Superconductivity in epitaxial thin films of Na$_x$CoO$_2$·yD$_2$O

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The observation of superconductivity in the layered transition metal oxide Na$_x$CoO$_2$·yH$_2$O (K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature (London) 422, 53 (2003)) has caused a tremendous upsurge of scientific interest due to its similarities and its differences to the copper based high-temperature superconductors. Two years after the discovery, we report the fabrication of single-phase superconducting epitaxial thin films of Na$_x$CoO$_2$·1.3D$_2$O grown by pulsed laser deposition technique. This opens additional roads for experimental research exploring the superconducting state and the phase diagram of this unconventional material.

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Superconductivity in Na$_x$CoO$_2$·yH$_2$O is a property of the cobalt oxide planes. Like in the case of the cuprates, the phase diagram of sodium cobaltate encompasses several competing electronic phases [2, 3, 4], and there are many indications that the superconducting state is unconventional [5, 6]. While in high-temperature superconductors the two-dimensional character of the corresponding copper oxide planes is stabilized by the intrinsically strongly anisotropic crystal structure, in Na$_x$CoO$_2$ a complicated water intercalation process is needed to amplify this anisotropy and induce superconductivity. The main difficulties in fabricating high-quality bulk material of Na$_x$CoO$_2$·yH$_2$O are the following: First, sodium can be inhomogeneously distributed in the entire bulk sample, resulting in an ill-defined doping level. Second, impurity Co oxides such as CoO and Co$_3$O$_4$ are likely to grow due to the high volatility of sodium. Third, it is difficult to avoid the formation of Na$_2$CoO$_3$ in conventional bulk sample fabrication. As a result, high-quality single crystals or bulk samples of Na$_x$CoO$_2$·yH$_2$O are rare, and it is even more difficult to obtain clean surfaces for optical spectroscopy and tunnelling experiments in this material. While high-quality thin films of high-temperature superconductors has allowed a large variety of phase-sensitive experiments to explore the symmetry of the superconducting order parameter, corresponding studies have thus far not proven possible for water-intercalated sodium cobaltate, due to the lack of superconducting thin films. Thin-film deposition techniques offer major advantages in the synthesis of high-quality samples, such as a well-defined vacuum and oxidizing environment. Recently, epitaxial growth of high-quality, "dry" Na$_x$CoO$_2$ films by pulsed laser deposition on SrTiO$_3$ substrates has been reported [7, 8]. In these thin films, phase purity was established within the detection limits of x-ray diffraction in four-circle geometry, and flat surfaces are obtained. As a further milestone, we now report the fabrication of superconducting thin films of Na$_x$CoO$_2$·yH$_2$O.

The control and the determination of the sodium contents are essential to the growth of Na$_x$CoO$_2$. For bulk materials, methods such as inductively coupled plasma atomic emission spectroscopy (ICP-AES) and energy dispersive x-ray (EDX) analysis are available, but the results are often difficult to interpret due to the presence of the above mentioned impurity phases. These methods cannot be applied to thin films, because the material quantity is too low. However, it is well known that for doped oxide materials the lattice parameters depend strongly on the doping level. A well-known example are the high-temperature superconductors, see for instance Ref. [9]. For Na$_x$CoO$_2$, the in-plane lattice constant a shows almost no dependence on doping, but doping does have a significant effect on the c-axis parameter (see Fig. 1). With increasing Na contents, positive charge accumulates between the CoO$_2$ layers, and as a result, the c-axis shrinks. The linear decrease of the c-axis lattice constant with increasing Na content is illustrated in Fig. 1. For x = 0.85 and 0.95 there is a large change in the crystal structure from point group 194 to 165. In the doping range from x = 0.25 to x = 0.85 the c-axis parameter varies linearly with doping. The a-axis parameter varies only about 20 pm throughout the whole doping range.

Figure 1: Lattice parameters from literature for independently refined diffraction and ICP-AES measurements for different x in Na$_x$CoO$_2$. Between x = 0.85 and 0.95 there is a large change in the crystal structure from point group 194 to 165. In the doping range from x = 0.25 to x = 0.85 the c-axis parameter varies linearly with doping. The a-axis parameter varies only about 20 pm throughout the whole doping range.
parameter with increased doping is a useful and accurate, albeit indirect, tool to determine the sodium contents of Na$_x$CoO$_2$.

In order to obtain superconducting Na$_x$CoO$_2$·$y$H$_2$O thin films, it is necessary to intercalate water into samples with doping levels of about $x = 0.3$. This goal can be achieved by first stabilizing Na$_x$CoO$_2$ thin films with $x \approx 0.6$ on SrTiO$_3$ (001) substrates [9]. For obtaining a film at the desired composition $x = 0.3$, it is vital to provide a strong oxidizing agent to deintercalate Na$^+$ ions. In principle, this can be accomplished by the standard Br$_2$·CH$_3$CN-solution method, which is also used for bulk synthesis [1]. However, we have found that NO$_2$·BF$_4$ is superior to the conventional method, as Br is avoided and the deintercalation time scale is considerably accelerated. The decisive step is the intercalation of water into the thin films. In contrast to bulk materials, single-phase thin films cannot be simply immersed into water, because the thin films tend to peel off the substrate. Only a much milder method allows the successful fabrication of superconducting thin films. Oxygen flow with 100% humidity supplied by a $D_2$O bath at a well-defined temperature (19°C) is provided to the sample over several days (196 h). In contrast to alternative preparation routes, this method also yields a clean and smooth surface (see Fig. 2), which is a necessary prerequisite for meaningful surface-sensitive measurements. X-ray diffraction clearly confirms the synthesis of correctly water-intercalated sodium cobaltate Na$_x$CoO$_2$·$yD_2$O epitaxial thin film with the desired doping level $x = 0.3$ and water content $y = 1.3$ (see Fig. 3).

The water-intercalated Na$_x$CoO$_2$·$yD_2$O thin films indeed show superconductivity for $x = 0.3$ and $y = 1.3$ with $T_{C,zero}$ about 4.2 K (see Fig. 4). The relatively sharp superconducting transition with a width of 1.5 K in the resistivity vs. temperature curve confirms the high quality of the thin films. Above the critical temperature, the thin films show metallic behavior up to room temperature with almost linear slope, similar to the high-temperature superconductors.

As a first flavor of the experimental possibilities which are opened through the achievement of these high quality Na$_x$CoO$_2$ thin films we present in Fig. 5 the far-infrared dielectric response function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, at $T = 10$ K of a series of water-free samples that cover a wide range of doping from $0.31 < x < 0.84$. Displayed are the real parts of the optical conductivity, $\sigma_1 = \omega/4\pi\varepsilon_2$ and of the dielectric function, $\varepsilon_1$, as measured directly by spectral ellipsometry using the ANKA synchrotron light source at Forschungszentrum Karlsruhe [10] (the contributions of the SrTiO$_3$ or the LaAlO$_3$ substrates are subtracted). The inset displays the evolution of the corresponding squared plasma frequency, $\omega_p^2 = \frac{4\pi n}{m^*}$, with $n$.
separated by an insulating region at half filling of $x$ in Na$_x$CoO$_2$ films on SrTiO$_3$ (S) or LaAlO$_3$ (L) substrates. The free carrier plasma frequency, $\omega_p^2$ (see inset) clearly tracks the phase diagram of sodium cobaltate [4] consisting of two metallic regions that are separated by an insulating region at half filling of $x = 1/2$.

![Figure 5: Real parts of optical conductivity and dielectric function as a function of doping $x$ in Na$_x$CoO$_2$ films on SrTiO$_3$ (S) or LaAlO$_3$ (L) substrates. The free carrier plasma frequency, $\omega_p^2$ (see inset) clearly tracks the phase diagram of sodium cobaltate [4] consisting of two metallic regions that are separated by an insulating region at half filling of $x = 1/2$.]

the carrier density and $m^*$ their effective mass, that has been deduced with a Drude-Lorentz fitting function. The free carrier response evidently exhibits a very strong and characteristic variation as a function of Na content. It has fairly sharp maxima near $x = 1/3$ and $2/3$ that are separated by a deep minimum near $x = 1/2$. It has indeed previously been noted that the range of $x = 1/2$ separates two metallic regions with high conductivity for $x < 0.5$ and $x > 0.5$ [2, 3]. Notably, a correspondingly rapid variation in the FIR electronic response was not observed in previous optical measurements on single crystals [11, 12]. This suggests that the films can offer significant advantages concerning the homogeneity (in particular concerning the Na content) and the surface quality that is critical for the Na$_x$CoO$_2$ · yD$_2$O is an $f$-wave superconductor [14] which would make this material the most exotic one discovered so far. Following the successful example of high-temperature superconductors, high-quality superconducting thin films of water-intercalated sodium cobaltate thus promise to enhance our knowledge about this complex material.

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