

Unconventional superconductivity in $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$ and proximity to a magnetically ordered phase

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Muon spin relaxation (μSR) measurements on the new layered cobalt oxide superconductor $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ and its parent, non-superconducting compounds, have revealed unconventional nature of superconductivity through: (1) a small superfluid energy which implies a surprisingly high effective mass of the charge carriers, approximately 100 times the bare electron mass; (2) the superconducting transition temperature T_c scaling with the superfluid energy following the correlations found in high- T_c cuprate and some other two-dimensional superconductors; (3) an anisotropic pairing without broken time-reversal symmetry; and (4) the proximity of a magnetically ordered insulating phase at $\text{Na}_{0.5}\text{CoO}_2$ below $T_N = 53$ K.

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Muon spin relaxation (μSR) measurements have been very effective in demonstrating unconventional superconductivity in high- T_c cuprate (HTSC) and organic superconductors. The absolute value of the measured penetration-depth λ established correlations between n_s/m^* (superconducting carrier density / effective mass) and T_c [1-3] which, together with the pseudogap behavior, suggest a formation of paired charge carriers occurring possibly at a temperature significantly higher than the condensation temperature T_c [3,4]. The temperature dependence of λ indicated d-wave pairing symmetry and line nodes in the energy gap [5,6]. Zero-field μSR studies revealed and elucidated static magnetic order in parent/relevant compounds of HTSC [3].

To these superconductors based on strongly correlated electrons, the recent discovery of superconductivity in $\text{Na}_{0.35}\text{CoO}_2$ intercalated with 1.3 H_2O [7] has added a unique compound which has highly 2-dimensional (2-d) conducting planes of cobalt oxide in a triangular lattice structure with geometrical spin frustration. The original idea of resonating valence bonds was developed for this geometry [8], but no superconducting system in this geometry has been known before the new cobalt oxide compound. Although extensive studies have been started [9-15], detailed characteristics of this system are yet to be demonstrated by conclusive experimental data sets.

We performed muon spin relaxation (μSR) measurements at TRIUMF in superconducting $\text{Na}_{0.35}\text{CoO}_2$ intercalated with 1.3 D_2O per formula unit, as well as in anhydrous Na_xCoO_2 with the Na concentration $x = 0.35, 0.5,$ and 0.64 . The samples were prepared at Princeton as described in earlier reports [14,15], and pressed into disc-shaped pellets with diameters of 6 mm. Electron microscopy of the pressed pellet samples indicates

that the 2-d cobalt oxide planes of the hydrated samples are essentially aligned. The susceptibility (χ) measurements showed superconducting $T_c = 4.2$ K for the sample with D_2O . The superconducting sample and $\text{Na}_{0.35}\text{CoO}_2$, sensitive to air exposure, were transported to TRIUMF in sealed containers. Measurements were performed at $T \geq 25$ mK using a dilution cryostat.

We first describe Zero-field (ZF) μSR [16] studies of magnetic order in non-superconducting anhydrous Na_xCoO_2 . Recent resistivity and susceptibility studies by Foo et al. [15] showed that the $x = 0.64$ system can be characterized as the “Curie-Weiss” metal, $x = 0.35$ as a “paramagnetic” metal, while $x = 0.5$ exhibits a transition from a high-temperature metal to low-temperature insulator at $T = 53$ K. In Fig. 1(a), we show the ZF- μSR time spectra of these systems. In the $x = 0.5$ system, the spectra above $T = 53$ K show slow relaxation without oscillation, i.e., a line shape expected for systems with nuclear dipolar fields without static magnetic order of Co moments. Below $T = 53$ K, a clear oscillation sets in, together with a rather fast damping. Below $T = 20$ -25 K, we see two frequencies beating. Figure 1(b) shows the temperature dependence of these frequencies. The amplitude of the damping signal indicate that all the muons feel a strong static magnetic field below $T = 53$ K. The static magnetic order sets in at the onset of a metal-insulator transition, and the establishment of the second frequency takes place at $T = 20$ K, which roughly corresponds to the “kink” temperature in the resistivity shown in the inset. Although a conclusive picture requires neutron scattering studies, it seems that one of two interpenetrating Co spin networks acquires a long-range order below $T = 53$ K, followed by the other network establishing long-range order below 20 K. The spatial spin

correlation should be antiferromagnetic (AF), since susceptibility shows no divergence at $T = 53$ K [evidence against ferromagnetism], and the damping of the $T = 25$ mK data is significantly slower than that of the Bessel function expected for the incommensurate spin-density-wave (ISDW) states [17] [evidence against ISDW].

We also confirmed the absence of static magnetic order in anhydrous Na_xCoO_2 with $x = 0.35$ and 0.64 , down to $T = 25$ - 35 mK, as shown in Fig. 1(a). Static antiferromagnetic order was reported for $x = 0.75$ - 0.9 by earlier μSR studies [18]. Together, the present data establish a rather complicated evolution of the magnetic ground states from paramagnetic (PM) ($x = 0.35$) to AF (0.5) to PM (0.64) to AF (0.75) to ISDW (0.9), with increasing x . The ~ 2 MHz frequency in the $x = 0.5$ system is close to ~ 3 MHz in $x = 0.75$, suggesting that the ordered moment sizes in these systems are of comparable magnitudes. The existence of an insulating magnetic state in the vicinity of superconductivity resembles the case in the cuprates.

Intercalation of H_2O or D_2O into the Na_xCoO_2 yields superconducting systems in a rather narrow range of x [14]. ZF- μSR is a powerful tool to detect a static magnetic field due to the particular superconducting pairing states associated with Time-Reversal-Symmetry-Breaking (TRSB), as shown in the case of Sr_2RuO_4 [19]. We observed Gaussian damping of the muon asymmetry in ZF- μSR of $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$. This damping is due to nuclear dipolar fields, and the Gaussian shape comes from the initial decay of the Kubo-Toyabe function for nuclear dipolar broadening [16]. Since the recovery of this function was missing in our observable time range (up to $8 \mu\text{s}$), we fitted this damping with the simple Gaussian function $\exp(-\sigma^2 t^2/2)$. As shown in Fig. 2(a), the relaxation rate σ in ZF is independent of temperature between $T = 6$ K and $T = 25$ mK. The arrows with “TRSB” indicate the expected changes of σ for the TRSB fields having random directions and Gaussian distribution of width (RMS second moment) 1 G and 2 G, respectively, added quadratically to the nuclear dipolar fields. Our results rule out the existence of a TRSB field above the 1 G level. This is consistent with an earlier report [10], yet we extended the temperature range from 2 K to 25 mK. On a triangular lattice, d-wave pairing has coexisting real and imaginary parts, resulting in a TRSB field. The present data sets a rather severe constraint to the d-wave pairing cases.

μSR data in transverse external fields (TF) reflect field broadening due to the flux vortex lattice in type-II superconductors, from which one can derive the magnetic field penetration depth λ [3,5]. We performed TF- μSR measurements in superconducting samples intercalated with D_2O [Fig. 2 (a)(b)], with the external field TF = 200 G applied perpendicular to the aligned CoO planes. Figure 2(b) shows the muon spin relaxation rate, fitted to the Gaussian damping $\exp(-\sigma^2 t^2/2)$, with σ_n indicat-

ing the average relaxation rate in the normal state. If the observed change in TF=200 G were due to a mechanism sensitive to ZF- μSR , we would have observed a change of the ZF relaxation rate to the level indicated by the “TF” arrow in Fig. 2(a). Thus, we proceed our discussion by assuming that the increase of σ in TF in Fig. 2(b) is solely due to the in-plane penetration depth λ_{ab} . By quadratically subtracting σ_n from the observed relaxation rate σ_{exp} , we obtained the relaxation rate σ_{sc} due to superconductivity as shown in Fig. 3. In separate measurements (not shown), we found essentially no dependence of σ_{sc} on TF in the range between 100 G and 2 kG, which assures no involvement of 2-d pancake vortex formation [5].

In Fig. 3, we compared the temperature dependence of $\sigma_{sc}(T) \propto \lambda^{-2}$ of $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$ with various models, in a fit of 16 data points with $\sigma(T = 0)$ as a free parameter. The observed results clearly disagree with curves of the two-fluid model (normalized chi square NCS=3.51) and s-wave BCS weak-coupling model (NCS=1.75, Durbin-Watson value of a normalized residual error correlations DW=1.11). Comparison with the scaled μSR results from YBCO [5] yields NCS=1.39 and DW=1.59, showing a rather poor agreement yet in a statistically acceptable range. For a 5% confidence level, a model with NCS>1.666 or DW<1.1 or DW>2.9 should be rejected, $1.1 < \text{DW} < 1.37$ or $2.63 < \text{DW} < 2.9$ is inconclusive, while $1.37 < \text{DW} < 2.63$ is comfortably acceptable.

For the cobalt oxide superconductors, several authors proposed f-wave models [13,20], which have a particular matching with the symmetry of triangular lattice. In Fig. 3, we also show a theoretical curve for an f-wave pairing, obtained by using a tight-binding fit of the LDA band calculation [13] and by assuming a separable effective interaction supporting a simple f-wave order parameter. In the present system, there is a large Fermi surface around the Γ point as well as six small hole-pockets near the K points. The line in Fig. 3 represents a case where nodes of f-wave symmetry exist only on the large Fermi surface and not on the six hole-pockets, while the order parameter on each Fermi surface has the same maximum value. This f-wave model gives a good agreement with the observed data with NCS=1.19 and DW=2.34.

These results rule out a fully isotropic energy gap. Before concluding a particular pairing symmetry, however, one has to test various other models with/without the possible effect of impurities. In ref. [11] the authors discussed anisotropy of the energy gap based on TF- μSR data with a few temperature points below T_c . Our finding of an anisotropic energy gap is consistent with earlier reports of a power-law T-dependence of the NMR relaxation rate $1/T_1$ as well as with the T-independent Knight shift of NMR [9] and μSR [10] below T_c .

The penetration depth λ is related to the superconducting carrier density n_s divided by the effective mass m^* as $\sigma(T) \propto \lambda^{-2} \propto [4\pi n_s e^2 / m^* c^2] [1 / (1 + \xi/l)]$, where

ξ is the coherence length and l denotes the mean free path. At this moment, it is difficult to prove the clean limit situation $\xi \ll l$ for the cobalt oxide superconductor, due to the lack of high-quality superconducting single crystals necessary to estimate the in-plane values of ξ and l . In the following, we proceed the discussion of the superfluid energy scale n_s/m^* by assuming the clean-limit, in view of an excellent conductivity in anhydrous $\text{Na}_{0.31}\text{CoO}_2$ crystals [15] and high H_{c2} values in polycrystalline superconducting specimens [21].

Derivation of the absolute values of λ and n_s/m^* is subject to modeling of flux vortex lattice line shapes, observed functional forms of field distribution, and angular averaging in the polycrystal samples. Based on the results of μSR measurements on c-axis aligned YBCO [22] and numerical works [23], we have adopted the conversion factor for polycrystal to aligned samples $\sigma_{aligned} \sim 1.4\sigma_{poly}$ to account for the effect of applying the TF perpendicular to the conducting planes of highly 2-d superconductors. For σ to λ conversion $\lambda = A/\sqrt{\sigma}$, we have adopted a factor $A = 2,700 [\text{\AA}(\mu\text{s})^{1/2}]$ for the Gaussian width σ . With these conversion factors, the values of λ_{ab} of polycrystalline samples of underdoped YBCO with $T_c \sim 60$ K [1] agree well with the value obtained using a single crystal specimen with comparable T_c in a more accurate line-shape analysis [5]. The above factor A gives $\lambda = 7,200 \text{\AA}$ for the in-plane penetration depth of the cobalt oxide system at $T \rightarrow 0$.

For highly 2-d superconductors, it is also interesting to study correlations between T_c and the 2-d superfluid density n_{s2d}/m^* which can be obtained by multiplying $\sigma_{aligned}$ with the average distance c_{int} of conducting planes. Figure 4 shows such a comparison, including the cuprates [3,22], alkali-doped (Hf/Zr)NCl with/without intercalation of THF (tetrahydrofuran) [24], and organic 2-d superconductors based on (BEDT-TTF) salts [6]. All the data points are taken using single crystal or aligned samples with TF perpendicular to the conducting planes, while ‘‘cuprate’’ lines represent polycrystal results [1,3] after the factor 1.4 correction. We find that T_c of all these 2-d superconductors could have a common relationship to the 2-d superfluid density n_{s2d}/m^* , which can be converted into corresponding 2-dimensional Fermi energy as given in the lower horizontal axis.

Based on correlations between T_c and the superfluid density in the cuprates, Emery and Kivelson [4] proposed a picture in which T_c is determined by phase fluctuations in the argument essentially identical to the Kosterlitz-Thouless (KT) theory [25]. In KT transitions, T_c and the superfluid density at the transition temperature T_{KT} are related with a universal system-independent relationship, which is shown by the T_{KT} line in Fig. 4. In Fig. 4, most of the points lie at about a factor 2-3 away in the horizontal axis from the T_{KT} line, which implies that the superfluid density undergoes about a 2-3 times reduction from the $T = 0$ value to the value near T_c where phase

fluctuations may destroy 3-d superconductivity. In the cuprates, this reduction could be related to excitations of nodal quasi particles, or classical thermal fluctuations, or some elementary excitations. Further studies for the origin of the T-dependence of $\sigma(T)$ could provide a key to understanding the correlations shown in Fig. 4.

If we assume the charge carrier density to be equal to the Na concentration, we obtain the in-plane effective mass of the cobalt-oxide superconductor to be about 100 times the bare electron mass m_e . A similar estimate for m^* was given in ref. [11]. The heavy mass can be expected for strongly correlated carriers in a triangular lattice [12]. The high effective mass is consistent with the electronic specific heat $C/T \sim 12$ [mJ/mole K²] of the superconducting cobalt oxide [26] just above T_c . This value can be compared to ~ 2 [mJ/mole K²] of $\text{YBa}_2\text{Cu}_3\text{O}_7$ [27]. After normalizing the values to a unit sheet area of conducting planes, C/T for the cobalt oxide becomes about 25 times larger than that for YBCO. In the non-interacting 2-d Fermi gas, C/T is proportional to m^* but independent of carrier density. Thus, within this approximation, we expect m^* of cobalt oxide to be 25 times that of the cuprates.

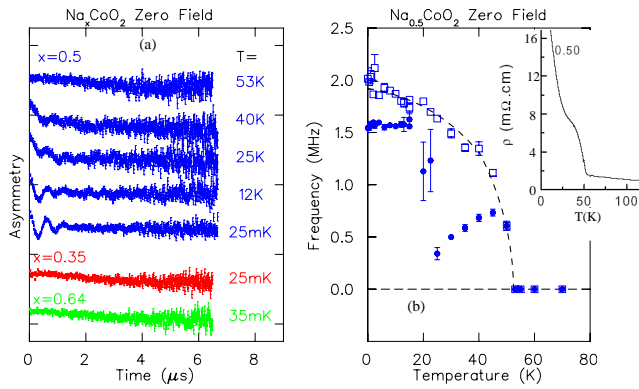
In conclusion, we have shown that the cobalt oxide superconductors have an anisotropic energy gap and a heavy effective mass $m^* \sim 100m_e$, without a TRSB field (limit given as 1 G). We established the existence of an antiferromagnetic insulating compound in the vicinity of the superconducting cobalt-oxide system without magnetic order, which suggests the possible involvement of magnetism in the superconducting mechanism.

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FIG. 1: (a) Muon spin relaxation time spectra observed in zero field in anhydrous Na_xCoO_2 with $x = 0.50, 0.35$ and 0.64 . (b) The muon spin precession frequency observed in the $x = 0.5$ system, shown with the resistivity in the inset [15].



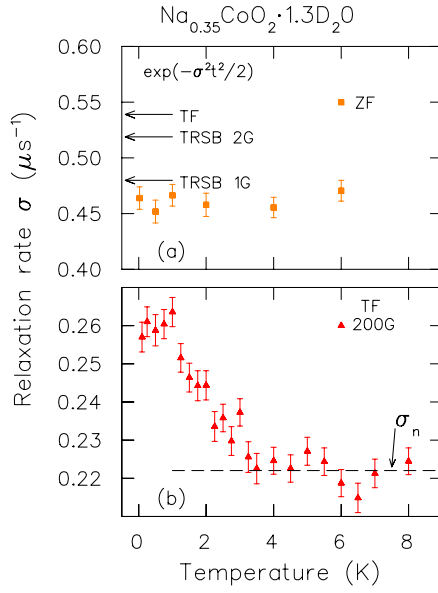


FIG. 2: Muon spin relaxation rate observed in a superconducting specimen of $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$, which has $T_c(\chi) = 4.2$ K from susceptibility χ . (a) shows results in zero field, while (b) in TF = 200 G applied perpendicular to the conducting planes. See text for the arrows in (a) and σ_n in (b).

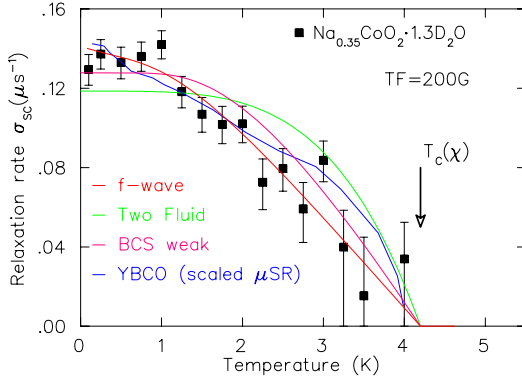


FIG. 3: Muon spin relaxation rate $\sigma_{sc}(T)$ due to superconductivity in $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$, with TF = 200 G applied perpendicular to the aligned conducting planes, obtained by quadratic subtraction of $\sigma_{sc}^2 = \sigma_{exp}^2 - \sigma_n^2$, where σ_{exp} and σ_n are shown in Fig. 2(b). The results are compared with fits to several models and the scaled plot of μSR results on $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ (YBCO) [5].

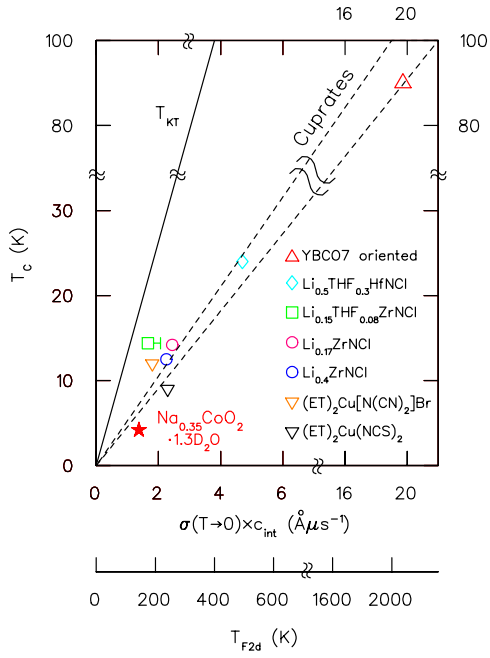


FIG. 4: A comparison of highly 2-d superconductors in a plot of T_c versus $\sigma_{sc}(T=0)$, multiplied by the average interlayer distance c_{int} of the conducting planes. Data points are from aligned pellet or single-crystal specimens [6,22,24], while the dotted lines are from ceramic specimens of YBCO [1-3] after a factor 1.4 correction. For $\sigma \times c_{int} \propto n_{s2d}/m^*$, we show the corresponding Fermi temperature T_{F2d} of the 2-d electron gas.