

Evidence for Nodal Quasiparticles in Electron-Doped Cuprates from Penetration Depth Measurements

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(Received 18 February 2000)

The in-plane magnetic penetration depth, $\lambda(T)$, was measured down to 0.4 K in single crystals of electron-doped superconductors, $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ (PCCO) and $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ (NCCO). In PCCO, the superfluid density varies as T^2 from 0.025 up to roughly $0.3T/T_c$ suggestive of a d -wave state with impurities. In NCCO, $\lambda(T)$ shows a pronounced upturn for $T < 4$ K due to the paramagnetic contribution of Nd^{3+} ions. Fits to an s -wave order parameter over the standard BCS range ($T/T_c = 0.32$) limit any gap to less than $\Delta_{\min}(0)/T_c = 0.57$ in NCCO. For PCCO, the absence of paramagnetism permits a lower temperature fit and yields an upper limit of $\Delta_{\min}(0)/T_c = 0.2$.

PACS numbers: 74.25.Nf, 74.72.Jt

There is by now a consensus that the hole-doped high- T_c cuprates exhibit d -wave pairing symmetry [1–10]. For electron-doped cuprates [11] the issue has been controversial. While most theories for the mechanism of high temperature superconductivity are insensitive to the sign of the carriers, some predict that n and p type materials will have different pairing symmetry, making its determination an important challenge [12,13]. Early microwave measurements of the penetration depth in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ (NCCO) were interpreted within an s -wave model [14–16]. However, Cooper pointed out that the power-law dependence for $\lambda(T)$ indicative of a nodal order parameter could be masked by a large paramagnetic contribution from Nd^{3+} ions [17]. Newer microwave measurements by Kokales *et al.*, performed on the same samples used in this paper, have revealed an upturn and power-law temperature dependence and are consistent with the data reported here [18]. Measurements of $\lambda(T)$ using single grain boundary junctions [19] have favored a gapped state. Some tunneling measurements favor an s -wave order parameter, albeit with significant departures from an isotropic weak coupling Bardeen-Cooper-Schrieffer (BCS) picture [20], while others report a zero-bias conductance peak [21–23]. Half-integral flux indicative of d -wave pairing [4] was recently reported in tricrystal experiments with both NCCO and $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ (PCCO) films [24].

In this letter we report measurements of $\lambda(T)$ down to 0.4 K in single crystals of both NCCO and PCCO. Lower temperatures and higher resolution combine to permit a more precise determination of the temperature dependence of $\lambda(T)$ than any previously reported. In NCCO, a large paramagnetic contribution is observed below 4 K. In non-magnetic PCCO, we find an overall T^2 variation of the superfluid density up to $T/T_c \approx 0.3$, suggesting the presence of nodal quasiparticles in the presence of strong impurity scattering.

Single crystals of $\text{R}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ ($R = \text{Nd}$ or Pr) were grown using a directional solidification technique and annealed in argon to achieve optimal superconducting properties [25]. Normal state resistivity varied as T^2 with the residual resistivity $\rho(0) = 20\text{--}50 \mu\Omega \text{ cm}$. The penetration depth was measured with an 11 MHz tunnel-diode-driven LC resonator [26–28]. Samples were mounted on a movable sapphire stage with temperature controllable from 0.4 to 100 K. The low noise level, $\Delta f_{\min}/f_0 \approx 5 \times 10^{-10}$, results in a sensitivity of $\Delta\lambda \leq 0.5 \text{ \AA}$ for our samples [$0.5 \times 0.5 \times 0.02 \text{ mm}$]. The large anisotropy of these materials ($\lambda_c/\lambda_{ab} \approx 30\text{--}80$ [15]) forces one to apply the rf field perpendicular to the conducting planes. Otherwise, the frequency shift will be dominated by changes of the interplane penetration depth, for which there exists no straightforward connection to the pairing symmetry. A semianalytical solution for the rf susceptibility of a platelet sample of square base $2w \times 2w$ and thickness $2d$ in this orientation was analyzed in Ref. [28]. At low temperatures the frequency shift, $\Delta f \equiv f(T) - f(0)$, is related to the change in penetration depth, $\Delta\lambda \equiv \lambda(T) - \lambda(0)$, via $\Delta f = -G\Delta\lambda$, with a calibration constant $G = V_s f_0 / [2V_0(1 - N)R]$, where N is the effective demagnetization factor, V_s is the sample volume, V_0 is the effective coil volume, f_0 is the resonance frequency in the absence of a sample, and $R \approx 0.2w$ is an effective dimension [28]. Because of penetration of the magnetic field from the top and bottom surfaces, R differs significantly from $R = w/2$ obtained for an infinite bar [6]. The sample and apparatus dependent constant $\Delta f_0 \equiv V_s f_0 / [2V_0(1 - N)]$ is measured by moving the sample out of the coil *in situ*. The overall calibration was tested with samples of Nb, YBCO, and BSCCO and gave $d\lambda/dT$ within 10% of the reported values [6–8].

In order to determine the normalized superfluid density, $\rho_s \equiv [\lambda(0)/\lambda(T)]^2$, it is necessary to know the absolute magnitude of the penetration depth, $\lambda(0)$. Measured

values of $\lambda(0)$ in NCCO vary from 1000–2600 Å [14,15,29,30]. The only reported value for PCCO, $\lambda(0) \approx 1000$ Å, was estimated from lower critical field H_{c1} measurements which may suffer from demagnetization and vortex effects [31]. We have developed a new technique to determine $\lambda(0)$ from the frequency shift, obtained by warming a sample coated with a thin layer of Al above $T_c(\text{Al})$ [32]. This technique applied to PCCO gave $\lambda(0) \approx 2500 \pm 100$ Å [32] which will be used as an upper estimate in this paper.

In Fig. 1 we plot the penetration depth for PCCO sample 1 along with several fits. The fitting range was 5 K to ensure the validity of the low temperature BCS expansion for an isotropic s -wave state, $\Delta\lambda = \lambda(0) \times \sqrt{\pi\Delta(0)/2T} \exp[-\Delta(0)/T]$ [1]. In each case, the small negative offset $A = \lambda(0) - \lambda(0.4 \text{ K})$ was determined as a fit parameter. The solid line is a fit with 188 data points to a power law, $\Delta\lambda = A + BT^2$, with $B = 3.70 \pm 0.01 \text{ Å/K}^2$ and $\chi^2 \approx 8.2$. The short dotted line shows the best fit to the BCS s -wave expression. With both $\lambda(0)$ and $\Delta(0)$ as free parameters we obtained $\Delta(0)/T_c = 0.538 \pm 0.002$ and $\lambda(0) = 426 \pm 3$ Å. The s -wave fit is somewhat worse than the power law ($\chi^2 \approx 17.6$) and gives an unrealistic value for $\lambda(0)$. The dash-dotted line shows the s -wave fit where $\Delta(0)/T_c$ was fixed at the weak-coupling BCS value (1.76). In this case an unrealistically large $\lambda(0) = 13570 \pm 50$ Å was obtained. For comparison, the dotted line is a plot of the BCS expression with $\Delta(0)/T_c = 1.76$ and set to a more realistic value of $\lambda(0) = 2500$ Å.

If the order parameter is an anisotropic s wave, then the minimum gap value determines the low temperature asymptotic behavior. The BCS functional form for $\Delta\lambda$ still holds, but with Δ_{\min} replacing the isotropic gap. The temperature range over which this asymptotic form is valid is now reduced accordingly. For an isotropic

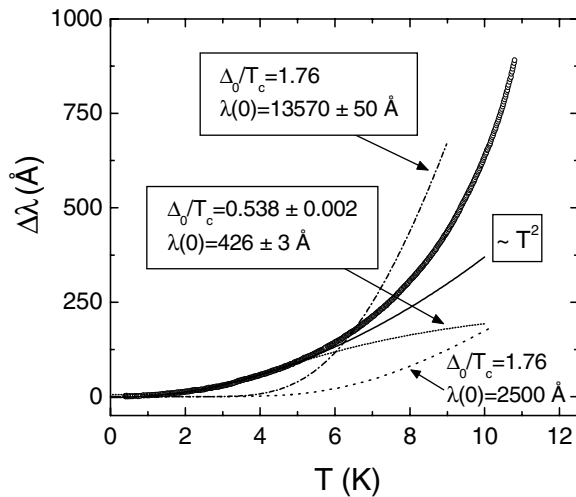


FIG. 1. Low temperature variation of the penetration depth $\Delta\lambda(T)$ in PCCO single crystal. Lines show fits to different models described in the text.

gap, $\Delta(0)/T_c = 1.76$, the range of validity in reduced temperature is $(T/T_c)_{\max} = t_{\max} \approx 0.32$ [1]. For an anisotropic gap, simple rescaling forces the range of validity down to $t_{\max} \approx 0.18\Delta_{\min}(0)/T_c$. Without *a priori* knowledge of $\Delta_{\min}(0)/T_c$, we do not know t_{\max} , and so it is necessary to successively reduce the range until the gap value obtained from the fit becomes independent of the range. Following this procedure for PCCO, with $\lambda(0) = 2500$ Å fixed, we find that $\Delta(\min)/T_c$ extrapolates to 0.20 ± 0.05 as $t_{\max} \rightarrow 0$. The same procedure for Nb yields $\Delta(0)/T_c = 1.74 \pm 0.02$, as expected. This stricter criterion would imply that any residual gap is less than 11% of the isotropic BCS value.

The overall best fit for sample 1 was achieved for a $T^{2.25 \pm 0.01}$ power law ($\chi^2 \approx 2.1$). Although this may appear unphysical, it is important to recall that the integer power laws expected for a nodal order parameter strictly apply to the normalized superfluid density, ρ_s , and not the measured quantity, $\Delta\lambda$. If $\rho_s = 1 - c_n T^n$ then $\Delta\lambda$ has corrections of order T^{2n} , and a fit to $\Delta\lambda$ can result in an artificial intermediate power (e.g., 2.25). This distinction is clearly evident in high quality, untwinned YBCO above 10 K [27].

In Fig. 2 we plot, for sample 1, normalized superfluid density, $\rho_s \approx [1 + \Delta\lambda(T)/\lambda(0)]^{-2}$, vs $(T/T_c)^2$ for three choices of $\lambda(0)$ spanning the range of reported values. $\lambda(0) = 1200$ Å yields $1 - \rho_s \sim (T/T_c)^2$ up to 8.4 K, while larger choices for $\lambda(0)$ reduce the range of pure quadratic behavior. For comparison we show data taken for Nb in the same apparatus. Up to $T/T_c = 0.5$, the Nb data fits the low temperature BCS expansion perfectly with $\Delta(0)/T_c = 1.74 \pm 0.02$, giving us confidence that the measurement technique is sound.

With an exponent of $n = 2.25$, sample 1 is our weakest candidate for a nodal order parameter. Figure 3 shows

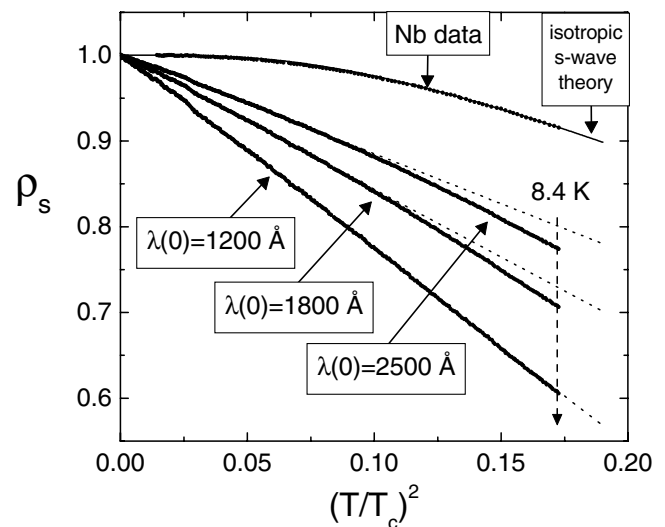


FIG. 2. Superfluid density ρ_s vs $(T/T_c)^2$, calculated assuming $\lambda(0) = 1000, 1500,$ and 2000 Å. The dotted lines indicate pure quadratic power law. The solid line shows isotropic s -wave behavior.

data for samples 1, 2, and 3 (offset for clarity) and the same Nb data with a fit to the BCS form. Samples 2 and 3 have power laws much closer to $n = 2$. In this plot we have chosen the largest value of $\lambda(0)$ in order to cast the power-law model in the most unfavorable light (i.e., smallest range of pure quadratic behavior). We conclude that the superfluid density in PCCO is best described by a quadratic power-law variation with temperature.

There are currently two theories for a quadratic power law in d -wave superconductors. Kosztin and Leggett showed that the divergence of the effective coherence length near the nodes of a d -wave order parameter yields $1 - \rho_s \sim T^2$ due to nonlocal electrodynamics [33]. Nonlocality is predicted to arise for the orientation used here (field perpendicular to conducting planes) below $T_{\text{nonlocal}} \approx \xi(0)\Delta(0)/\lambda(0)$, where $\xi(0)$ is the coherence length. In electron-doped cuprates, $T_{\text{nonlocal}} \approx 0.5\text{--}2.5$ K within our current knowledge of superconducting parameters. Since we observe a quadratic temperature dependence up to 8–10 K in some samples, nonlocality is unlikely to be the source. A stringent test for nonlocality would require a comparison between this data and $\lambda(T)$, obtained from the $H \parallel ab$ plane orientation. However, the $H \parallel ab$ orientation involves the interplane penetration depth, as discussed earlier.

Impurity scattering in the unitary limit provides a more plausible explanation for the quadratic dependence of $\rho_s(T)$ [2,6]. In the “dirty d -wave” scenario, $\rho_s(T)$ will cross over from a linear to quadratic temperature dependence below $T^* \approx 6 \ln 2 \gamma / \pi$, where $\gamma \approx 0.63 \times \sqrt{\Gamma \Delta(0)}$ and Γ is a scattering rate parameter, proportional to the impurity concentration [2]. The slope $d\lambda/dT^2|_{T \rightarrow 0} \approx \pi \lambda(0) / [6\gamma \Delta(0)]$. Casting this result in di-

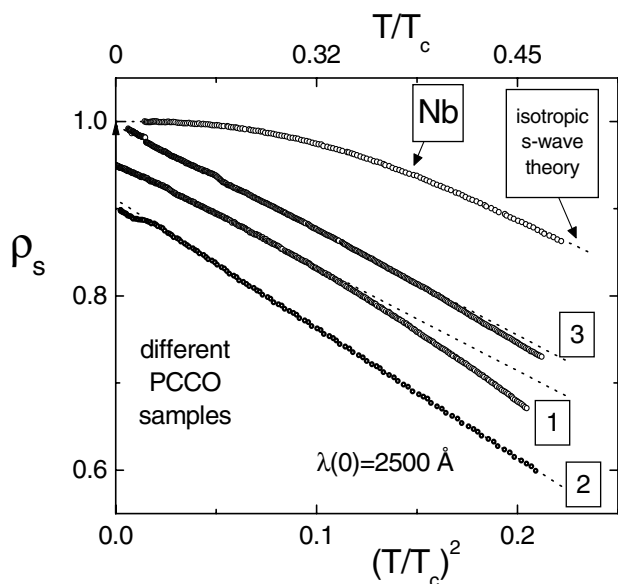


FIG. 3. ρ_s in three PCCO single crystals assuming $\lambda(0) = 2500$ Å (data offset for clarity). The dotted lines show T^2 fits at low temperatures. Also shown are the data for Nb and the calculated isotropic s -wave curve.

mensionless form gives $\Gamma/T_c \approx 0.28/[-d\rho_s/d(T/T_c)^2]$. In Fig. 4 we plot T_c vs Γ/T_c for all five samples studied. Samples 1, 2, and 3 are marked. The transitions in some samples were broad and two different criteria were used to estimate T_c —onset of the diamagnetic signal and the inflection point of the $\Delta\lambda(T)$ curve. Since no impurities were deliberately added, the spread in T_c may reflect slight differences in annealing and thus carrier density, which in turn will affect the scattering rate. Figure 4 shows T_c suppression with increased scattering rate as expected for a d -wave state with impurity scattering [2]. Γ/T_c is at least 10 times larger than the rate observed in clean YBCO [6,7].

We now discuss measurements of $\lambda(T)$ in NCCO. This compound has been studied much more thoroughly than PCCO and was cited as first evidence for s -wave pairing in e -doped materials [14,15]. However, Nd^{3+} ions introduce a large paramagnetic background and influence the measured penetration depth [17]. With magnetic permeability $\mu(T) = 1 + C/(\Theta + T)$, the measured penetration depth is given by $\lambda(T) = \lambda_L(T)\sqrt{\mu(T)}$, where λ_L is the London penetration depth, C is a Curie-Weiss constant, and Θ is the characteristic temperature for antiferromagnetic interaction [17]. To fit the data, we take $\Theta = 1.2$ K from neutron scattering [34] and specific heat [35] measurements. For C we have chosen two representative values $C = 0.3$ and 0.05 , calculated by assuming the effective magnetic moment of Nd^{3+} ions to be $2.4\mu_B$ [17] and $1\mu_B$, respectively.

Figure 5 shows $\Delta\lambda(T)$ measured in a single crystal of NCCO. The inset shows the low temperature range. Below $T \approx 4$ K there is a pronounced upturn, which we attribute to the paramagnetic contribution of Nd^{3+} ions. The upper solid line in the inset of Fig. 5

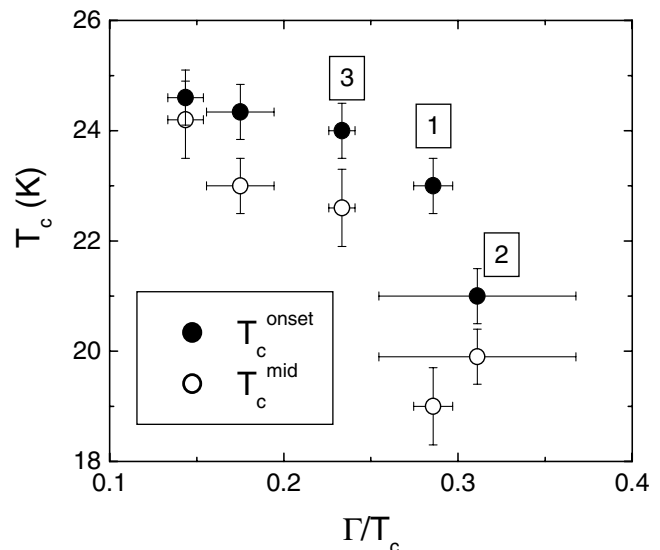


FIG. 4. T_c versus scattering parameter Γ/T_c determined using five PCCO crystals. Filled symbols show T_c^{onset} defined as the onset of diamagnetism. Open symbols show T_c^{mid} defined as the inflection point on $\Delta\lambda(T)$.

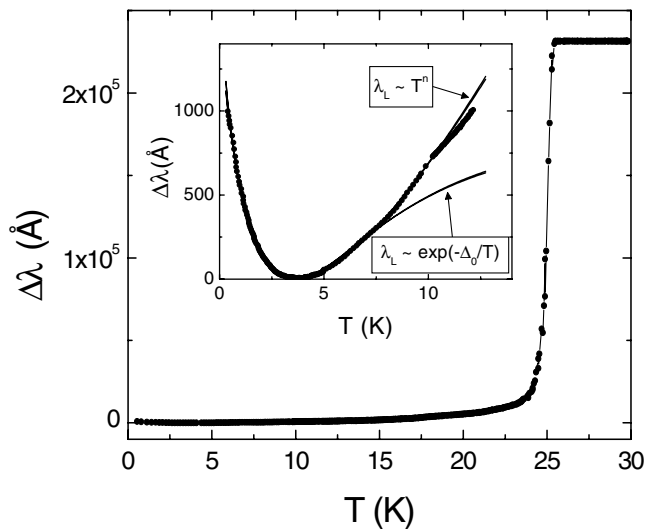


FIG. 5. $\Delta\lambda(T)$ in NCCO single crystal. Inset: low temperature range. Lines are the fits assuming a power law or an s -wave temperature dependence for the London penetration depth $\lambda_L(T)$ as described in the text.

shows the power-law fit ($\lambda_L \propto T^n$) which yields $n = 1.35 \pm 0.03$ and $n = 1.40 \pm 0.03$ for $C = 0.3$ and 0.05 , respectively. (Fits for the two different values of C are indistinguishable on this scale.) The lower line shows analogous fits to the low temperature s -wave expression from which we obtain $\Delta(0)/T_c = 0.569 \pm 0.006$ and $\Delta(0)/T_c = 0.573 \pm 0.006$. Fits were obtained from data up to $t = 0.32$. The higher temperature data is shown for completeness. Changing the value of Θ from 1.2 to 2 also had a small effect on the fit parameters. The value of $\Delta(0)/T_c$ is close to that obtained in PCCO. Again, for a strict test we should fit over a correspondingly reduced temperature range. However, the dominant paramagnetic contribution below $t < 0.16$ renders this procedure meaningless. The $n = 1.4$ exponent obtained from the power-law fit is closer to the clean d -wave limit and could imply that after correction for paramagnetism, unitary-limit scattering in NCCO is smaller than in PCCO.

In conclusion, we have measured the penetration depth $\lambda(T)$ in electron-doped PCCO and NCCO single crystals down to 0.4 K. In nonmagnetic PCCO, ρ_s decreases quadratically with temperature up to $t \approx 0.3$, consistent with a dirty d -wave (gapless) scenario. The correlation between T_c and the rate of change of superfluid density is also consistent with this picture. In NCCO, a large paramagnetic contribution to the penetration depth was observed. $\lambda_L(T)$ was found to vary as $T^{1.4}$. For both materials, a fit over the same temperature range to an s -wave model sets an upper limit of $\Delta(0)/T_c = 0.57$ but requires unrealistically small values $\lambda(0)$. For PCCO, the test can be made more stringent and we reduce the upper limit to $\Delta_{\min}(0)/T_c = 0.2$.

We thank J. R. Cooper, A. A. Abrikosov, S. M. Anlage, N. Goldenfeld, P. J. Hirschfeld, R. Klemm, L. Taillefer, A. Mourachkine, Y. Yeshurun, and C. C. Tsuei for useful dis-

cussions and communications. This work was supported by the Science and Technology Center for Superconductivity Grant No. NSF-DMR 91-20000. Work in Maryland is supported by Grant No. NSF-DMR 97-32736.

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