Effect of Hydrostatic Pressure on the Superconductivity in $Na_xCoO_2\cdot yH_2O$

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Abstract

The effect of hydrostatic pressure on the superconducting transition temperature of $Na_{0.35}CoO_2\cdot yH_2O$ was investigated by ac susceptibility measurements up to 1.6 GPa. The pressure coefficient of T_c is negative and the dependence $T_c(p)$ is nonlinear over the pressure range investigated. The magnitude of the average $dlnT_c/dp \approx -0.07$ GPa⁻¹ is comparable to the pressure coefficient of electron-doped high- T_c copper oxide superconductors with a similar value of T_c . Our results provide support to the assumption of two-dimensional superconductivity in $Na_{0.35}CoO_2\cdot yH_2O$, which is similar to the cuprate systems, and suggest that intercalation of larger molecules may lead to an enhancement of T_c .

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The recent discovery of superconductivity in two-dimensional CoO₂ layers in the compound Na_{0.35}CoO₂·yH₂O has attracted attention because of its possible similarity to the high- T_c superconductivity in CuO_2 -planes of the cuprate systems but with a different spin state associated with Co.¹ The compound appears to be the first superconducting layered metal oxide involving 3d-transition metals other than copper. The de-intercalation of Na⁺ ions accompanied by an intercalation of water molecules results in a combined doping and c-axis expansion effect effectively reducing the interlayer coupling between the CoO₂ planes and enhancing the two-dimensional character of the structure. Magnetic susceptibility measurements have shown a diamagnetic drop below 5 K ascribed to the onset of superconductivity although the estimated volume fraction is only of the order of 10 \% of the value for perfect diamagnetism. The high-field dependence of the susceptibility resembles that of the high- T_c copper oxides, with little change of the onset but an appreciable broadening of the superconducting transition under increasing magnetic field. Because of these similarities and the fact that the removal of water suppresses the superconductivity it was suggested that the large separation of the CoO₂ layers and the reduced interaction between them is essential for stabilizing the superconducting state.¹

The major difference to the square CuO_2 planes of the cuprates is the triangular symmetry of the Co-lattice that may lead to possible frustration effects in the magnetic structure of the antiferromagnetically interacting cobalt spins. Theoretical treatments therefore employ the t-J model on a planar triangular lattice.^{2,3,4} Different magnetic and superconducting orders, e.g. d-wave superconductivity,² a time-reversal-symmetry-breaking $d_{x^2-y^2} + id_{xy}$ ground state,³ and spin triplet superconductivity⁴ have been proposed. To distinguish between different theoretical proposals and to facilitate our basic understanding of superconductivity in $\text{Na}_{0.35}\text{CoO}_2\cdot\text{yH}_2\text{O}$ far more experimental work needs to be conducted. In particular, the dependence of the superconducting state on the interlayer coupling is of interest. The CoO_2 interlayer coupling should be tuned reversibly by changing the distance between the planes (c-axis lattice parameter) without affecting the chemical composition, i.e. the content of sodium and water. This can be achieved by applying hydrostatic pressure. Because of the strong lattice anisotropy and the weak bonding between the layers (the water molecules are electrically neutral although polarized) it is expected that the compression of the c-axis increases the interlayer coupling and has a major effect on the superconductivity.

We have measured the superconducting T_c of $Na_{0.35}CoO_2 \cdot yH_2O$ powder by ac magnetic

susceptibility experiments in a hydrostatic pressure environment up to 1.6 GPa. The observed decrease in T_c of up to 10 % at 1.6 GPa indicates the importance of a reduced interlayer coupling for stabilizing the superconducting ground state in this compound.

The $Na_xCoO_2 \cdot yH_2O$ powder was synthesized as described in Ref. 1 and 5. The xray spectrum shows the reflections of the hexagonal space group P6₃/mmc with lattice parameters a=2.820 Å and c=19.593 Å. The structural parameters are in good agreement with the recently reported data. Magnetic susceptibility measurements indicate the onset of superconductivity at 4.7 K, the magnitude of the diamagnetic signal at 2 K in field and zero field cooling runs are comparable with data of Ref. 1. Before starting the high pressure experiment the sample was carefully checked with respect to chemical compatibility with the liquid pressure transmitting medium (a 1:1 mixture of 3M Fluorinert FC70/FC77). The pressure medium was mixed with the sample powder and the dc susceptibility of the mixture was measured using the SQUID magnetometer (Quantum Design). No change or degradation in the superconducting properties of the mixture as compared to the original powder was detected. For high-pressure ac susceptibility measurements a dual coil was mounted onto a plastic frame with a 1.3 mm diameter, 5 mm long concentric inner space accommodating the sample powder and a small piece of high purity (99.9999 %) lead for in situ pressure measurements. The superconducting transition of the lead induced a small diamagnetic signal in the pickup coil and the pressure was determined from the shift of the lead transition temperature.⁶ The coil was inserted into a Teflon container filled with the Fluorinert pressure medium and pressure was generated by a beryllium-copper piston cylinder clamp.⁷ The pressure cell was inserted into a ⁴He dewar that allowed the control of temperature between room temperature and 1.2 K. The temperature below 45 K was measured by a germanium resistor built into the pressure clamp close to the sample position. The inductance was measured with an LR 700 mutual inductance bridge (Linear Research) at a frequency of 19 Hz.

The inductance, I(T), measured at different pressures is shown in Fig. 1 (for clarity not all sets of acquired data are shown). The superconducting transition is well resolved and the onset of diamagnetism causes the decrease of the inductance signal below T_c . The vertical drop of I(T) close to 7 K in Fig. 1 indicates the diamagnetic signal from the superconducting transition of the lead manometer and it was used for pressure determination. With increasing pressure the superconducting transition of the $Na_{0.35}CoO_2 \cdot yH_2O$ powder shifts to lower

temperature and the transition becomes slightly sharper. It is remarkable that the shape and the overall drop of the susceptibility curves do not change appreciably with pressure which indicates that the sample is stable at the applied hydrostatic pressure. There is no sign of a possible chemical decomposition or loss of water during the experiments. After acquiring the highest pressure data the pressure was almost completely released (a residual pressure of 0.04 GPa was measured) and the susceptibility curve was found in good agreement with the ambient pressure data taken at the start of the experiments. These data are marked by filled squares in Fig. 1. This again shows that the sample is stable and the superconducting properties are reversible under hydrostatic pressure. The $T_c(p)$ as estimated from the onset of the diamagnetic signal (see inset of Fig. 1) is displayed in Fig. 2. For low pressure the change of T_c is relatively small. With increasing pressure the T_c decreases faster resulting in a non linear dependence $T_c(p)$ as shown in Fig. 2. The solid line is a fit of the data to a parabolic pressure dependence, $T_c(p) = 4.68 - 0.0047~p - 0.183~p^2$ (T_c in K and p in GPa). At the highest pressure of this experiment (1.53 GPa) the superconducting transition dropped to 4.2 K. Extrapolating the parabolic dependence to $T_c=0$ yields a critical pressure of $p_c \simeq 5$ GPa. The recovery of the T_c after pressure release is indicated by the filled square in Fig. 2 (in contrast to the open circles denoting data estimated within the increasing pressure cycle). It should be noted that in the present experiments the pressure medium was frozen at the superconducting transition temperature. This may result in deviations from pure hydrostatic conditions and small pressure gradients throughout the sample space could be expected. Any pressure medium, even He gas at elevated pressure, will solidify at these low temperatures. In order to check on possible pressure gradients we have evaluated the width of the diamagnetic drop of the ac susceptibility in passing the superconducting transition of the lead manometer. The cooling speed was electronically controlled as low as 0.01 K/min. The width of the lead transition (as measured between the 90 % and 10 % drop of the susceptibility) was even at the highest pressure still below 0.01 K and only slightly larger than the zero pressure value of 0.008 K. If the small difference is attributed to a pressure gradient across the volume of the lead sample the inhomogeneity is less than 0.005 GPa at the maximum pressure of 1.6 GPa. With the Na_{0.35}CoO₂·yH₂O samples linear dimension being about 10 times the size of the lead the possible pressure gradients are still small and should not affect the results significantly.

A negative pressure coefficient of T_c is frequently observed in low- as well as high- T_c

compounds. In low- T_c (i.e. BCS-like, phonon-mediated) superconductivity the negative pressure shift of T_c can be explained by a decrease of the electron-phonon coupling constant, λ . λ is proportional to the electronic density of states (DOS) and to the inverse of the average square of the phonon frequency. The application of pressure usually results in an increase of the phonon frequency (phonon "hardening" effect) and, in many instances, in a decrease of T_c , as was recently discussed, for example, in MgB₂.8 The high-T_c cuprate superconductors exhibit both, positive as well as negative pressure coefficients, depending on the compound and the doping state. For some hole-doped copper oxides a negative dT_c/dp was reported in the overdoped regime and partially attributed to a pressure-induced charge transfer but it was also shown that this charge transfer is not the only factor affecting the pressure shift of T_c (for an extensive discussion see Ref. 9). Na_{0.35}CoO₂·yH₂O is, however, an electron-doped system. This has to be taken into account if the present data are compared with the high- T_c cuprates. For electron-doped cuprates, e.g $\mathrm{Sm_{1.88}Ce_{0.12}CuO_{4-y}}$, the pressure coefficient of T_c was found to be negative for a large number of systems with different chemical composition and (electron) doping. 9,10 Thereby, a universal relation between the relative pressure coefficient, $d\ln T_c/dp$, and T_c was proposed.¹⁰ According to this relation the pressure coefficient for a sample with $T_c=4.7$ K should be of the order of -0.1 to -0.15 GPa⁻¹. The T_c -p relation shown in Fig. 2 is nonlinear, however, estimating the average pressure change of T_c yields a value of $d\ln T_c/dp=-0.07$ GPa⁻¹and calculating the slope of $T_c(p)$ at the high pressure end of the graph we get $d\ln T_c/dp=-0.1$ GPa⁻¹. These values are in fair agreement with the typical pressure coefficient of an electron-doped high- T_c superconductor with a similar ambient pressure T_c .

In the discussion of the pressure effects the lattice anisotropy has to be considered since even hydrostatic pressure may result in different compression ratios along the main crystallographic directions. In optimally doped YBCO, for example, the dT_c/dp varies in sign and magnitude for compression along a-, b-, and c-axis resulting in a very small overall pressure shift of T_c under hydrostatic pressure conditions. The lattice anisotropy in $Na_{0.35}CoO_2 \cdot yH_2O$ is significant due to the huge expansion of the c-axis after intercalation of water and the compression is expected to be anisotropic as well. High pressure x-ray investigations can distinguish the compression of a- and c-axis and are therefore highly desirable. For the current discussion we assume that the two-dimensionality and the expansion of the

c-axis by intercalation of water in Na_{0.35}CoO₂·yH₂O is the key to understand the superconductivity (this is at least assumed in all previous publications). 1,2,3,4 Then it is naturally to expect that a pressure induced decrease of the c-axis length results in a suppression of the superconducting state. However, the effects of in-plane compression are not clear and need to be investigated separately. Uniaxial pressure experiments using single crystals of Na_{0.35}CoO₂·yH₂O (not currently available) can help to separate the different contributions. A pressure induced charge transfer to the CoO₂-layers (as discussed for the cuprate superconductors) is unlikely as long as the intercalated water molecules remain neutral and the valence of the Na-ions is +1. The non-linear decrease of T_c observed in our investigation is equally unusual and interesting. It may suggest the possible existence of large dispersion in the energy spectrum of the compound near its Fermi surface.

In conclusion, we have investigated the dependence of the superconducting T_c of $Na_{0.35}CoO_2\cdot yH_2O$ upon hydrostatic pressure up to 1.6 GPa. The pressure coefficient is negative and $T_c(p)$ shows a strong nonlinearity. The sign and magnitude of the relative pressure coefficient are compatible with similar data of electron-doped cuprates. Our results indicate that the superconductivity in this compound may originate from the apparent two-dimensionality of the CoO_2 planes similar to the CuO_2 layers of the electron-doped copper oxides.

Acknowledgments

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- FIG. 1: ac susceptibility of Na_{0.35}CoO₂·yH₂O measured at different pressures. The data are normalized to the susceptibility value at 5 K. The superconducting transition temperature was estimated from the onset of the diamagnetic signal, as indicated by the arrow in the inset. The sequence of pressure application follows the values listed in the figure. The filled squares denote the data set acquired after pressure was released.
- FIG. 2: Pressure dependence of T_c of Na_{0.35}CoO_{2·y}H₂O. The open circles are data taken at increasing pressure, the filled square indicates T_c after the pressure was completely released. The numbers indicate the chronological order of the pressure changes.
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