Single crystal growth and investigation of Na$_x$CoO$_2$ and Na$_x$CoO$_2$ yH$_2$O

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Abstract

A systematic study of Na$_x$CoO$_2$ ($x=0.50$ - 0.90) and Na$_x$CoO$_2$yH(D)$_2$O ($x=0.26$ - 0.42, $y=1.3$) has been performed to determine phase stability and the effect of hydration on the structural and superconducting properties of this system. We show that a careful control of the Na deintercalation process and hydration dynamics is possible in single crystals of this system. Furthermore, we give experimental evidence that the dependence of the superconducting transition temperature on Na content is much weaker than reported earlier. Implications of this effect for the understanding of the superconducting phase diagram are discussed.

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I. INTRODUCTION

The recently discovered superconductor \( \text{Na}_x\text{CoO}_2\text{yH}_2\text{O} \) has attracted considerable attention as being the first superconducting cobaltite and due to evidence for important electronic correlations. Its superconducting transition temperature of maximum \( T_c \approx 5 \) K exhibits a composition dependence, decreasing for both underdoped and overdoped materials, as observed in the cuprates. This suggests that a detailed characterization of the electronic and magnetic behavior of this new type of materials and their interplay with structural peculiarities may contribute to a more fundamental understanding of the high \( T_c \) superconductivity in cuprates, such as the layered crystal structure, magnetic susceptibility, electronic anisotropy, irreversibility lines and superconducting parameters \( \lambda_{ab}, H_{c2} \).

The physical properties are determined by the amount of sodium and water in \( \text{Na}_x\text{CoO}_2\text{yH}_2\text{O} \) via their influence on the Co valence state and the resulting local distortions of the \( \text{CoO}_6 \) octahedra present in the structure. The compound \( \text{Na}_x\text{CoO}_2 \) shows manifestations of frustration in its physical properties, because Co occupies a triangular lattice and the exchange interactions are antiferromagnetic. The close relationship between structural and electronic properties establishes itself also on the Fermi-Surface that is expected to show features of strong nesting. Furthermore, there exists evidence that superconductivity might have an unconventional order parameter. When water is introduced into the compound, it exhibits chemical and structural instabilities. The \( \text{Na}^+ \) ions are at least partially mobile at elevated temperatures and may order at low temperatures in dependence of composition and sample treatment. The same is proposed for the \( \text{Co}^{4+}/\text{Co}^{3+} \) charge state on the triangular lattice.

All of these features make the study of the physical and chemical properties of the compounds difficult. However, nearly all the studies reported so far have been made on either sintered specimens or poorly characterized polycrystalline samples. These materials are often found to be inhomogeneous, especially with respect to the distribution of \( \text{Na}^+ \) ions in the lattice and in the intergranular spaces, the \( \text{Na}_2\text{O} \) decomposition of the compound, and with respect to the intercalation of water. In polycrystalline samples water may in part accumulate in intergranular spaces. The possible presence of second phases leaves a degree of uncertainty when interpreting the structure and the electrical and superconducting properties as function of composition, i.e. establishing a superconducting phase diagram.
This problem may be circumvented by the use of high quality single crystals whose chemical composition and crystal structure can be properly determined.

When growing Na\textsubscript{x}CoO\textsubscript{2} single crystals, considerable difficulties appear on account of the high Na\textsubscript{2}O vapor pressure, which increases exponentially from 10\textsuperscript{-5} to 10\textsuperscript{-3} torr with heating to temperatures between 500 and 800 °C, followed by a noticeable evaporation. Therefore ceramic powders were synthesized using additional Na\textsubscript{2}CoO\textsubscript{3} for compensation of the Na loss during heating\textsuperscript{2,11} or a "rapid heat-up" technique\textsuperscript{12} to avoid the formation of a non-stoichiometric compound. Solution growth by using NaCl flux\textsuperscript{13} was performed that unfortunately lead only to thin crystals (<0.03 mm) or non-stoichiometric and possibly contaminated samples. To obtain the superconducting phase the crystal must be hydrated by chemical oxidation\textsuperscript{1}. The compound can be partially decomposed during the oxidation process, leading to highly defective crystals containing Na-poor phases.

In this contribution we present a single crystal growth method to prepare large and high quality single crystals and demonstrate their chemical, thermal, and structural behavior and electric properties under dry and humid conditions.

II. EXPERIMENTAL

Single crystals were grown in an optical floating zone furnace (Crystal System Incorporation, Japan) with 4 x 300 W halogen lamps installed as infrared radiation sources. Starting feed and seed materials were prepared from Na\textsubscript{2}CO\textsubscript{3} and Co\textsubscript{3}O\textsubscript{4} of 99.9% purity with the nominal composition of Na\textsubscript{x}CoO\textsubscript{2}, where \(x=0.50, 0.60, 0.70, 0.75, 0.80, 0.85\) and 0.90, respectively. Well-mixed powders were loaded into alumina crucibles and heated at 750 °C for a day. The heated powders were reground and calcined at 850 °C for another day. They were then shaped into cylindrical bars of \(\approx 6 \times 100\) mm by pressing at an isostatic pressure of \(\approx 70\) Mpa and then sintered at 850 °C for one day in flowing oxygen to form feed rods.

The sintered feed rod was premelted with a mirror scanning velocity of 27 mm/h by travelling the upper and lower shafts, respectively, to densify the feed rod. After premelting the \(\approx 20\) mm rod long was cut and used as a first seed and hereafter the grown crystal was used as a seed. The feed rod and the growing crystal were rotated at 15 rpm in opposite directions. In an attempt to reduce the volatilization of Na and obtain stoichiometric and large crystals, we applied travelling rates of 2 mm/h under pure oxygen flow of 200 ml/min
FIG. 1: DTA-TG analysis by melting single crystalline Na$_{0.7}$CoO$_2$ heated 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, (b) temperature dependence of the weight loss.

throughout the growing procedure.

To obtain superconductivity the Na was partly extracted by placing crystals in a 6.6 mol Br$_2$/CH$_3$CN solution during 100 hours and then washed out the solution by H$_2$O or D$_2$O. Alternatively, the electrochemical technique was also applied, using an aqueous solution of NaOH as an electrolyte to partially extract Na. This technique needs a longer time for deintercalation and the resulting superconducting transitions are generally sharper.

Thermogravimetric and differential thermal analysis (TG-DTA) was performed to study the melting behavior as well as the time and temperature dependence of the water loss in the compound. Single crystal XRD measurements were carried out with the X-ray diffractometer (Philips PW 1710) using Cu $K_{\alpha}$ radiation, a scanning rate of 0.02 degrees per minute, and $\theta$ - 2 $\theta$ scans from 5 to 90 degrees. The lattice parameters obtained from XRD data were refined using the commercial program PowderCell. The chemical composition was determined by energy dispersive X-ray (EDX) including microanalysis. The as-grown crystals were cleaved parallel to the $a$ axis and the composition of Na and Co was determined across the cleaved section.
III. RESULTS AND DISCUSSIONS

A. DTA-TG analysis

The melting behavior of a Na$_{0.7}$CoO$_2$ crystal was investigated by DTA-TG measurements and with a high temperature optical microscope. A small single crystal was loaded in a Pt crucible and then heated in the DTA-TG apparatus (NETZSCH STA-449C) at 7.5 °C/min up to 1200-1250 ºC in flowing oxygen. Two peaks with onset $T_1=1035$ ºC and $T_2=1092$ ºC on the DTA curve correlate very well with a weight loss observed by TG, as shown in Figs. 1(a) and (b), respectively. No weight changes were observed below 980 ºC.

The high temperature optical microscope study of the crystal reveals that the liquid phase appears at $T_1=1035$ ºC but the solid phase (crystal) still remains up to $T_2=1092$ ºC, exhibiting a coexistence of solid and liquid phases. Our investigations indicate that thermal decomposition of Na$_{0.7}$CoO$_2$ is accompanied by a weight loss down to 96.2 wt.% and the compound decomposes into a sodium-rich liquid and a cobalt-rich solid phase$^{15,16}$, assuming chemical reaction of the melt as follows, Na$_x$CoO$_2$ $\rightarrow$ CoO + Liquid (Na-rich) + xO$_2$ - (T $>$ 1100 ºC) $\rightarrow$ [Na$_x$CoO$_{1.65}$]* (*=homogeneous melt).

The dissolution of CoO occurs in the Na-rich melt and by taking up oxygen from the environment. Thus, it results in an increase of weight because the oxidation state of cobalt is significantly higher in the melt, i.e., Co$^{+2.7}$, according to the chemical reaction equation shown above. A sharp weight loss down to 95.5 wt.% occurs at $T_2=1092$ ºC and the melt starts to get homogeneous and stable. A nearly constant weight of 95.5 - 94.9 wt.% is obtained in the temperature range of 1120 - 1200 ºC, where the melt becomes homogeneous. A monotonic weight loss of melt may happen under constant heating. Evidently, the melting behavior described so far indicates that the compound melts incongruently.

B. Crystal growth, morphology and composition

When sintering Na$_x$CoO$_2$ at high temperatures the decomposition of Na$_2$O can cause a weight loss and lead to an inhomogeneous compound. During growth a white powder of Na$_2$O is observed to volatilize and deposit on the inner wall of the quartz tube. By weighing a total weight loss $\approx$6 wt.% is estimated. This value is in agreement with the data shown in Fig. 1(b), neglecting the tiny loss of oxygen caused by the change of cobalt valence state.
FIG. 2: A typical Na$_{0.7}$CoO$_2$ single crystal ingot obtained by optical floating zone technique.

The main loss of Na$_2$O is found during the premelting procedure, estimated to be ≈5 wt.%. This is probably caused by incompletely reacted Na$_2$O when the mixtures are calcined and sintered prior to premelting. An additional ≈1 wt.% loss is estimated after the crystal growth.

During growth, we observed that the molten zone is rather stable and Na$_x$CoO$_2$ single crystals with a sodium content of $x=0.70 - 0.90$ is easily formed. In contrast, it is hard to grow the compound with $x=0.50 - 0.60$. The analysis of EDX indicates that as-grown Na$_x$CoO$_2$ with $x<0.6$ consists of multi phases like, Na$_2$O, CoO$_2$ and Na-poor phases.

Large and high quality single crystals were obtained with a growth rate of ≈2 mm/h in flowing oxygen atmosphere. Figure 2 shows a typical crystal ingot of Na$_{0.7}$CoO$_2$. The 001 face is readily cleaved mechanically due to the layered structure of the compound. Figure 3(a) displays one half of the crystal platelets with the 001 face of several cm$^2$ area cleaved from an ingot with a sharp scalpel. Figure 3(b) shows the other half after water intercalation. Crystal grains are found to grow preferably along the $a$ crystallographic axis, parallel to the rod axis.

A convex growth interface is observed to be the boundary between the regions of smaller and larger diameter of the crystal ingot, as shown in Fig. 3. The smaller one is formed when the molten zone was at lower temperatures and the larger one is formed at higher temperatures. Therefore, the unequal diameter for an ingot indicates that temperature fluctuations occurred at the molten zone during growth. According to the temperature-composition relationship a fluctuation of heating temperature may result in a composition change of the molten zone, leading to an inhomogeneous compound. Figure 3(a) shows that many tiny crystal grains of CoO$_2$ gather at the boundary of the growth front. These grains can be removed after the deintercalation treatment, as shown in Figs. 3(b) and (c), respectively. It is important to maintain a stable molten zone by applying a constant...
FIG. 3: Two halves of an as-grown crystal ingot with the (001) surface. (a) the as-cleaved half Na$_{0.7}$CoO$_2$ showing the CoO$_2$ inclusions gathering at the growth boundary and (b) the other half Na$_{0.3}$CoO$_2$•H$_2$O showing the removal of the CoO$_2$ inclusions after deintercalation followed by hydration, (c) the enlarged CoO$_2$ inclusions.

heating temperature for growing a high quality single crystal.

Single crystal XRD powder diffraction of Na$_{0.7}$CoO$_2$ gives the following lattice parameters and cell volume of the space group P63/mmc: $a=2.8278(4)$ Å, $c=10.9073(0)$ Å, $v=75.54$ Å$^3$. Sintered powders show a slightly different XRD patterns with $a=2.8230(2)$ Å, $c=10.9628(8)$ Å.

For the determination of Na/Co compositions using EDX the crystal was scanned through a segment of 3 mm along the growth direction taking the average of four measured points in the central and edge region of the crystal. It is found that the Na content varied with the temperature fluctuations during growth. At the beginning of the growth the temperature fluctuations are high and cause a high variation of the composition, $\Delta x \approx 0.11$, determined within 2 cm from the seeding part of the ingot. Following the seeding part the variation of
Na content is smaller, $\Delta x \approx 0.06$, when the molten zone is maintained in a stable state by a constant temperature. A volatilized white $\text{Na}_2\text{O}$ powder accumulates on the inner wall of the quartz tube after the growth is completed. The loss of Na may result to a reduction of its concentration in the as grown crystal. The white $\text{Na}_2\text{O}$ powders also form on the surface of crystals if the samples are stored under ambient conditions. Therefore the grown crystals must be stored in an evacuated container or a desiccator to avoid decomposition.

C. Sodium extraction and water intercalation

The superconducting phase $\text{Na}_x\text{CoO}_2\cdot y\text{H}_2\text{O}$ ($0.26 \leq x \leq 0.42$, $y \approx 1.3$) is obtained by chemically extracting (deintercalation) sodium from $\text{Na}_x\text{CoO}_2$, followed by hydration. Single crystals of $\text{Na}_{0.7}\text{CoO}_2$ were placed in the oxidizing agent $\text{Br}_2/\text{CH}_3\text{CN}$ for around 100 hours, and then washed with acetonitrile. The change of sodium content of the resulting crystals is generally proportional to the bromine concentration in the $\text{CH}_3\text{CN}$ agent. A crystal of $\text{Na}_x\text{CoO}_2$ with $x=0.3$ can result from a 6.6 mol $\text{Br}_2/\text{CH}_3\text{CN}$ treatment only after a long extraction time of more than a week. The Na extraction of the compound was also carried out by the electrochemical method. The composition $\text{Na}_{0.3}\text{CoO}_2$ could be achieved in aqueous solution of NaOH using a constant current of 0.5 mA and a voltage of 1.0 V for over 10 days. Comparing the published 1 to 5 days extraction time for the $\text{Na}_{0.7}\text{CoO}_2$ powders\textsuperscript{1,3} the crystal needs longer time to complete the extraction, also depending on the dimension of the sample. The slower extraction reaction in single crystals compared to a powder is related to the higher perfection and longer period of Na-O-Na within the NaO layers. In powder samples variations of the bonding are expected on a nanometer scale. Before and after the extraction treatment the sodium composition distribution across the crystals was determined by EDX.

The superconducting phase is then obtained by immersing the deintercalated samples for a week in $\text{H}_2\text{O}/\text{D}_2\text{O}$, or sealing the samples in a water vapor saturated container at room temperature. After hydration/deuteration a large increase in thickness is visible to the naked eyes and the morphology exhibits "booklet"-like layered cracks perpendicular to the $c$ axis. The sodium intercalant layer expands with decreasing Na content, because the Na removal results in Co oxidation ($\text{Co}^{3+}$ ions oxidized to smaller $\text{Co}^{4+}$ ions) and thus the $\text{CoO}_2$ layers are expected to shrink.\textsuperscript{1,2} This suggests that a decreased bonding interaction
FIG. 4: Schematic drawing of the layered structures for (a) non-hydrated Na$_{0.61}$CoO$_2$ and (b) fully hydrated Na$_{0.33}$CoO$_2$.1.3H$_2$O.

between layers with decreasing Na content may result in a readily cleaving plane. Figures (a) and (b) illustrate the layered structures of the non- and fully hydrated phases of the compound, respectively. According to the layered structure of Na$_x$CoO$_2$, 24 Co-O bonds in the layer of CoO$_2$ form an octahedral CoO$_6$ with high bonding energy and therefore the layer is structurally robust, while the bonding energy is much weaker in the NaO layer because the Na$^+$ mobility is high and the number of bonds Na1-O is 6 and Na2-O only 4/3. Therefore the Na layer readily collapses to leave the CoO$_2$ layer terminated as the outer-most surface of the crystal. Moreover, the insertion of water induces two additional intercalated layers of H$_2$O between NaO and CoO$_2$, i.e., from Co-Na-Co to Co–H$_2$O–Na–H$_2$O–Na–Co, which results in the expansion of the c lattice constant from 11.2 to 19.6 Å. The hydrogen in the new intercalated H$_2$O layer bonds extremely weakly to the NaO and CoO layers. Therefore this compound is exceptionally unstable with respect to a change of thermal, mechanical or


FIG. 5: Three typical morphologies showing the layered structure of Na$_x$CoO$_2$ single crystal. (a) After cutting an as-grown Na$_{0.7}$CoO$_2$ single crystal, (b) the cracked layers perpendicular to the $c$ axis of the Na$_{0.3}$CoO$_2$ crystals after deintercalation, (c) the "booklet"-like structure of the Na$_{0.3}$CoO$_2$1.3H$_2$O after hydrated by H$_2$O.

humidity environment. Under ambient, oxidizing and humid conditions the crystal exhibits three typical morphologies, as shown in Figs. 5(a), (b) and (c), respectively.
FIG. 6: Single crystal X-ray diffraction patterns for Na$_{0.3}$CoO$_2y$H$_2$O measured by immersing the sample in D.I. water. The initial crystal contained the phases of $y=0.6$ and 0.

D. Behavior of the crystals upon hydration and dehydration

To study the phase formation and problems with rehydration we have performed detailed x-ray diffraction experiments as function of time. Single crystals of non-hydrated Na$_{0.3}$CoO$_2$ have been partially hydrated in humid air to form Na$_{0.3}$CoO$_20.6$H$_2$O under ambient conditions. These crystals were immersed in water with the $c$ surface exposed to air. Each measurement of the 002 reflections was carried out for a short time of $\approx3$ minutes to avoid that the x-ray emits off the sample surface due to the rapid expansion of crystal thickness during the hydrating process. We show in Fig. 6 that the increase of intensity of the 002 reflection (corresponding to $y=1.3$) is accompanied by a decrease of intensity of the other two 002 reflections (corresponding to $y=0.6$ and 0, respectively). This is indicative of the increase of the volume of hydrated phase $y=1.3$ while decreasing the non-hydrated and par-
tial hydrate phases, \( y = 0 \) and 0.6. After a one day hydration the sample becomes completely "wet". This is indicated by the 002 reflections for the \( y = 1.3 \) and 0.6 phases and the disappearance of the 002 corresponding to the non-hydrated phase \( y = 0 \). Note that the 002 reflection of the partial hydrate with \( y = 0.6 \) still exists until a further hydration up to 10 days. In the meantime the XRD pattern shows a continuously increasing volume fraction of \( y = 1.3 \) phase reaching approximately 100%. This suggests that the initial hydration process takes place with two-water molecules per unit cell (corresponding to \( y = 0.6 \)) inserted into the Na plane, and followed by a group of four (corresponding to \( y = 1.3 \)) located in vacancies of the extracted Na sites.

The hydrated volume of a crystal is a function of hydration time since the water diffuses gradually in the \( ab \) plane whereas the \( c \) face is robust and no diffusion path exists along the \( c \) axis. A fully hydrated phase \( y = 1.3 \), exhibiting superconductivity, is achieved after 10 days for a crystal of 2x2 mm\(^2\) in the \( a/b \) direction, concomitant with the disappearance of the partial hydrates of the other two 002 reflections, as shown in Fig. 6. This indicates that Na-vacant sites can be completely occupied by water molecules when a longer diffusion time is allowed for creating a water-saturated environment during the hydration process.

A thermogravimetric analysis can be used to monitor the loss of water and stability of the hydrated phases as function of temperature and time. Figure 7 shows the temperature dependence of water loss for an over hydrated sample (\( y = 1.8 \)) under a slow heating rate of 0.3 °C /min in flowing oxygen. The fastest loss of water occurs between 20 and 50 °C and is then again increasing upon further heating. The sample weight is characterized by several relatively broad plateaus in weight that are attributed to phases with \( y = 1.8, 0.9, 0.6, 0.3 \) and 0.1 for temperatures near 28, 50, 100, 200 and 300 °C, respectively. These data suggest the existence of the following majority phases at the respective temperatures: \( \text{Na}_{0.3}\text{CoO}_2\text{.}1.8\text{H}_2\text{O} \ (c=19.75 \text{ Å}), \text{Na}_{0.3}\text{CoO}_2\text{.}0.9\text{H}_2\text{O} \ (c=13.85 \text{ Å}), \text{Na}_{0.3}\text{CoO}_2\text{.}0.6\text{H}_2\text{O} \ (c=13.82 \text{ Å}) \) and \( \text{Na}_{0.3}\text{CoO}_2\text{.}0.3\text{H}_2\text{O} \ (c=12.49 \text{ Å}) \) and \( \text{Na}_{0.3}\text{CoO}_2\text{.}0.1\text{H}_2\text{O} \ (c=11.20 \text{ Å}) \). A change of \( \Delta y = 0.33 \) corresponds to the removal of one water molecule per unit cell. A complete removal of water (\( y = 0 \)) from the compound takes place at temperatures over 600 °C.

Analysis of DTA-TG confirms that the fully hydrated superconducting phase (\( y = 1.3 \)) is rather unstable between 20 and 50 °C due to the rapid loss of water. However, the superconducting phase can be reformed easily by rehydration. The inset of Fig. 7 shows the time dependence of the loss of water at room temperature. A rapid loss of water from \( y = 1.8 \)
FIG. 7: Thermogravimetric analysis of an over hydrated Na$_{0.3}$CoO$_2$1.8H$_2$O single crystal heated at 0.3 K/min in flowing oxygen. Inset: time dependence of the weight loss for the same specimen at room temperature in flowing oxygen. Initial mass of the sample was 112.965 mg. The loss was approximately 19 mg after heating and rehydrating.

to 0.6 occurs in one and a half hours and then no further weight loss is observed during one day. XRD reveals that the flat plateau corresponding to a semi hydrated Na$_{0.3}$CoO$_2$0.6H$_2$O with $y=0.6$ appears to be a metastable phase under ambient conditions. This observation is in conflict with that for polycrystalline powders$^2$.

The fact of the matter is that a single crystal is only one domain containing crystal-water while powder samples consist of countless tiny grains with additional intergrain water. Furthermore, the loss or absorption of water in a large single crystal is slower and more well-defined compared to powders due to the diffusion path along the Na-layer.
FIG. 8: The $00l$ reflections showing the mixture of cells and the lattice constants for the various hydrates of $\text{Na}_0.3\text{CoO}_2_y\text{H}_2\text{O}$ under different ambient conditions. (a) From humid to dry air for 2 days, (b) from humid to dry air for 5 days, (c) from dry to humid air for 5 days. Symbol A represents the phase of $y=0$ for $a=2.82$ Å and $c=11.195$ Å, C: $y=0.3$ for $a=2.82$ Å and $c=12.478$ Å, D: $y=0.6$ for $a=2.82$ Å and $c=13.815$ Å, B: $y=1.3$ for $a=2.82$ Å and $c=19.710$ Å.

E. Mixture of cells

As shown in the TGA data, a fully hydrated sample can release water under ambient conditions to form partial hydrates. On the other hand, moisture from air can also be absorbed by a non-hydrated sample to form hydrated phases. In order to quantitatively identify the hydrated phases in the crystal, the fully hydrated or non-hydrated samples were placed in a humid or dry atmosphere. They were then investigated by XRD and the results show a clear shift in the positions of the $00l$ reflections for both samples, yielding several variations in the $c$ axes of the unit cells, as shown in Figs. (a-c). The fully hydrated phase
FIG. 9: Time dependence of the out-of-plane resistivity $\rho_c$ of a Na$_{0.3}$CoO$_2$YH$_2$O single crystal during a hydration process. The number given as footnote at the plateaus is hydration time in hours.

of Na$_{0.3}$CoO$_2$1.3H$_2$O is exposed to dry air at ambient conditions for 2 and 5 days, resulting in the formation of four and three mixed phases, as shown in Figs. (a) and (b), respectively. Exposing a non-hydrated Na$_{0.3}$CoO$_2$ to humid air for 5 days results in two additional phases of Na$_{0.3}$CoO$_2$0.3H$_2$O and Na$_{0.3}$CoO$_2$0.6H$_2$O, as shown in Fig. (c). Note that the phase with $y=0.6$ is always observed in the crystals under ambient conditions. Nevertheless, to prevent a fully hydrated phase from losing water we suggest that the samples be stored in a saturated humid atmosphere. Non-hydrated samples can be stored in an evacuated container to prevent decomposition from absorbing water in air.

F. Electrical properties

We have performed transport experiments of the out-of-plane resistivity $\rho_c$ as function of time to further characterize the hydration dynamics. The initially non-hydrated single crystal Na$_{0.3}$CoO$_2$ was immersed in D.I. water throughout the whole experiment. In contrast to measurements of powder samples in humid air, this configuration reduces the influence of internal and external surfaces and allows a full and continuous hydration. Furthermore,
the out-of-plane resistivity $\rho_c$ measured in four-point geometry should be less affected by the intrinsic Na ion conductivity.

In Fig. 9 and its inset plateaus and steps of the resistivity are given with increasing hydration time followed by a continuous and then more gradual decrease. Noteworthy is the similar resistivity reached after 8 hours compared to the initial state. This implies that, although irreversible by nature, the hydration process has also reversible stages. During hydration the water molecules enter the compound to intercalate between the $\text{CoO}_2$ and Na layers. The $\text{CoO}_2$ layers are separated by a trilayer of $\text{H}_2\text{O}/\text{Na}/\text{H}_2\text{O}$. The dominant effect is to expand the $c$-axis lattice parameters, from about 11.2 Å without water (non-superconducting phase $\text{Na}_{0.3}\text{CoO}_2y\text{H}_2\text{O}$, $y=0$) to 12.5 Å (semi hydrated phase, $y=0.6$) and then to 19.5 Å when the system becomes superconducting ($y=1.3$) (see Fig. 6). This is related to an enlarged interlayer distance from 5.6 Å to 6.9 Å and then to 9.8 Å. The stepwise increase from $t_0$ to $t_5$ occurs at a constant chemical doping level and suggests that the increase of spacing between the $\text{CoO}_2$ layers leads to the resistivity increase. We propose that the rapid steps followed by plateaus map the dynamics of domains of hydration that are pinned at the random potential of the local defect landscape. The more gradually decrease of resistivity for $t>12$ hours must therefore be related to a more homogeneous state of the system.

There is an interesting correlation between the $\text{CoO}_2$ layer and the superconducting transition temperature, i.e., the Co-O distance decreases with increasing $T_c$. The layer thickness of $\text{CoO}_2$ changes from 1.93 Å for non-superconducting phase to 1.84 Å for superconducting phase. It is clear that the layer thickness of $\text{CoO}_2$ shrinks after reaching full hydration or doping to $y=1.3$ and a change in the oxidation state of Co occurs, because the oxidation state directly corresponds to the carrier density in the $\text{CoO}_2$ layers and some electron transfer off the cobalt. Recently, also a relation between the $c$ axis parameter and the superconducting transition temperature has been discussed. Nevertheless, the change of the room temperature resistivity during the hydration process is not only influenced by the expansion of spacing in the system but also by a redistribution of the charge in $\text{CoO}_2$ layer.
FIG. 10: 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: optimum $T_c \approx 4.9$ K with $x=0.42$ as ZFC and FC measurement.

G. Superconductivity

The superconducting properties of the fully hydrated single crystals were characterized by a.c. susceptibility using a SQUID magnetometer. Zero field cooling measurements with 10 Oe applied field are presented in Fig. 10. Superconducting transition temperatures $T_c=2.8 - 4.9$ K with $x\approx0.28 - 0.42$ are observed, respectively. Some of our samples showed strong diamagnetic a.c. signals and a superconducting volume fraction as high as 20%. The transition width for each sample is different, which is very likely caused by an inhomogeneous sodium concentration and partial hydration that affect the superconducting state of Na$_x$CoO$_2$1.3H$_2$O. The $T_c$ values vary with Na content, showing the highest $T_c$ at 4.9K with $x=0.42$ given in the inset of Fig. 10. As shown in the inset the onset of the superconducting transition is identical with the divergence of FC and ZFC data.

Figure 11 is the plot of $T_c$ as function of sodium concentration of Na$_x$CoO$_2$1.3H$_2$O. For samples with $x \leq 0.22$ and $x \geq 0.47$ there is no superconducting transition detectable. These
FIG. 11: Superconducting phase diagram as a function of Na content. The dashed line is a guide to the eye. The dashed bar marks the metal-insulator transition observed in non-hydrated Na$_{0.5}$CoO$_2$.

Data agree to some extent with a recent study that shows a constant $T_c$ for Na contents up to 0.37$^{10}$. However, they conflict with the superconducting "dome" of $T_c(x)$ demonstrated for powder samples$^3$. This latter dependence motivated the proposal of intrinsic critical concentrations $x_{cr1} \approx 1/4$ and $x_{cr2} \approx 1/3$ related to charge ordering instabilities of the Co$^{3+}$/Co$^{4+}$ $^{20}$. In the present single crystal study the upper limit is shifted to much higher concentrations, $x_{cr2} \approx 0.45$. This implies, that a charge ordering at $x_{cr2} \approx 1/3$ is not relevant to suppress $T_c$.

However, the superconducting phase extends now close to the phase line where non-hydrated Na$_{0.5}$CoO$_2$ shows a metal-insulator transition$^{10}$. This is evidence for an importance of electronic correlations at higher $x$ in the hydrated system. It is interesting to note that the Néel transition $T_N \approx 20$K is also only observed for higher Na concentrations $x > 0.75$ in non-hydrated crystals, and that this ordering temperature does not change appreciably with $x$. Bulk antiferromagnetic order has been proven using myon spin rotation and other thermodynamic experimental techniques$^6$. The exact nature of the ordering, however, is still needed to further investigate.

Evidence for superlattice formation and electronic instabilities either due to Na or Co$^{3+}$/Co$^{4+}$ charge ordering are recently accumulating for non-hydrated Na$_x$CoO$_2$ with
$x=0.5$, but also to some extend for other stoichiometries$^{21,22}$. Hydration contributes to the charge redistribution due to its effect on the CoO$_2$ layer thickness and the formation of Na(H$_2$O)$_4$ clusters that shield disorder of the partially occupied Na sites. The above mentioned instabilities should influence the superconducting state as they modulate the electronic density of states and change nesting properties of the Fermi surface$^{8,9}$. Further studies are needed to investigate a possible interrelation of Na content, hydration and structural details on well-characterized samples with highest $T_c$.

IV. CONCLUSION

Using TG-DTA we found that Na$_x$CoO$_2$ is an incongruently melting compound, and single crystals can be grown using the optical floating zone technique. Both non-hydrated and fully hydrated crystals are exceptionally sensitive under ambient conditions. Study of XRD and TG indicates that the semi-hydrated phase Na$_x$CoO$_2$0.6H$_2$O is more stable than the other compositions under ambient conditions. The XRD patterns show the presence of cells corresponding to the coexistence of several different hydrated phases in rehydrated samples. The superconducting transition temperature of Na$_x$CoO$_2$1.3H$_2$O is only weakly influenced by the Na content. Highest $T_c \approx 4.9$ K is found for $x \approx 0.42$, i.e. in the proximity of a metal-insulator transition observed in the non-hydrated phase with $x=0.5$. The hydrated compound is strongly unstable concerning its chemical, structural and electrical properties. We therefore propose to carefully reinvestigate the recently claimed evidence for unconventional superconductivity on single crystals.

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