Muon Spin Relaxation Measurements of $Na_xCoO_2 \cdot yH_2O$

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Using the transverse field muon spin relaxation technique, we measure the temperature dependence of the magnetic field penetration depth λ, in the $Na_xCoO_2 \cdot yH_2O$ system. We find that λ, which is determined by the superfluid density n_s and the effective mass m^*, is very small and on the edge of the TF-μSR sensitivity. Nevertheless, the results indicate that this system obeys the Uemura relation. By comparing λ with the normal state electron density, we conclude that m^* of the superconductivity carrier is 70 times larger than the mass of bare electrons. Finally, the order parameter in this system cannot be described by a complete gap over the entire Fermi surface.

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The discovery of the new superconductor $Na_xCoO_2 \cdot yH_2O$ caused excitement in the unconventional superconductivity community. Of main interest are three questions: (i) Does this superconductor satisfy the Uemura relation? (ii) What is the gender of this material; is it a relative of cuprates, heavy fermions, metallic superconductors, or a class of its own? (iii) What is the symmetry of the order parameter and does it have nodes? Regarding the first question, one of the most universal correlations among the unconventional superconductors is the relation between the transition temperature T_c and the width of the transverse field muon spin rotation (TF-μSR) line at low temperatures, $\sigma(0) \propto \lambda^{-2}$, where λ is the magnetic field penetration depth λ. Uemura *et al.* [1] were able to show that the same relation holds for underdoped cuprates, bismuthates, Chevrel phase, and organic superconductors. This relation has no explanation in the framework of the BCS theory, and it is usually explained in terms of phase coherence establishment in a theory of local fluctuations of the order parameter [2]. It is interesting to know if $Na_xCoO_2 \cdot yH_2O$ also obeys this relation. The second question would be addressed by the absolute value of $\sigma(0)$. For the third question, several works have given contradictory answers. For example, ^{59}Co NMR or nuclear quadrupole resonance measurements by Kobayashi *et al.* [3] and Waki *et al.* [4] suggest the existence of a coherence peak indicating a complete gap over the Fermi surface. In contrast, Fujimoto *et al.* [5] and Ishida *et al.* [6] found no coherence peak, questioning the previous result. Therefore, an additional and different experimental approach is required. A possible approach is to measure the temperature dependence of λ. At low temperatures, λ is sensitive to low-lying excitations, and in the case of a complete gap $\lambda(T) - \lambda(0)$ should vary exponentially as a function of T. On the other hand, nodes in the gap lead to a power-law dependence of this penetration depth difference.

The aim of this work is to measure the temperature dependence of λ with TF-μSR in $Na_xCoO_2 \cdot yH_2O$. TF-μSR is a very useful way to study superconductors in the mixed state and has proven to be very useful in cuprates investigations. In this method, 100% spin polarized muons are implanted in the sample, which is cooled in a field perpendicular to initial muon spin. Above T_c, where the external field penetrates the sample uniformly, the second moment of the field distribution at the muon stopping site $\langle \Delta B^2 \rangle$ is relatively small and determined only by fields produced by nuclear moments. Consequently, the muon spins rotate in a coherent way and weak depolarization of the muon ensemble is observed. When the sample is cooled below T_c, a flux lattice (FLL) is formed in the sample resulting in an inhomogeneous field and, therefore, a larger second moment at the muon site. This increase in $\langle \Delta B^2 \rangle$ leads, in turn, to a high muon spin depolarization rate in the sample. The penetration depth is related to the field distribution width by

$$\langle \Delta B^2 \rangle = \left(\frac{0.00\,371 F \Phi_0^2}{\lambda_\perp^4} \right)^{1/2}, \tag{1}$$

where $\lambda_\perp$ is the in-plane penetration depth, Φ_0 is the flux quanta, and $F \sim 0.44$ for anisotropic compounds [7].

Because of the large beam spot (2×2 cm^2) in some of our measurements, and the need to minimize background signal from muons that miss the sample, we used polycrystalline. This type of sample is also expected to have better doping homogeneity compared to single crystals. The $Na_{0.7}CoO_2$ was prepared by solid state reaction [8] from mixtures of Co and Na_2CoO_3. This sample was intercalated as in Ref. [9] using a solution of Br_2 in CH_3CN, with Br_2 to Na molar ratio of 3. Then the material was washed in water and dried. The resulting compound was identified as $Na_{0.3}CoO_2 \cdot 1.3H_2O$ [10]. The transition temperature was measured using a home-built dc magnetometer. In Fig. 1 we show the field cooled magnetization measured in a field of 50 G. The T_c of the sample is about 3.5 K. In the inset, we show the magnetization vs the applied field in zero field cooling conditions, measured at 1.8 K. As can be seen in the figure, the lower critical field H_{c1} is about 30 G.

The μSR experiments were done on the MuSR spectrometer at the ISIS spallation source at the Rutherford-Appelton Lab in the United Kingdom, and in the general purpose spectrometer (GPS) instrument on the πM3 beam line at PSI Switzerland. At ISIS, we used the ^{3}He sorb cryostat which allows a base temperature of about 350 mK. The sample was cooled in a field of 400 G, which is above H_{c1}. At PSI, the base temperature available was 1.6 K, and we measured in field cooled conditions in fields of 400 G and 3 kG. It has been reported that $Na_{0.3}CoO_2 \cdot 1.3H_2O$ is a very unstable system. It decays into another hydrated phase which is nonsuperconducting. The system is sensitive to temperature and humidity. For that reason, we used a cell which allowed the sample to be cooled without losing the water content. The cell and the window were made of titanium, a material in which the muon polarization relaxes very slowly. Although this material is superconducting below 400 mK, its H_c is lower than our working field of 400 G. We tried to minimize as much as possible the exposure of the sample to dry and warm atmospheres. The sample was exposed to laboratory atmosphere for no more than a few minutes before it was sealed in the cell. The magnetization of the samples was measured to be the same before and after the ISIS experiment.

The nuclear moment of the Co and the protons leads to relatively large $\langle \Delta B^2 \rangle$ and causes the muon polarization to relax quite fast in $Na_xCoO_2 \cdot yH_2O$ even in the normal state. Combined with the fact that this compound might be an extreme type II SC with a very large penetration depth, we expect only a small contribution to the relaxation from the formation of the flux lattice. Usually, $\lambda \sim 10^4$ Å is considered as the limit of the TF-μSR technique. Here we expect values of that order, so very high statistics runs are needed. In addition, the use of the ISIS facility which is optimized for weak relaxation is an advantage. The MuSR spectrometer in ISIS consists of 32 counters arranged on two circles. For demonstration purposes, we combine all 32 counters using a rotating reference frame (RRF) transformation and binning, and depict in Figs. 2(a) and 2(b) the imaginary and real rotation signals, respectively, at both the highest and lowest temperatures. A small but clear difference is seen in the relaxation rate between these two temperatures especially after 4 μs.

However, for analysis purposes, in order not to degrade the data by the RRF transformation, we fitted the 32 raw histograms separately. The same holds for the GPS spectrometer which contains only three counters in TF mode. We did not group the counter histograms nor bin them in the fits. The fit function is Gaussian since in powder samples it describes the data sufficiently well. To account for muons that missed the sample, we used two Gaussian relaxation functions, one with very slow relaxation representing muons hitting the Ti cell. The overall function is given by

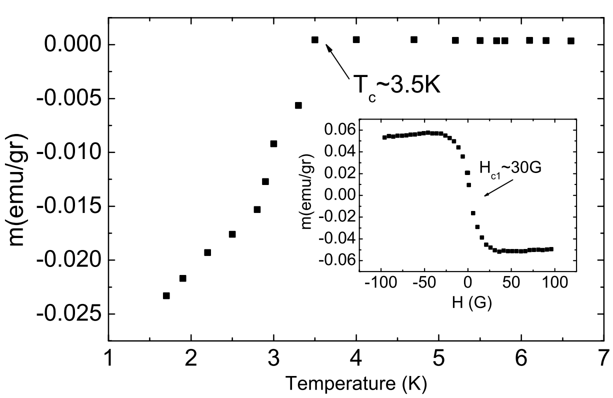

FIG. 1. Magnetization measurements of the $Na_xCoO_2 \cdot yH_2O$ vs temperature. The transition temperature is 3.5 K. Inset: M vs H for the same sample. $H_{c1} \sim 30$ G.

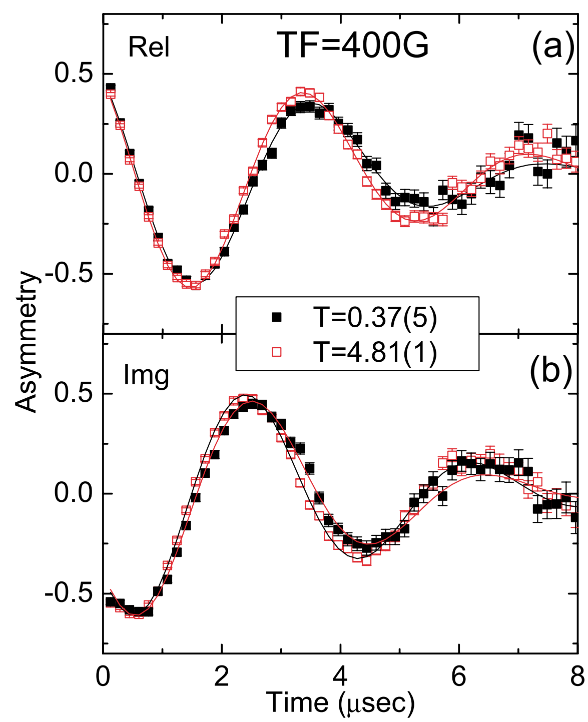

FIG. 2 (color online). Transverse field μSR data at two different temperatures taken at ISIS in 400 G. Both real and imaginary data are shown in a reference frame rotating at $\gamma_\mu \times 380$ G.

$$A(t) = A_0 \exp\left(-\frac{(\sigma t)^2}{2}\right)\cos(\gamma B t) + A_{\mathrm{cell}} \exp\left(-\frac{(\sigma_{\mathrm{cell}} t)^2}{2}\right)\cos(\gamma B_{\mathrm{cell}} t),$$

where A_0 and A_{cell} are the initial asymmetries, σ and σ_{cell} are the relaxation rates, and B and B_{cell} are the averaged fields in the sample and cell, respectively. The results of the fit for the PSI data indicate that around 7% of the muons missed the sample. In ISIS, the background signal is negligible due to the larger sample used. In the inset of Fig. 3, we show σ vs temperature for the data taken in PSI in 400 G and in 3 kG, and in ISIS at 400 G.

As can be seen, the change in relaxation in passing through T_c is quite small; between 4 and 2 K it is only about 5% of the normal state relaxation σ_n. As mentioned before, σ_n stems from nuclear moments and seems to be field independent. Below T_c, the relaxation is from a combination of nuclear moments and the flux lattice formed in the sample. When the origin of the relaxation is a convolution of two distributions, it results in a multiplication of two relaxation functions in the time domain. Since both the nuclear moments and the flux lattice in a powder sample generate Gaussian field distributions, we can obtain the FLL part by $\sigma_{\mathrm{FLL}} = \sqrt{\sigma^2 - \sigma_n^2}$. In Fig. 3, we show σ_{FLL} as a function of temperature below T_c. This figure includes all the data from PSI and ISIS. Measurements at two temperatures, below and above T_c, were conducted in both facilities to check consistency, and indeed they agree with each other. Unfortunately, due to experimental problems we do not have at present data between 0.37 and 1.6 K. However, this has no impact on our conclusions. As one can see, there is no field dependence, as expected for a compound with $H_{c2} \sim 61$ T [11]. The penetration depth λ at base temperature is calculated from Eq. (1) and $\sigma_{\mathrm{FLL}} = \gamma_\mu \sqrt{\langle \Delta B^2 \rangle}$, where $\gamma_\mu = 85.16$ MHz/kG is the gyromagnetic constant of the muon. This calculation gives $\lambda = 9100(500)$ Å at $T = 0.37$ K, which is very large, and on the order of what is considered as the limit of TF-μSR. Indeed, the error bars on $\sigma_{\mathrm{FLL}}(T)$ are quite big and there is scatter in the data.

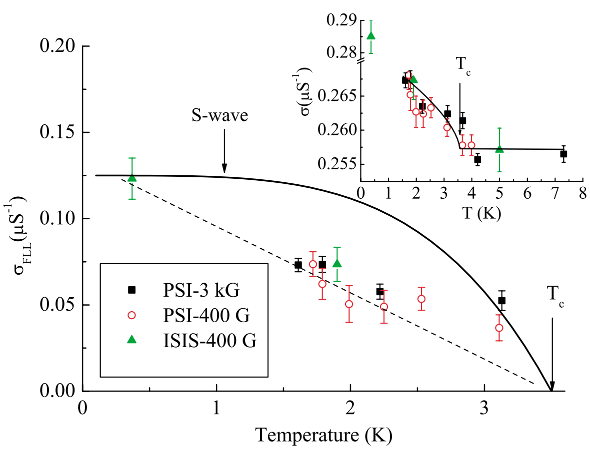

FIG. 3 (color online). The part of the muon relaxation associated with the flux lattice formation σ_{FLL} as a function of temperature. The solid line is the temperature dependence predicted by the two-fluid model and an S-wave gap. The dashed line is a guide to the eye. Inset: The total muon relaxation rate, as taken in ISIS and PSI in a field of 400 G and 3 kG.

Nevertheless, it is possible to compare the superfluid density of the $Na_{0.3}CoO_2 \cdot 1.3H_2O$ system with that of other unconventional SC and see if it agrees with the Uemura relation. In Fig. 4, we depict the original Uemura line using data only from the high temperature superconductors $YBa_2Cu_3O_y$ (YBCO) [1], $La_{1-x}Sr_xCuO_4$ (LSCO) [1], and $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$ [CLBLCO(x)] [12]. Underdoped and overdoped samples are presented with solid and open symbols. The $\sigma_{\mathrm{FLL}} = 0.125(10)$ at $T = 0.37$ K and $T_c = 3.5$ K fall exactly on this line. For comparison, we added the data for Nb, which is a BCS type II SC with $T_c = 9.26$ K.

Next, we discuss the gender of $Na_{0.3}CoO_2 \cdot 1.3H_2O$. Assuming 0.3 free electrons per Co [13], we get for our system a free electron density of about $3.8 \times 10^{21}/\mathrm{cm}^3$, which is comparable with the value for optimally doped YBCO. The free electron density of Nb, for example, is $5.56 \times 10^{22}/\mathrm{cm}^3$, about an order of magnitude higher than in $Na_{0.3}CoO_2 \cdot 1.3H_2O$. Using the London equation,

$$1/\lambda^2 = 4\pi n_s e^2 / m^* c^2, \qquad (2)$$

where n_s is the superconducting carrier density and m^* is the effective mass of these carriers, we can calculate the superfluid density. The separation of n_s/m^* is impossible using μSR alone and it is very hard in general. We can get useful insight from the comparison with Nb. Assuming that roughly all the normal state carriers contribute to the

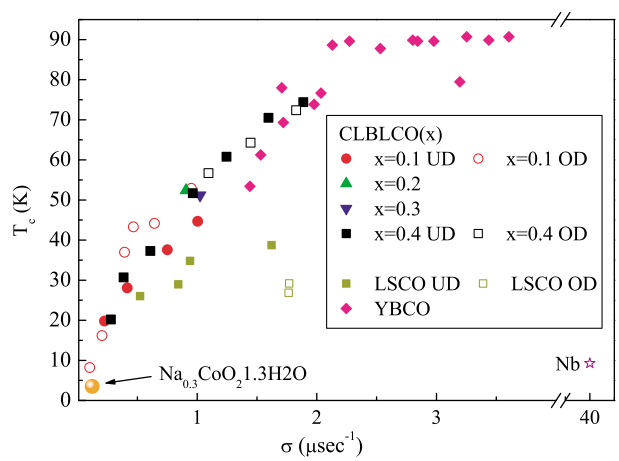

FIG. 4 (color online). The Uemura plot showing T_c vs the muon relaxation rate σ at the lowest temperature for LSCO, YBCO, and CLBLCO(x) cuprates, and for Nb. The results from $Na_xCoO_2 \cdot yH_2O$ fall on the line defined by the cuprates.

superconductivity, so that at $T \rightarrow 0$ the superfluid density equals the free electron density, we can extract the effective mass of the carrier from λ. In the case of Nb, we get an effective mass $m^* \sim 3m_e$; on the other hand, for $Na_{0.3}CoO_2 \cdot 1.3H_2O$ we get $m^* \sim 75m_e$. Despite this crude estimation, the mass is huge and comparable to the effective masses of the heavy fermion superconductors. It is much larger than the mass that the same calculation will yield for YBCO ($m^* \sim 2m_e$), for example. In fact, thermopower [10] and specific-heat measurements [14,15] point to the narrow band character of the $Na_xCoO_2 \cdot yH_2O$ system which results in an enhancement of the electron mass.

Finally, it is clear from Fig. 3 that the temperature dependence of σ_{FLL} is inconsistent with the phenomenological "two-fluid" model prediction: $\sigma(T) \propto 1-(T/T_c)^4$ [16]. The fact that σ_{FLL} does not saturate even at low temperatures indicates that the gap is incomplete. Higemoto *et al.* [17] reached a similar conclusion based on muon Knight shift results.

In summary, we performed TF-μSR experiments on a sample of $Na_{0.3}CoO_2 \cdot 1.3H_2O$. The temperature dependence of the penetration depth λ indicates that superconductivity in this system is unconventional and that the order parameter has nodes. The value of the relaxation rate at low temperature agrees with the well-known prediction of the Uemura line. Comparing the normal state carrier density with the superfluid density reveals an unusually heavy superconductive carrier.

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[1] Y. J. Uemura *et al.* Phys. Rev. Lett. **66**, 2665 (1991).
[2] V. J. Emery and S. A. Kivelson, Nature (London) **374**, 434 (1995).
[3] Y. Kobayashi, M. Yokoi, and M. Sato, cond-mat/0306264.
[4] T. Waki *et al.*, cond-mat/0306036.
[5] T. Fujimoto *et al.*, Phys. Rev. Lett. **92**, 047004 (2004).
[6] K. Ishida *et al.*, cond-mat/0308506.
[7] E. H. Brandt, Phys. Rev. B **37**, 2349 (1988).
[8] T. Kawata, Y. Iguchi, K. Takahata, and I. Terasaki, Phys. Rev. B **60**, 10 584 (1999).
[9] K. Takada *et al.*, Nature (London) **422**, 53 (2003).
[10] B. Fisher *et al.*, J. Phys. Condens. Matter **15**, L571 (2003).
[11] H. Sakurai *et al.*, Phys. Rev. B **68**, 132507 (2003).
[12] A. Keren, A. Kanigel, J. S. Lord, and A. Amato, Solid State Commun. **126**, 39 (2003).
[13] R. E. Schaak *et al.*, Nature (London) **424**, 527 (2003).
[14] H. D. Yang *et al.*, cond-mat/0308031.
[15] B. G. Ueland *et al.*, cond-mat/0307106.
[16] M. Tinkham, *Introduction to Supeconductivity* (McGraw-Hill, New York, 1996).
[17] W. Higemoto *et al.*, cond-mat/0310324.