Sodium Ion Ordering in double-layered and triple-layered Na\textsubscript{x}CoO\textsubscript{2}
HENNY ZANDBERGEN, Dept. of Chemistry and Princeton Materials Inst., Princeton University; National Centre for HREM, Dept. of Nanoscience, Delft University of Technology

The layered sodium cobalt oxide Na\textsubscript{x}CoO\textsubscript{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\textsubscript{0.7}CoO\textsubscript{2}, and Na\textsubscript{1.0}CoO\textsubscript{2} The structure of Na\textsubscript{x}CoO\textsubscript{2} is based the stacking of triangular O-Co-O layers with Na planes. The Co atoms are in edge-sharing CoO\textsubscript{6} octahedra. For the starting compound Na\textsubscript{0.7}CoO\textsubscript{2}, the Na\textsuperscript{+} ions are in a trigonal prismatic coordination whereas for Na\textsubscript{1.0}CoO\textsubscript{2} the Na\textsuperscript{+} 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\textsubscript{0.7}CoO\textsubscript{2} and Na\textsubscript{1.0}CoO\textsubscript{2} respectively. For Na\textsubscript{0.7}CoO\textsubscript{2} as well as Na\textsubscript{1.0}CoO\textsubscript{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\textsubscript{0.7}CoO\textsubscript{2} as starting material, the most strongly developed superlattice is found for the composition Na\textsubscript{0.5}CoO\textsubscript{2}. With Na\textsubscript{1.0}CoO\textsubscript{2} as starting material, the most strongly developed superlattice is found for the compositions Na\textsubscript{0.75}CoO\textsubscript{2} and Na\textsubscript{0.5}CoO\textsubscript{2}. In particular the superstructure Na\textsubscript{0.75}CoO\textsubscript{2} of is very complicated.

In collaboration with M.L. Foo, Department of Chemistry and Princeton Materials Institute, Princeton University, Princeton, NJ 08544 USA; Q. Xu and V. Kumar, National Centre for HREM, Department of Nanoscience, Delft University of Technology, Rotdamenseweg 137, 2628 AL Delft, The Netherlands ; L. Viciu, Department of Chemistry and Princeton Materials Institute, Princeton University; Q. Huang, NIST Center for Neutron Research, NIST, Gaithersburg, MD 20899; and R.J. Cava, Department of Chemistry and Princeton Materials Institute, Princeton University.