Muon Spin Relaxation Measurements in Na$_2$CoO$_2$ · yH$_2$O

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Using the transverse field muon spin relaxation technique we measure the temperature dependence of the magnetic field penetration depth $\lambda$ in the Na$_2$CoO$_2$ · yH$_2$O system. We find that $\lambda$, which is determined by superfluid density $n_s$ and the effective mass $m^*$, is very small and on the edge of the TF-$\mu$SR sensitivity. Nevertheless, the results indicate that the order parameter in this system has nodes and that it obeys the Uemura relation. By comparing $\lambda$ with the normal state electron density we conclude that $m^*$ of the superconductivity carrier is 70 times larger than the mass of bare electrons.

The discovery of the new superconductor Na$_2$CoO$_2$ · yH$_2$O caused excitement in the unconventional superconductivity community. Of main interest are three questions: (I) what is the symmetry of order parameter and does it have nodes? (II) what is the gender of this material; is it a relative of the cuprates, the heavy fermions, metallic superconductors, or a class in its own? and (III) does this superconductor satisfy the Uemura relation? Regarding the first question, several works have given contradictory answers. For example $^{59}$Co NMR/NQR measurements by Kobayashi et. al. [1] and Wakiby et. al. [2] suggest the existence of a coherence peak indicating a complete gap over the Fermi surface. In contrast, Fujimoto et. al. [3] and Ishida et. al. [4] 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 the magnetic field penetration depth $\lambda$. At low temperatures, $\lambda$ 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. A study of $\lambda$ can help addressing the other two questions as well. For the third 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-$\mu$SR) line at low temperatures, $\sigma(0) \propto \lambda^{-2}$. Uemura et. al. [5] were able to show that the same relation holds for the underdoped cuprates, the bismuthates, Chevrel-phase and the organic superconductors. This relation has no explanation in the frame-work 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 [6]. It is interesting to know if Na$_2$CoO$_2$ · yH$_2$O also obeys this relation. The second question would be addressed by the absolute value of $\sigma(0)$.

The aim of this work is to measure the temperature dependence of $\lambda$ with TF-$\mu$SR in Na$_2$CoO$_2$ · yH$_2$O. TF-$\mu$SR is a very useful way to study superconductors in the mixed state. 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 a 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

$$\langle \Delta B^2 \rangle = \left( \frac{0.00371 F \Phi_0^2}{\lambda_\perp^4} \right)^{1/2}$$ (1)

where $\lambda_\perp$ is the in-plane penetration depth, $\Phi_0$ is the flux quanta, and $F \sim 0.44$ for anisotropic compounds [7].

Polycrystalline samples of Na$_{0.7}$CoO$_2$ were prepared by solid state reaction [8] from mixtures of Co and Na$_2$CoO$_3$. These samples were intercalated as in Ref. [9] using a solution of Br$_2$ in CH$_3$CN, 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$_2$ · 1.3H$_2$O [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 Gauss. The $T_c$ of the sample is about 3.5K. In the inset we show the magnetization vs. the applied field in zero field cooling conditions, measured at 1.8K. As can be seen in the figure the lower critical field $H_{c1}$ is about 35 G.

The sample was exposed to lab atmosphere for no more than a few minutes before it was sealed in the cell. The exposure of the sample to dry and warm atmospheres 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, $\lambda \sim 10^4 A$ is considered as the limit of the TF-$\mu$SR 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 consist of 32 counters arranged on two circles. For demonstration purpose we combine all 32 counters using a RRF transformation and binning, and depict in Fig 2(a) and (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 $\mu$sec.

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 3 counters in TF mode. We did not group the counter histograms nor bin them in the fits. The fit function is Gaussian since in a powder samples it describes the data sufficiently well. Also this Gaussian is not sensitive to core radius and to the symmetry of the flux lattice. To account for muon that missed the sample we used two Gaussian relaxation functions one with very slow relaxation representing muons hitting the Ti cell. The over all function is given by: $A(t) = A_0 \exp \left(-\frac{\omega t}{2}\right) \cos(\gamma B t) + A_{cell} \exp \left(-\frac{(\sigma_{cell}t)^2}{2}\right) \cos(\gamma B_{cell} t)$.

where $A_0$ and $A_{cell}$ are the initial asymmetries, $\sigma$ and $\sigma_{cell}$ 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 indicates 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 $\sigma$ 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 K and 2 K it is only about 5% of the normal state relaxation $\sigma_n$. As mentioned before, $\sigma_n$ 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: $\sigma_{FLL} = \sqrt{\sigma^2 - \sigma_n^2}$. In Fig 3 we show $\sigma_{FLL}$ as function of temperature below $T_c$. This figure includes all the data from PSI and ISIS, and the point at $T = 0.37 K$. Unfortunately, due to experimental problems we do not have at present data between 0.37 K and 1.6 K. As one can see there is no field dependence, as expected for a compound with $H_a \sim 61 T$ [12]. The penetration depth $\lambda$ at base temperature is calculated from Eq. 1 and $\sigma_{FLL} = \gamma \mu \sqrt{\langle B^2 \rangle}$ where $\gamma \mu = 85.16 M H z/kG$ is the gyromagnetic constant of the muon. This calculation gives $\lambda = 9100(500) \AA$ at
\( T = 0.37 \text{ K} \), which is very large, and on the order of what is considered as the limit of TF-\( \mu \)SR. Indeed, the error bars on \( \sigma_{FLL}(T) \) are quite big and there is scatter in the data. Nevertheless it is clear from Fig. 3 that the temperature dependence of \( \sigma_{FLL} \) is inconsistent with the phenomenological “two-fluid” model prediction: \( \sigma(T) \propto 1 - (T/T_c)^4 \) [14]. The fact that \( \sigma_{FLL} \) does not saturate even at low temperatures indicates that there are nodes in the gap. Higemoto et. al. [11] reached a similar conclusion based on muon Knight shift results which indicated a non-complete gap.

Next, we would like 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) [5], La_{1-x}Sr_xCuO_4 (LSCO) [5], and (Ca_{0.6}La_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y [CLBLCO(x)] [15]. Underdoped and overdoped samples are presented with solid and open symbols. The \( \sigma_{FLL} = 0.125(10) \) at \( T = 0.37 \text{ K} \) and \( T_c = 3.5 \text{ K} \) fall exactly on this line. For comparison we added the data for Nb, which is a BCS type II SC with \( T_c = 9.26 \text{ K} \).

Finally we discuss the gender of Na_{0.3}CoO_2 \cdot 1.3H_2O. Assuming 0.3 free electrons per Co [16], we get for our system a free electron density of about \( 3.8 \times 10^{21} / \text{cm}^3 \), which is comparable with the value for optimally doped YBCO. The free electron density of Nb, for example, is \( 5.56 \times 10^{22} / \text{cm}^3 \), about an order of magnitude higher than in Na_{0.3}CoO_2 \cdot 1.3H_2O. Using the London equation

\[
\frac{1}{\lambda^2} = 4\pi n_s e^2 / m^* c^2
\]

where \( n_s \) is the superconducting carriers density and \( m^* \) is the effective mass of this carriers we can calculate the superfluid density. The separation of \( n_s / m^* \) is impossible using \( \mu \)SR alone and it is very hard in general. But we can get useful insight from the comparison with Nb. Assuming that roughly all the normal state carriers contribute to the 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 \( \lambda \). In the case of Nb we get an effective mass \( m^* \sim 3 m_e \), on the other hand for Na_{0.3}CoO_2 \cdot 1.3H_2O we get \( m^* \sim 75 m_e \). 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 (\( m^* \sim 2 m_e \)), for example. In fact, thermopower [10] and specific-heat measurements [17,18] point to the narrow band character of the Na_{0.3}CoO_2 \cdot 1.3H_2O system which results in an enhancement of the electron mass.
FIG. 4. The Uemura plot showing $T_c$ vs. the muon relaxation rate $\sigma$ at the lowest temperature for LSCO, YBCO, and CLBLCO(x) cuprates, and for Nb. The results from Na$_{x}$CoO$_{2}$·$y$H$_{2}$O fall on the line defined by the cuprates.

In summary, we performed TF-\(\mu\)SR experiments on a sample of Na$_{0.3}$CoO$_{2}$·1.3H$_{2}$O. The temperature dependence of the penetration depth $\lambda$ 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 super-fluid density reveals an unusually heavy superconductive carrier.

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