Superconductivity and Field-Induced Magnetism in Pr$_{2-x}$Ce$_x$CuO$_4$ Single Crystals

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We report muon-spin rotation/relaxation ($\mu$SR) measurements on single crystals of the electron-doped high-$T_c$ superconductor Pr$_{2-x}$Ce$_x$CuO$_4$. In zero external magnetic field, superconductivity is found to coexist with Cu spins that are static on the $\mu$SR time scale. In an applied field, we observe a $\mu^+$-Knight shift that is primarily due to the magnetic moment induced on the Pr ions. Below the superconducting transition temperature $T_c$, an additional source of static magnetic order appears throughout the sample. This finding is consistent with antiferromagnetic (AFM) ordering of the Cu spins in the presence of vortices. We also find that the temperature dependence of the in-plane magnetic penetration depth $\lambda_{ab}$ in the vortex state resembles that of the hole-doped cuprates at temperatures above $\sim 0.2\ T_c$.

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While there now exists a large body of convincing experimental work on high-$T_c$ superconductors with hole-type carriers, the intrinsic properties of the electron-doped cuprates Pr$_{2-x}$Ce$_x$CuO$_4$ ($R \equiv$ La, Pr, Nd, Sm or Eu) have remained very elusive. Part of the problem stems from the difficulty of preparing single phase superconducting samples. An additional complication is the presence of both Cu and rare-earth ($R$) moments. The interplay between these two magnetic sublattices has been studied extensively in the undoped parent compounds R$_2$CuO$_4$. In Ce-doped samples, there is the possibility that the magnetic exchange interactions involving the CuO$_2$ planes play an important role in superconductivity. There is also some uncertainty about the symmetry of the superconducting order parameter. Although, recent phase sensitive and angle-resolved photoemission experiments are consistent with $d$-wave pairing symmetry, measurements of thermodynamic quantities such as the in-plane magnetic penetration depth $\lambda_{ab}$ generally do not show the expected linear temperature dependence at $T < T_c$ that is characteristic of a “clean” superconductor. Many of the early results for $\lambda_{ab}(T)$ in electron-doped cuprates were obtained in the Meissner phase of Nd$_{2-x}$Ce$_x$CuO$_4$ (NCCO) thin films and single crystals. While these results favored $s$-wave symmetry, it has since been recognized that the paramagnetism of the Nd ions strongly affects the low-$T$ behavior of $\lambda_{ab}(T)$ and $\lambda_{ab}(T)$. Consequently, attention has shifted primarily to the Pr$_{2-x}$Ce$_x$CuO$_4$ (PCCO) system, where crystal electric field (CEF) splitting of the Pr$^{3+}$ $J=4$ manifold results in a nonmagnetic singlet ground state. Unfortunately, more recent measurements of $\lambda_{ab}(T)$ in PCCO thin films and crystals using a variety of techniques have not yielded consistent results.

To avoid extrinsic effects related to the sample surface, we have utilized the $\mu$SR technique. $\mu$SR is a local probe of the bulk and is one of the few techniques that can measure $\lambda_{ab}(T)$ in the vortex state — sensitive to the supercurrents circulating around the vortex cores, rather than the screening currents which flow near the sample surface. Attempts to accurately measure $\lambda_{ab}(T)$ in NCCO by $\mu$SR have been precluded by the considerable Nd-moment contribution to the muon-spin depolarization rate. In this Letter, we report on the first $\mu$SR study of superconducting PCCO single crystals.

We studied three single crystals of PCCO grown by a directional solidification technique in Al$_2$O$_3$ crucibles using a CuO-based flux. Reduction of oxygen to induce superconductivity was achieved by encapsulating each single crystal in polycrystalline PCCO in the presence of flowing Ar at 900-1000 °C (Ref. 17). Here we report on representative data from one of the single crystals, noting that qualitatively similar results were obtained in a partial $\mu$SR study of the other two. The crystal was 0.07 mm thick, having an $a\cdot b$ plane surface area of $\sim 6.5$ mm$^2$ and a mass of 3.74 mg. Although resistivity measurements indicate a $T_c$ value of 25(1) K, bulk susceptibility measurements show that the diamagnetic signal assumes a constant value below $\sim 16$ K (see Fig. 1 inset).

The measurements were carried out on the M15 and M20B positive muon ($\mu^+$) beam lines at TRIUMF, Canada. In a $\mu$SR experiment the spin of the implanted $\mu^+$ precesses at a frequency $\omega_0 = \gamma_\mu B_\mu$, where $B_\mu$ is the local field at the $\mu^+$ site and $\gamma_\mu = 13.5534$ kHz G$^{-1}$ is the muon gyromagnetic ratio. The PCCO single crystals are the smallest samples studied to date by conventional $\mu$SR. Consequently, a special arrangement of scintilla-
the sample edges prevents flux from entering the bulk at shown in the inset of Fig. 2. In the ZFC case, pinning at
ried out under both field-cooled (FC) and zero-field
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Additional measurements carried out in a
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planes.

In ZF, the muon-spin polarization \( P(t) \) is relaxed by magnetic moments of electronic and nuclear origin. As shown in Fig. 1, the relaxation rate of the ZF-\( \mu \)SR signal in PCCO increases with decreasing \( T \). The absence of discrete frequency oscillations indicates that there is no onset of spontaneous magnetic order at temperatures above 2.3 K. Additional measurements carried out in a longitudinal-field geometry indicate that the muon spin is depolarized by randomly oriented internal fields which are static on the \( \mu \)SR time scale. Since the Pr ions have a nonmagnetic singlet ground state and the nuclear contribution to \( P(t) \) is small, we attribute the source of the magnetism to disordered Cu spins.

TF-\( \mu \)SR and magnetization measurements were carried out under both field-cooled (FC) and zero-field cooled (ZFC) conditions. Typical asymmetry spectra are shown in the inset of Fig. 2. In the ZFC case, pinning at the sample edges prevents flux from entering the bulk at \( T = 2.3 \) K and \( H < 300 \) Oe. Thus, the ZFC time spectrum in Fig. 2 resembles that observed in ZF. We note that this is also the case in high-quality \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) single crystals. Above 300 Oe, flux fully penetrates the sample at \( T = 2.3 \) K, but pinning centers prevent the formation of an equilibrium vortex lattice configuration. On the other hand, a well-ordered vortex lattice is achieved in the FC procedure. Fast Fourier transforms (FFT) of the corresponding muon-spin precession signals at \( H = 91 \) Oe are shown in Fig. 2. The FFT provides an approximate picture of the internal magnetic field distribution \( n(B) \) [18]. Above \( T_c \), the linewidth is due to the electronic and nuclear magnetic moments. Below \( T_c \), the lineshape is further broadened and becomes asymmetric as a result of the inhomogeneous field distribution created by a lattice of vortices. Because the contribution of the magnetic moments to the width of \( n(B) \) increases with increasing \( H \), we have restricted the current study to low magnetic fields.

The stopping site of the \( \mu^+ \) has previously been identified in the related undoped parent compound \( \text{Nd}_2\text{CuO}_4 \) as near an O atom midway between adjacent CuO_{2} layers [19]. Consistent with this site assignment, the TF-\( \mu \)SR signal in PCCO shows a single well resolved signal with an average frequency shifted relative to the Larmor precession frequency of \( \mu^+ \) in vacuum. The corresponding \( \mu^+ \)-Knight shift is

\[
K^\parallel_\mu = \frac{B_0 - \mu_0 H}{\mu_0 H} - 4\pi \left( \frac{1}{3} - N \right) \rho_{\text{mol}} \chi^\parallel(n),
\]

where \( B_0 \) is the average internal field sensed by the muons, the second term is a correction for Lorentz and bulk demagnetization fields, \( \rho_{\text{mol}} = 0.01744 \text{ mol/cm}^3 \) is the molar density of PCCO, and \( N \approx 1 \) is the demagnetization factor for a thin plate-like crystal. Figure 3 shows that \( K^\parallel_\mu \) scales linearly with \( \chi^\parallel \) above \( T_c \), indicating that the relative frequency shift is not induced by the \( \mu^+ \). In the normal state there are several contributions to \( K^\parallel_\mu \). Susceptibility measurements have established that the field-induced moment on the Pr ions dominates the magnetic response of PCCO, which depends little on Ce-doping [21]. Furthermore, as shown in the inset of Fig. 3, \( \chi \) is highly anisotropic due to strong crystalline electric-field (CEF) effects. For \( H \parallel c \), there are smaller contributions to \( \chi^\parallel \) from the tilting of the

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**FIG. 1:** Time evolution of the asymmetry (i.e. \( A(t) = AP(t) \), where \( A \) is the signal amplitude) in zero external field at \( T = 80 \) K, 40 K and 2.3 K. The initial muon-spin polarization was perpendicular to the \( \delta \)-axis. Inset: Temperature dependence of the resistivity (solid diamonds), and the bulk susceptibility at \( H \parallel c = 1 \) Oe under FC and ZFC conditions.

**FIG. 2:** FFTs of the muon-spin precession signal in PCCO. Below \( T_c \), the measurements were taken in an arbitrary sequence as a function of \( T \) under FC conditions. The dashed vertical line indicates the value of the external field \( H = 91 \) Oe. Inset: Asymmetry spectra taken at \( T = 2.3 \) K under both FC and ZFC conditions.
Cu moments out of the \( \hat{a} \hat{b} \) plane, Cu\(^{2+}\)-O\(^2-\)-Pr\(^{3+}\) superexchange interactions and from the polarization of the conduction electrons.\(^{21}\) The Pauli paramagnetic susceptibility \( \chi_0 \) of the conduction electrons gives rise to a \( T \)-independent Knight shift, \( K_0 = A_0 \chi_0 \), where \( A_0 \) is the contact hyperfine coupling constant. The field induced moment on the Pr ions results in a \( T \)-dependent susceptibility at \( H = 10 \) kOe applied parallel \( (\chi^\parallel) \) and perpendicular \( (\chi^\perp) \) to the \( c \)-axis. Right inset: magnetic field dependence of \( B_0 - \mu_0 H \) at \( T = 5 \) K and 25 K. Each data point at \( T = 5 \) K represents a single FC measurement.

\[ K_\mu^\parallel \approx K_0 + K_f^\parallel = K_0 + (A_c + A_{\text{dip}}^\parallel) \chi_f^\parallel, \]

where \( A_c \) and \( A_{\text{dip}}^\parallel \) are the contact hyperfine and dipolar coupling constants, respectively, and \( \chi_f^\parallel \approx \chi^\parallel - \chi_0 \). At the \( \mu^+ \) site we calculate \( A_{\text{dip}}^\parallel = -663.6 \) Oe/\( \mu_B \). The solid line in Fig. 3 is a fit to Eq. (2), yielding \( A_c = 3231 \) Oe/\( \mu_B \) and \( K_0 > -4480 \) ppm.

Below \( T_c \), there is a substantial increase of \( B_0 \) that nearly coincides with the increase of the diamagnetic signal under FC conditions (see Fig. 4). This cannot be explained by the reduction of \( \chi_0 \) that arises from the formation of Cooper pairs. We first considered the possibility that the increased field is a manifestation of the so-called paramagnetic Meissner effect\(^{22}\), but the diamagnetic response observed in both the FC and ZFC magnetization does not support this interpretation. A second possible origin, thought to be responsible for magnetorestriction enhancements\(^{23}\) and large diamagnetic shifts of \( B_0 \)\(^{24}\) in the superconducting state of the \( \text{RBa}_2\text{Cu}_3\text{O}_7-\delta \) system, is the \( R \)-moments induce screening currents in the CuO\(_2\) layers. However, here the Pr-moment is induced by the applied field, and thus is reduced below the normal-state value in regions well beyond the vortex cores. This is inconsistent with the FFTs in Fig. 2, which imply that all muons stopping in the sample see an increase in the local field. A third possible origin is that the vortices nucleate static Cu-spin order, as has been observed in the superconducting state of underdoped \( \text{La}_2-x\text{Sr}_x\text{CuO}_4\).\(^{25}\) We note that while the difference between \( B_0 \) in the superconducting and normal states is reduced with increasing \( H \), this does not imply that the additional source of field below \( T_c \) weakens. For example, the solid curve in Fig. 4 is a fit assuming \( B_0(T) = [(B_0^N)^2 + (B_\perp)^2]^{1/2} \), where \( B_0^N \) is the average internal field in the normal state and \( B_\perp \approx \) 43 G and 28 G, at 5 K and 10 K, respectively. This indicates that the additional field \( B_\perp \) that appears at the \( \mu^+ \)-site is primarily directed in the \( \hat{a} \hat{b} \) plane. Calculations show that this is consistent with the \( \text{La}_2\text{NiO}_4 \) spin-structure that has been observed with \( \mu \text{SR} \) in the parent compound \( \text{Nd}_2\text{CuO}_4 \) at low \( T \)\(^{19}\). Thus, long-range order of the Cu spins appears to be stabilized in PCCO by a low density of vortices, perhaps due to the close proximity of the superconducting and AFM phases.

The in-plane magnetic penetration depth \( \lambda_{ab} \) can be determined from the TF-\( \mu \text{SR} \) time spectra as described in Ref.\(^{12}\). In the normal state, the muon-spin precession signal is well described by the polarization function
\[ P(t) = e^{- (\sigma t)^\beta} \cos(\omega_t t + \phi), \]

where \( \beta \approx 1.6 \) and \( \sigma \) is the temperature-dependent depolarization rate. The TF-\( \mu \text{SR} \) time spectra below \( T_c \) were well fit to
\[ P(t) = e^{- (\sigma t)^\beta} \int n_v(B) \cos(\gamma_t B t + \phi) dB, \]

where \( n_v(B) \) is the field distribution of an hexagonal vortex lattice derived from Ginzburg-Landau theory, and \( \sigma_v \) is the depolarization rate due primarily to the effects of the magnetic moments — which occur on a length
scale that is $10^3$ times smaller than $\lambda_{ab}$. Fits at low $T$ which explicitly included a variable transverse field component $B_{1z}$ gave $\beta \approx 1.2$ and a diamagnetic shift for the $c$-axis component of field. However, $\lambda_{ab}(T)$ could not be reliably obtained in this manner due to the decreased sensitivity to $B_{1z}$ with increasing $T$ and the competition with other fitting parameters. Our analysis using Eq. (3) shows that $\sigma_c$ scales as $1/(T-\theta)$, where $\theta = -18(5)$ K. At low $H$, only a small fraction of the implanted muons stop near the vortex cores. As a result, the analysis is not very sensitive to the value of the coherence length $\xi_{ab}$. For example, increasing $\xi_{ab}$ from 30 Å to 60 Å changes $\lambda_{ab}(0)$ by less than 2%. Figure 5 shows the temperature dependence of $\lambda_{ab}^{-2}$. The absence of data below $T = 2.3$ K forbids an accurate determination of the limiting temperature dependence of $\lambda_{ab}^{-2}(T)$. However, above this $\lambda_{ab}^{-2}(0)/\lambda_{ab}^{-2}(T)$ shows reasonable agreement with that determined by $\mu$SR in the hole-doped systems La$_{2-\delta}$Sr$_\delta$CuO$_4$ and YBa$_2$Cu$_3$O$_{7-\delta}$. The solid curve in the inset of Fig. 5 is a fit of the PCCO data to $\lambda_{ab}^{-2}(T)=\lambda_{ab}^{-2}(0)[1-(T/T_c)^2]$, yielding $T_c = 15.9(2)$ K and $\lambda_{ab}(0) = 3369(73)$ Å. The values of $T_c$ and $\lambda_{ab}(0)$ indicate that the bulk of our sample is primarily underdoped. For example, Meissner state measurements in Ref. 13 on an underdoped PCCO film reported $\lambda_{ab}=3100$ Å. This same study showed evidence for a crossover from $s$-wave to $d$-wave behavior in the underdoped regime.

In conclusion, we have observed the onset of static magnetic order in the superconducting state of underdoped PCCO single crystals with a field applied perpendicular to the CuO$_2$ plane. This result is consistent with vortex-induced AFM ordering of the Cu spins throughout the sample. In addition, our measurements of $\lambda_{ab}^{-2}(T)$ in the vortex state appear consistent with hole-doped cuprates down to $\sim 0.2 T_c$. However, a unique determination of the low-temperature behavior by $\mu$SR awaits the availability of larger single crystals.

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