Sodium Ion Ordering in double-layered and triple-layered Na$_x$CoO$_2$
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The layered sodium cobalt oxide Na$_x$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 Na$_{0.7}$CoO$_2$, and Na$_{1.0}$CoO$_2$ The structure of Na$_x$CoO$_2$ is based the stacking of triangular O-Co-O layers with Na planes. The Co atoms are in edge-sharing CoO$_6$ octahedra. For the starting compound Na$_{0.7}$CoO$_2$, the Na$^+$ ions are in a trigonal prismatic coordination whereas for Na$_{1.0}$CoO$_2$ the 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 Na$_{0.7}$CoO$_2$ and Na$_{1.0}$CoO$_2$ respectively. For Na$_{0.7}$CoO$_2$ as well as Na$_{1.0}$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 Na$_{0.7}$CoO$_2$ as starting material, the most strongly developed superlattice is found for the composition Na$_{0.5}$CoO$_2$. With Na$_{1.0}$CoO$_2$ as starting material, the most strongly developed superlattice is found for the compositions Na$_{0.75}$CoO$_2$ and Na$_{0.5}$CoO$_2$. In particular the superstructure Na$_{0.75}$CoO$_2$ is very complicated.

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