Crystal growth, magnetism, transport and superconductivity of two dimensional sodium cobalt oxide single crystals

Dapeng Chen
University of Wollongong, dapeng@uow.edu.au

Recommended Citation

Unless otherwise indicated, the views expressed in this thesis are those of the author and do not necessarily represent the views of the University of Wollongong.
NOTE

This online version of the thesis may have different page formatting and pagination from the paper copy held in the University of Wollongong Library.

UNIVERSITY OF WOLLONGONG

COPYRIGHT WARNING

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.
Crystal Growth, Magnetism, Transport and Superconductivity of Two Dimensional Sodium Cobalt Oxide Single Crystals

A thesis submitted in fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY from UNIVERSITY OF WOLLONGONG by Dapeng Chen (B.C., M.E.) Institute for Superconducting and Electronic Materials 2008
DECLARATION

This is to certify that the work presented in this thesis was carried out by the candidate in the laboratories of the Institute for Superconducting and Electronic Materials (ISEM), at the University of Wollongong, NSW, Australia, and has not been submitted for a degree to any other institution of higher education.

Dapeng Chen

2008
ACKNOWLEDGMENTS

I would like to express my sincere appreciate and gratitude to my supervisors, Prof. Xiaolin Wang, Prof. S. X. Dou, and Prof. Chengtian Lin, for their continuous academic guidance, encouragement, and support during my three years of PhD study in the Institute for Superconducting and Electronic Materials at the University of Wollongong.

I would also like to express my gratitude to Dr. T. Silver, Dr. J. Horvat, Dr. Alex Pan, Dr. Aihua Li, and Mr. Xun Xu, for their contributions in measurements, useful discussions, and suggestions.

This work would not have been completed without the help of Dr. J. Stempfer, G. Götz, K.-H. Bender, and C. Bush from the Max Planck Institute for Solid State Research, Germany; Prof. Guoqing Zheng and K. Matamo from Okayama University; J. Laverock and S. B. Dugdale from the University of Bristol; R. L. Meng and Prof. C. W. Chu from the University of Houston; J. A. Duffy, J. Wooldridge, G. Balakrishnan, and M. R. Lees from the University of Warwick; A. Andrejczuk, M. Itou, and Y. Sakurai from the Japan Synchrotron Radiation Research Institute; and Hui Zhang from Kunming University of Science and Technology. I would like to sincerely thank all of them for their great collaboration.

My special thanks to all my colleagues at ISEM, and all the members and technicians at the Faculty of Engineering for their friendly help and assistance in using the facilities.
I would also like to acknowledge the University of Wollongong for providing me with two scholarships – an International Postgraduate Research Scholarship (IPRS) and a University Postgraduate Award (UPA) with top-up award.

Finally I wish to thank my family members and my friends for their patience and support.
Table of Contents

ABSTRACT ................................................................................................................................. 1

CHAPTER 1 INTRODUCTION ....................................................................................................... 5
  1.1. INTRODUCTION .................................................................................................................. 5

CHAPTER 2 LITERATURE REVIEW ON SODIUM COBALTATES .............................................................. 12
  2.1. INTRODUCTION .................................................................................................................. 12
  2.2. TWO-LAYER Na_xCoO_2 .................................................................................................... 13
    2.2.1. Polycrystalline samples and physical properties .......................................................... 13
    2.2.2. Effects of elemental doping ........................................................................................ 21
    2.2.3. Thin film growth and physical properties .................................................................... 22
    2.2.4. Single crystal growth and physical properties ............................................................. 24
      2.2.4.1. Single crystal growth by the flux method ................................................................. 24
      2.2.4.2. Single crystal growth by optical floating zone method ........................................... 26
    2.2.5. Theoretical explanations ............................................................................................. 29
  2.3. CHARGE ORDERED INSULATOR Na_0.5CoO_2 ....................................................................... 30
    2.3.1. Crystal structure of Na_{0.5}CoO_2 ................................................................................ 30
    2.3.2. Magnetic structure of Na_{0.5}CoO_2 ............................................................................. 34
    2.3.3. Other physical properties of Na_{0.5}CoO_2 ................................................................. 37
  2.4. UNUSUAL PHYSICAL PROPERTIES PHASE γ'-Na_{0.75}CoO_2 .............................................. 39
    2.4.1. Crystal structure .......................................................................................................... 39
    2.4.2. Sodium pattern and magnetic structure of Na_{0.75}CoO_2 ........................................... 40
    2.4.3. Crystal growth and physical property measurements .................................................. 43
4.2. EXPERIMENT ........................................................................................................... 98

4.3. RESULTS AND DISCUSSION .................................................................................... 99

4.3.1. Superconductivity .............................................................................................. 99

4.3.2. Evidence for d-wave pairing in the cobalt oxide superconductor Na$_x$CoO$_2$ · $1.3H_2O$ .................................................................................................................... 103

4.3.3. Elliptical hole pockets in the Fermi surfaces of hydrated sodium cobalt oxides ......................................................................................................................... 105

4.4. CONCLUSION ........................................................................................................ 107

CHAPTER 5 MAGNETIC ANISOTROPY OF TWO-LAYER NA$_x$COO$_2$ SINGLE CRYSTALS ................................................................. 109

5.1. INTRODUCTION .................................................................................................. 109

5.2. EXPERIMENT ...................................................................................................... 109

5.3. RESULTS AND DISCUSSION .............................................................................. 110

5.4. CONCLUSION ...................................................................................................... 118

CHAPTER 6 STUDIES OF SINGLE CRYSTAL GROWTH AND ANISOTROPIC MAGNETIC PROPERTIES OF NON-STOICHIOMETRIC THREE-LAYER SODIUM COBALT OXIDES ....................................................................................... 120

6.1. INTRODUCTION .................................................................................................. 120

6.2. EXPERIMENT ...................................................................................................... 122

6.3. RESULTS AND DISCUSSION .............................................................................. 124

6.3.1. Crystal growth ................................................................................................. 124
List of Figures

Fig. 1.1. The similarities and discrepancies between cobaltates and cuprates. The crystal structure of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ [9] is on the left, and the crystal structure of Bi2212 is on the right. 7

Fig. 1.2. Illustration of the four lamp ellipsoidal infra-red image furnace for TSFZ. 10

Fig. 2.1. Structural views of $Na_{0.7}CoO_2$ (left) and $Na_xCoO_2 \cdot yH_2O$ (right), where Na and $H_2O$ sites are partially occupied. $Na_{0.7}CoO_2$ was prepared by solid-state reaction under oxygen gas flow. A fivefold excess of $Br_2$ with respect to the Na content was dissolved in acetonitrile ($CH_3CN$). A well pulverized powder of $Na_{0.7}CoO_2$ was immersed in the $Br_2/CH_3CN$ solution for 5 days to de-intercalate Na ions; then the product was filtered, washed with $CH_3CN$ and distilled water, and finally dried in ambient atmosphere [9]. 14

Fig. 2.2. The phase diagram of non-hydrated $Na_xCoO_2$ [10]. 18

Fig. 2.3. The renewed magnetic phase diagram of $Na_xCoO_2$. $\mu_1$-AF, antiferromagnetism of $Co^{3.5+\delta}$; AF, antiferromagnetism of $Co^{3.5-\delta}$; FM, ferromagnetism of $Co^{3.5-\delta}$; MM, metamagnetism of $Co^{3.5-\delta}$; SC, superconductivity; and SDW, spin density wave. The open and filled circles stand for the ferromagnetic transition points for $Na_{0.52}CoO_2$ and $Na_{0.55}CoO_2$, respectively. The inset figure shows the magnetic structure proposed for $x = 0.55$ with field $H//c$ plane [36].
Fig. 2.4. Model for the Na planes of Na$_{0.71}$CoO$_2$ (left) and electron diffraction pattern of Na$_{0.71}$CoO$_2$ (right). The Na planes at both $z = 0$ and $z = 1/2$ are given. Occupied Na positions are given as black dots and Na vacancies by open circles. X indicates the positions of the underlying Co atoms. On the right of each model, it is indicated whether the Na atoms are at a Na1 or a Na2 site [29].

Fig. 2.5. An optical micrograph of a sample prepared by Fujita et al. (left) [61], and typical Na$_{0.7}$CoO$_2$ single crystals packeted parallel to the ab plane (middle and right) [68].

Fig. 2.6. Typical Na$_{0.82}$CoO$_2$ single crystal grown by the floating-zone technique in an image furnace ($\Phi 6 \times 80$ mm$^3$).

Fig. 2.7. The crystal structure of Na$_{0.5}$CoO$_2$ obtained from $\gamma$-Na$_x$CoO$_2$, showing layers of edge-shared CoO$_6$ octahedra and the triangular prismatic coordination of Na within the intermediary layers [87].

Fig. 2.8. [001] diffraction patterns of Na$_{0.5}$CoO$_2$: (a) pattern of commensurate superstructure was taken almost immediately expose to the electron beam, (b) pattern of incommensurate superstructure was taken after exposure to the electron beam; (c) diffraction pattern taken at about 100 K with extra
reflections; such diffraction patterns were only observed in a few areas. White arrows in (b) indicate the first and second order superstructure reflections of the central spot and the 110 spot. (d) Model for the Na planes of Na$_{0.5}$CoO$_2$. Both the Na planes on $z = 0$ and $z = 1/2$ are given. Occupied Na positions are shown as black dots and Na vacancies by open circles. X indicates the positions of the underlying Co atoms. On the right of each model it is indicated whether the Na atoms are at a Na1 or a Na2 site [29].

Fig. 2.9. The crystal structures of NaCoO$_2$ phases ($x = 0.6$, 0.5) derived from three-layer NaCoO$_2$. The smaller and larger black spheres represent Co and sodium ions, respectively, while the grey spheres are the oxygen ions.

Fig. 2.10. Magnetic susceptibilities measured for a single crystal of Na$_{0.5}$CoO$_2$ with a field of 1 T parallel and perpendicular to c. At 87 K, the anomaly is very small for $H//c$, while the anomalies are significant at 53 K for directions of $H$ that are both perpendicular and parallel to the c-axis [93].

Fig. 2.11. Magnetic structures proposed [93] for Na$_{0.5}$CoO$_2$ are shown with ordered pattern of Na atoms. The close relationship between the ordering patterns of the Na atoms and the Co moments can be seen.

Fig. 2.12. Model of the spin arrangement in Na$_{0.5}$CoO$_2$. The two CoO$_2$ layers in the magnetic unit cell are depicted, and, for clarity, only Co ions are shown [16].
Fig. 2.13. The crystal structures of Na$_{0.75}$CoO$_2$ derived from three-layer NaCoO$_2$. The small and large black spheres represent Co and sodium ions, respectively, while the grey spheres are the oxygen ions [96].

Fig. 2.14. Neutron diffraction results showing ordering of Na$^+$ (left [111]) and the Na ion ordering pattern proposed for $x = 0.75$ (right)[113].

Fig. 2.15. Left: The magnon dispersion of Na$_{0.75}$CoO$_2$ parallel to the (00l) direction, measured on IN8 at a temperature of 1.5 K. Right: The magnetic structure on which the spin-wave model is based, showing the two exchange constants $J_{ab}$ and $J_c$, and the spin directions [114].

Fig. 2.16. (a) The ordered A-type antiferromagnetic structure in the a-c plane, with an external magnetic field $B$ applied parallel to the magnetic moments. (b) Above a critical field $B_{cf}$ the system undergoes a spin-flop transition to a phase with spins at an angle $\theta$ to the c axis [115].

Fig. 2.17. Left [96]: The crystal structure of Na$_{0.92}$CoO$_2$. Smaller and larger black spheres represent Co and sodium ions, respectively, while the grey spheres are the oxygen ions. Right [130]: The crystal structure of Na$_{0.6}$CoO$_2$. 47
Fig. 2.18. (a) and (b) show the two [001] diffraction patterns observed for Na$_{0.64}$CoO$_2$ [29]. The arrows indicate the incommensurate vectors $q_1$ and $q_2$ in (a), and the circles indicate the extra reflections in (b).

Fig. 2.19. Structural models [148] for the Na$_x$CoO$_2$ · 1.4(D$_2$/H$_2$O) superconductor: Left: $P6_3/mmc$ structure of the $\gamma$-Na$_x$CoO$_2$ derived superconductor. The figure in the middle shows the $D_2$O ice structure [153]. The figure on the right shows the crystal structure of the $\alpha$-Na$_x$CoO$_2$ derived superconductor (R-3m) [150].

Fig. 2.20. The superconducting phase diagram for Na$_x$CoO$_2$ · 1.3H$_2$O. Inset shows the schematic structure [152].

Fig. 2.21. (a) $T_c$ vs. Co valence for superconducting cobaltate. The left curve is from titration data, while the right hand curve describes oxidation states based solely on Na content, from Schaak et al. [152]. (b) The variation of the $c/a$ ratio as a function of the cobalt oxidation state. The inset show the variation of the $H_3O^+$ content of particular samples as determined from measurements of the Na content and the Co oxidation state. Dashed lines are only guides to the eye [14].

Fig. 3.1. DTA-TG analysis by melting single crystalline Na$_{0.67}$CoO$_2$, with heating at 7.5 °C/min up to 1200–1250°C in flowing oxygen. $T_1 = 1035°C$, $T_2 = 1092°C$. (a)
The melting behavior of the compound, and (b) the temperature dependence of the weight loss.

Fig. 3.2. Typical Na$_{0.82}$CoO$_2$ (upper) and Na$_{0.75}$CoO$_2$ (lower) single crystal ingots obtained by the optical floating zone technique.

Fig. 3.3. 001 XRD patterns showing pure $\gamma$-phase Na$_{0.82}$CoO$_2$ (upper panel) and $\gamma$-phase Na$_{0.75}$CoO$_2$ (lower panel). The split peaks are CuKa$_1$ and CuKa$_2$ for the higher and lower intensity, respectively.

Fig. 3.4. Two halves of an as-grown crystal ingot with a cleaved 001 surface: (a) As-cleaved half ingot of Na$_{0.7}$CoO$_2$, showing CoO$_2$ inclusions gathered at the growth boundary (b) The other half of the ingot transformed to Na$_{0.3}$CoO$_2$ · yH$_2$O, showing the removal of the CoO$_2$ inclusions after de-intercalation followed by hydration. (c) The enlarged CoO$_2$ inclusions.

Fig. 3.5. Typical terraced pits on the (110) face of as-grown Na$_{0.7}$CoO$_2$ single crystal.

Fig. 3.6. (a) HRTEM image showing the layered structure of a Na$_{0.7}$CoO$_2$ single crystal; (b) HRTEM image of an edge dislocation in the same crystal.
Fig. 3.7. Sodium distributions along the growth direction for the as-grown Na$_{0.75}$CoO$_2$ single crystal before and after Na-extraction.

Fig. 3.8. Typical crystal morphologies showing the layered structure of Na$_x$CoO$_2$ single crystals. Intercalant layers appeared after de-intercalation using (a) Br$_2$/CH$_3$CN solution (2 days) and (b) H$_2$O to wash out Na ions. (c) “Booklet”-like crystals obtained by the electrochemistry method using NaOH solution (7 days); (d) the same electrochemistry method crystals after a further washing with D$_2$O.

Fig. 3.9. The 002 reflections show the hydration dynamics of the water molecule intercalation in Na$_{0.3}$CoO$_2$. The process indicates that two water molecules (y = 0.6, n = 2) are inserted into a formula unit initially and that this is followed by a group of four to form a fully hydrated phase (y = 1.3, n = 4) [40].

Fig. 3.10. XRD patterns and lattice constants for Na$_{0.3}$CoO$_2$·yH$_2$O under changing ambient conditions: (a) From humid to dry air for 2 days after full hydration. (b) From humid to dry air for 5 days after full hydration. (c) From dry to humid air for 5 days before hydration.

Fig. 3.11. Time dependence of the 002 counts for y = 0, 0.6 and 1.3, respectively, indicating that the volume of the fully hydrated y = 1.3 phase increases while the y = 0 phase rapidly decreases. The y = 0.6 phase is rather stable.
Fig. 3.12. Thermogravimetric analysis of an over-hydrated (15 days) Na$_{0.3}$CoO$_2$·1.8H$_2$O (112.9650 mg) sample, showing the temperature dependence of the weight loss for the compound heated at 0.3 °C/min in flowing oxygen. Inset: the derivative curve. 86

Fig. 3.13. The 0 0 l X-ray diffraction pattern for Na$_{0.3}$CoO$_2$·yH$_2$O showing the mixture of hydrates with y = 0, 0.3, 0.6, 0.9, and 1.8, respectively [40]. 87

Fig. 3.14. Thermogravimetric results from another sample of partially hydrated Na$_{0.3}$CoO$_2$·0.9H$_2$O (107.7800 mg). 88

Fig. 3.15. (a) Time dependence of the in-plane and the out-plane resistivity for Na$_{0.3}$CoO$_2$·yH$_2$O single crystal during a constant hydration process. (b) Schematic representation of the structures of the possible ordered phases with y = 0, 0.3, 0.6, 0.9, and 1.3, respectively. 90

Fig. 3.16. Time dependence of the in-plane (left) and out-of-plane (right) resistivity, $\rho_{ab}$ and $\rho_c$, of Na$_{0.3}$CoO$_2$ single crystals. 92

Fig. 4.1. Zero field Cooling (ZFC) magnetic characterization of the Na$_x$CoO$_2$·1.3H$_2$O single crystals showing the onset $T_c(x)$. Inset: ZFC and FC measurements showing that the optimum $T_c \approx 4.9$ K with x = 0.42 [70]. 100
Fig. 4.2. Revised superconducting \((Na_xCoO_2 \cdot 1.3H_2O)\) and non-superconducting \((Na_xCoO_2)\) phase diagrams schematically combined. My susceptibility data (open circles) is compared to earlier data (small solid squares) and theoretical estimations (thin dashed curve). The arrows in red SC area mark a proposed charge ordering instability at \(x = 1/4\) and \(x = 1/3\) that is not evident in my data [152]. Green bars mark the report of charged ordered phases at \(x = 0.5\), 0.60, and 0.65. For \(x = 0.5\), a metal–insulator transition (MIT) is observed. The composition \(x = 0.5\) separates the behavior of the magnetic susceptibility into a paramagnetic metallic and a Curie–Weiss-like regime. The antiferromagnetic (AF) phase shows an approximately composition-independent critical temperature \(T_N\) and fades out for a composition of \(x \leq 0.75\).

Fig. 4.3. Temperature dependence of the Knight shift for \(Na_xCoO_2 \cdot 1.3H_2O\) with the magnetic field (3.82 T) applied along the a-axis (data from Ref. [165]). The arrow indicates \(T_c\) under the field.

Fig. 4.4. The magnetic-field dependence of the \(^{59}\)Co Knight shift (K) along the a-axis direction at \(T = 1.7\) K, where \(\Delta K = K_0(T = 4.2\) K) - \(K_0(T = 1.7\) K). The curve is a fit to \(-\Delta K \propto \sqrt{H / H_c}\).

Fig. 4.5. A simulation of a Fermi surface comprising a central hexagonal sheet (representing the \(a_{1g}\) hole sheet) and six \(e'_g\) elliptical hole pockets (left) together with the experimental Fermi surface of \(Na_{0.35}CoO_2 \cdot 1.3D_2O\).
obtained from the reconstruction of five Compton profiles for each composition (right). The boundary of the first Brillouin zone is indicated. 107

Fig. 5.1. X-ray diffraction patterns for Na$_x$CoO$_2$ single crystals cleaved along the growth direction. All the peaks can be attributed to the (00l) orientation. 111

Fig. 5.2. X-ray rocking curves for the as-grown Na$_{0.82}$CoO$_2$ crystal (Mo K$_\alpha$-radiation). 112

Fig. 5.3. Temperature dependence of the susceptibility of Na$_{0.82}$CoO$_2$ and Na$_{0.87}$CoO$_2$ measured in a field of 1 T. The open and closed symbols are for the magnetic field applied parallel and perpendicular to the (001) direction, respectively. 113

Fig. 5.4. Temperature dependence of the susceptibility for Na$_{0.42}$CoO$_2$ sample measured with the field parallel and perpendicular to the (001) direction. 115

Fig. 5.5. $\chi_{ab}(T)$ versus $\chi_c(T)$ for single crystals of Na$_x$CoO$_2$ ($x = 0.42, 0.82, \text{and} 0.87$). 116

Fig. 6.1. As-grown single crystal of $\alpha$-NaCoO$_2$ (left) and the cleaved crystal from the last grown part of the ingot (right). 126
Fig. 6.2. X-ray diffraction patterns for $\alpha$-NaCoO$_2$ single crystals cleaved along the growth direction. All the peaks can be attributed to (00l).

Fig. 6.3. Rietveld refinement pattern for the as-grown $\alpha$-Na$_{0.92}$CoO$_2$ crystal. The observed diffraction intensities and the calculated patterns are represented by the plus signs and the solid lines, respectively. The pattern at the bottom represents the difference. Short bars below the observed and calculated patterns indicate the positions of allowed Bragg reflections.

Fig. 6.4. Temperature dependence of the susceptibility for Na$_{0.92}$CoO$_2$ sample measured with field parallel and perpendicular to the (001) direction. Inset shows the data measured in 1 and 5 T with field parallel to (001).

Fig. 6.5. Temperature dependence of the susceptibility for Na$_{0.93}$CoO$_2$ sample measured in a field of 1 T. The open and closed symbols are for the magnetic field applied perpendicular and parallel to the (001) direction, respectively. Inset shows low temperature results at different parallel magnetic fields.

Fig. 6.6. $\chi_{ab}$ versus $\chi_c$ for $\alpha$-Na$_x$CoO$_2$ with $x = 0.91$, 0.92, and 0.93.

Fig. 6.7. Temperature dependence of the susceptibility for Na$_{0.91}$CoO$_2$ sample measured with three different magnetic field directions.

Fig. 7.1. X-ray rocking curves for the as-grown Na$_{0.91}$CoO$_2$ crystal (Mo K$_\alpha$-radiation).
Fig. 7.2. The raw resistance vs. temperature data for the sample. Inset: Definition of contact arrangement.

Fig. 7.3. The temperature dependence of the in- and out-of-plane resistivity of \( \text{Na}_{0.91}\text{CoO}_2 \) single crystals deduced from Montgomery-type analysis.

Fig. 7.4. Resistivity ratio \( \rho_c/\rho_{ab} \) and susceptibility ratio \( \chi_c/\chi_{ab} \) for Na\(_{0.91}\)CoO\(_2\) crystal measured with the field parallel and perpendicular to the (001) direction. Inset: Temperature dependence of the susceptibility for the same sample.

Fig. 7.5. Temperature dependence of the electrical resistivity for Na\(_{0.91}\)CoO\(_2\) crystal. The solid lines are fits to the experimental data using Eq. (1).

Fig. 7.6. Temperature dependence of the electrical resistivity for a Na\(_{0.91}\)CoO\(_2\) crystal. The solid lines are fits to the experimental data using Eq. (3). The inset shows a plot of log (\( \rho \)) vs. \( T^{0.25} \) below 20 K.
List of Tables

Table 2.1. Structure details and unit cell parameters of Na$_x$CoO$_2$ · yH$_2$O at room temperature. 53

Table 3.1. Possible co-existent phases in the Na$_x$CoO$_2$ single crystals and their crystallographic data. 65

Table 5.1. Summary of magnetic data for Na$_{0.82}$CoO$_2$ and Na$_{0.87}$CoO$_2$. 117

Table 6.1. Crystallographic data for Na$_{0.92}$CoO$_2$ in the space group R-3m. 128

Table 6.2. Summary of magnetic data for three-layer Na$_x$CoO$_2$. 135
ABSTRACT

The objective of this work was to study the single crystal growth of Na$_x$CoO$_2$ by the optical floating zone technique and the intrinsic properties of the high quality single crystal samples thus produced. The properties of the superconductors derived from it will also be reported.

This thesis, after a literature review on the Na$_x$CoO$_2$ family and the superconductors derived from it, reports a systematic study on growing Na$_x$CoO$_2$ (x = 0.32–1.00) and Na$_x$CoO$_2$ · yH$_2$O (x = 0.22–0.47, y = 1.3). The experiments demonstrate that nearly pure α- (x = 0.90–1.00) and α’- (x = 0.75) phases of Na$_x$CoO$_2$ crystals could be obtained using the optical floating zone method, while other phases with lower sodium content, x < 0.70 (β-phase with x = 0.55, 0.60 and γ-phase with x = 0.65 and 0.70, respectively), are observed always to contain Na$_2$O, Co$_3$O$_4$, and Na-poor phases. There is experimental evidence that the dependence of the superconducting transition temperature on Na content is much weaker than reported earlier. Implications of the Na effect for understanding of the structure, thermoelectricity, and superconducting phase diagram are discussed.
Na-extraction and hydration were carried out on the $\alpha$- and $\alpha$-samples to obtain the superconducting phase. Hydrated single crystals exhibit cracked layers perpendicular to the $c$-axis, due to a large expansion when the water is inserted into the structure. A study of intercalation/de-intercalation was performed to determine the stability of the hydrated phase and the effects of hydration on the structure of the compound. X-ray diffraction and thermogravimetric experiments were used to monitor the processes of accommodation of water molecules and their removal from the crystal lattice. The initial intercalation process takes place with two water molecules (corresponding to $y = 0.6$) inserted in a formula unit, followed by a group of four ($y = 1.3$) to form a $\text{Na(H}_2\text{O)}_4$ cluster. Thermogravimetric analysis suggests that de-intercalation occurs with the removal of the water molecules one by one from the hydrated cluster at elevated temperatures of approximately 50, 100, 200, and $300^\circ\text{C}$. My investigations reveal that the hydration process is dynamic and that water molecule intercalation and de-intercalation follow different reaction paths in an irreversible way.

This thesis also contains intensive studies on the cobalt oxide superconductors $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ based on $^{59}\text{Co}$ nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) measurements. For the sample with $x = 0.26$ and critical temperature $T_c = 4.6$ K, it was found that the spin–lattice relaxation rate, $1/T_1$, shows a $T^3$ variation below $T_c$ and down to very low temperatures, which indicates the presence of line nodes in the superconducting (SC) gap function. The spin susceptibility below $T_c$ for these samples was also studied via Knight shift measurements. The spin part of the Knight
shift decreases below $T_c$ in both the $a$- and $c$- directions, indicating a singlet spin state of the Cooper pairs. The results strongly suggest that the superconducting state is a d-wave state. Based on bulk measurements of the electron momentum distribution, using the technique of x-ray Compton scattering, the evidence that small, elliptically shaped pockets do indeed exist in the Fermi surface of cobalt oxide superconductors was presented.

The magnetic properties of two-layer $\text{Na}_x\text{CoO}_2$ ($x = 0.42, 0.82,$ and $0.87$) were studied. The magnetic susceptibility measurements revealed considerable anisotropy along $H//ab$ and $H//c$ for the as-grown single crystals. It was found that an antiferromagnetic transition with Neél temperature, $T_N = 21$ K, occurred for the $x = 0.82$ sample, and there was a paramagnetic phase for the $x = 0.87$ sample over a wide temperature range from 2 to 300 K, while the sample with $x = 0.42$ showed a monotonic increase of $\chi$ with increasing temperature above $\sim 100$ K. In addition, the $x = 0.82$ sample had the largest derived anisotropic $g$-factor ratio ($g_{ab}/g_c \approx 1.30$), whereas the sample with $x = 0.42$ was nearly isotropic ($g_{ab}/g_c \approx 0.96$).

Magnetic susceptibility measurements on three-layer $\alpha$-$\text{Na}_x\text{CoO}_2$ ($x = 0.91, 0.92,$ and $0.93$) showed that the magnetic properties depend strongly on $x$. The compound was found to be antiferromagnetic at $T_N \approx 20$ K for $x = 0.91$ and $x = 0.92$, and paramagnetic for $x = 0.93$. In-plane and out-of-plane anisotropy were observed for the $x = 0.91$ crystals. In addition, the anisotropic $g$-factor ratio ($g_{ab}/g_c$) derived from the anisotropic
susceptibility along H//ab and H//c decreased significantly as the sodium composition increased from x = 0.91 to x = 0.93.

A systematic study was also carried out on the conduction mechanism and the anisotropy of the electrical transport properties of the α-Na$_{0.91}$CoO$_2$ single crystals. The resistivity was found to show a large anisotropy along the ab plane and the c axis. The resistivity below the metal-to-insulator transition temperature (20 K) can be well fitted by the variable-range hopping model. The high temperature range can be fitted well by

$$\rho(T) = \rho_0 + A\omega_s/\sinh^2(h\omega_s/2k_BT) + BT^{7/2},$$

both for the in-plane and the out-of-plane behaviours. Such behaviour provides evidence for small polaron and spin-wave scattering metallic conduction in heavily Na-doped sodium cobaltate.