$ shows smaller OMR than that of Na$_{0.71}$CoO$_2$ and Na$_{2/3}$CoO$_{1.98}$, which infers a shorter carrier lifetime in a more disordered Na$_{2/3}$CoO$_2$ as expected. On the other hand, LMR is typically derived from spin effect, where the negative LMR is most likely associated with the suppression of spin scattering due to the field

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\chi_c$ (cm$^3$/mole)</th>
<th>$C$ (cm$^3$ K/mole)</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_{2/3}$CoO$_2$</td>
<td>0.00049(3)</td>
<td>0.099(2)</td>
<td>96(2)</td>
</tr>
<tr>
<td>Na$<em>{2/3}$CoO$</em>{1.98}$</td>
<td>0.00054(5)</td>
<td>0.109(2)</td>
<td>60(2)</td>
</tr>
<tr>
<td>Na$_{0.71}$CoO$_2$</td>
<td>0.00034(2)</td>
<td>0.106(1)</td>
<td>62(1)</td>
</tr>
</tbody>
</table>

#### Table I. Summary of magnetic-susceptibility data analysis for Na$_{2/3}$CoO$_2$, Na$_{2/3}$CoO$_{1.98}$, and Na$_{0.71}$CoO$_2$ fitted using equation $\chi_c + C/(T-\theta)$ in the range of $\sim 100$–300 K.
alignment of localized moment. We find that the LMR in Na$_2$CoO$_2$ is nearly half of that in Na$_{0.71}$CoO$_2$ and Na$_{2/3}$CoO$_1.98$ at low temperature, which suggests less spin scatterers in the system. Again, the main point is the similarity between Na$_{0.71}$CoO$_2$ and Na$_{2/3}$CoO$_1.98$ and their contrast with Na$_{2/3}$CoO$_2$. We also remark that the extraction of carrier density from Hall coefficient data is not possible because of its strong temperature dependence due to strongly correlated nature.

IV. CONCLUSIONS

In summary, using single-crystal samples of well-controlled oxygen and sodium content, we have provided strong evidence to resolve the controversy of superlattice ordering found in Na$_x$CoO$_2$ of $x=0.71$ and 2/3. Synchrotron x-ray Laue diffraction results indicate that there is no sodium ordering in Na$_{2/3}$CoO$_2$ at room temperature while Na$_{2/3}$CoO$_1.98$, which has identical Co valence to that of Na$_{0.71}$CoO$_2$, shows identical $\sqrt{3}a \times \sqrt{3}a \times 3c$ simple hexagonal superstructure to that of Na$_{0.71}$CoO$_2$, also with nearly identical magnetic and transport properties. These results imply that Na$_{0.71}$CoO$_2$ with $\sqrt{3}a \times \sqrt{3}a \times 3c$ superlattice is the most stable structure at this particular concentration while Na$_{2/3}$CoO$_1.98$ of identical average Co valence possesses a nearly identical Na superstructure and magnetic properties with the help of oxygen defect generation. This proposed model is supported in part by the higher resistivity found in Na$_{2/3}$CoO$_2$ without Na superstructure. Studies on Na ion ordering based on screened intersodium interaction without considering the involved oxygen deficiency could result in misleading prediction or interpretation.

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