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### **Sodium Ion Ordering in double-layered and triple-layered $\text{Na}_x\text{CoO}_2$**

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The layered sodium cobalt oxide  $\text{Na}_x\text{CoO}_2$  is studied by electron diffraction for a wide range of sodium contents,  $0.15 < x < 0.75$ . This range in compositions is obtained by removal of Na by various methods for the starting materials  $\text{Na}_{0.7}\text{CoO}_2$ , and  $\text{Na}_{1.0}\text{CoO}_2$ . The structure of  $\text{Na}_x\text{CoO}_2$  is based the stacking of triangular O-Co-O layers with Na planes. The Co atoms are in edge-sharing  $\text{CoO}_6$  octahedra. For the starting compound  $\text{Na}_{0.7}\text{CoO}_2$ , the  $\text{Na}^+$  ions are in a trigonal prismatic coordination whereas for  $\text{Na}_{1.0}\text{CoO}_2$  the  $\text{Na}^+$  coordination is octahedral. Prismatic coordination occurs when the close packed oxygen planes directly adjacent to the Na plane have the same projection into the basal plane (A-Na-A), whereas octahedral coordination of Na occurs when the directly adjacent oxygen planes have different projections (A-Na-B) into the basal plane. Due to this difference in stacking the a axis is about 1.08 nm and 1.65 nm for  $\text{Na}_{0.7}\text{CoO}_2$  and  $\text{Na}_{1.0}\text{CoO}_2$  respectively. For  $\text{Na}_{0.7}\text{CoO}_2$  as well as  $\text{Na}_{1.0}\text{CoO}_2$  a series of superstructures are observed, which can be explained with ordered Na ion-Na vacancy superlattices. The structural principle for some of the observed ordering schemes, particularly near  $x=0.5$ , is, surprisingly, the presence of lines of Na ions and vacancies rather than simply maximized Na-Na separations. With  $\text{Na}_{0.7}\text{CoO}_2$  as starting material, the most strongly developed superlattice is found for the composition  $\text{Na}_{0.5}\text{CoO}_2$ . With  $\text{Na}_{1.0}\text{CoO}_2$  as starting material, the most strongly developed superlattice is found for the compositions  $\text{Na}_{0.75}\text{CoO}_2$  and  $\text{Na}_{0.5}\text{CoO}_2$ . In particular the superstructure  $\text{Na}_{0.75}\text{CoO}_2$  is very complicated.

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