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

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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
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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 $\alpha$- (x = 0.90–1.00) and $\acute{\alpha}$- (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 ($\beta$-phase with x = 0.55, 0.60 and $\gamma$-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 \(\tilde{\alpha}\)-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\(^\circ\)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 $\text{Na}_x\text{CoO}_2 (x = 0.42, 0.82, \text{ and } 0.87)$ 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 Néel 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 ~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 $\alpha$-$\text{Na}_x\text{CoO}_2 (x = 0.91, 0.92, \text{ and } 0.93)$ 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 $\alpha$-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

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

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.