Evidence for nodal quasiparticles in electron-doped cuprates from penetration depth measurements

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The in-plane magnetic penetration depth, $\lambda(T)$, was measured down to 0.4 K in single crystals of electron-doped superconductors, Pr$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ (PCCO) and Nd$_{1.85}$Ce$_{0.15}$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 $\Delta_{min}(0)/T_c = 0.2$.

There is by now a consensus that the hole-doped high-$T_c$ cuprates exhibit d-wave pairing symmetry [1, 4]. For electron-doped cuprates [1] the issue remains unresolved. 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 NCCO were interpreted within an s-wave model [4, 10]. 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 sample used in this paper, have revealed an upturn and power-law temperature dependence and are consistent with our data [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 BCS picture [20], while others report a zero-bias conductance peak [21, 23]. Half-integral flux indicative of d-wave pairing [1] was recently reported in tricrystal experiments with both NCCO and 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 R$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ (R=Nd or Pr) were grown using directional solidification technique and annealed in argon to achieve optimal superconducting properties [25]. Penetration depth was measured using an 11 MHz tunnel-diode driven LC resonator [26, 28]. Samples were mounted on a movable sapphire stage with temperature controllable from 0.4 K to 100 K. The low noise level, $\Delta f_{min}/f_0 = 5 \times 10^{-10}$, results in a sensitivity of $\Delta \lambda \leq 0.5$ Å for our samples [0.5 × 0.5 × 0.02 mm]. The large anisotropy of these materials ($\lambda_c/\lambda_ab \approx 30-80$ [13]) 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 semi-analytical solution for the rf susceptibility of a platelet sample of square base $2w \times 2w$ and thickness $2d$ in this orientation was analyzed in detail in Ref. [28]. At low temperatures the frequency shift, $\Delta f = f(f(T) - f(0))$, is related to the change in penetration depth, $\Delta \lambda = \lambda(T) - \lambda(0)$, via $\Delta f = -G\Delta \lambda$, with the calibration constant $G = V_sf_0/[2V_0(1 - N)]$, 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]. Although this result is similar to the known solution for an infinite slab in parallel field [3], the effective dimension $R$ differs significantly from $R = w/2$ obtained for an infinite bar. This difference is due to penetration of the magnetic field from the top and bottom surfaces. 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 reported values [1, 5]. 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 \([14,15,29,30]\). In PCCO the only reported value, \( \lambda(0) \approx 1000 \) Å, was estimated from the measurements of the lower critical field \( H_{c1} \) and is less reliable due to demagnetization and possible vortex effects \([32]\). We recently developed a new technique for determining \( \lambda(0) \) from the frequency shift obtained by warming a sample coated with a thin layer of Al above \( T_c(Al) \). A detailed description of this procedure will be published elsewhere \([33]\). This technique applied to PCCO gave \( \lambda(0) = 2500 \pm 100 \) Å \([32] \) which will be used as an upper estimate in this paper.

![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.](image)

In Fig. 1 we plot the penetration depth for PCCO sample 1 along with several fits. The fitting range was 5 K to assure validity of the low temperature BCS expansion for an isotropic s-wave state, \( \Delta\lambda = \lambda(0)/\sqrt{\pi} \Delta(0)/2T \exp(-\Delta(0)/T) \). In each case, the small negative offset \( A = \lambda(0) - \lambda(0.4K) \) 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 \( B = 3.70 \pm 0.01 \) Å/K² 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 \( \Delta_{min} \) replacing the isotropic gap. The temperature range over which this asymptotic form is valid is now reduced accordingly. For an isotropic gap, \( \Delta(0)/T_c = 1.76 \), the range of validity in reduced temperature is \( (T/T_c)_{max} = t_{max} \approx 0.32 \). 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 \( \Delta(0)/T_c \) extrapolates to \( 0.20 \pm 0.05 \) as \( t_{max} \to 0 \). 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, \( \rho_s \), and not the measured quantity, \( \Delta\lambda \). If \( \rho_s = 1 - c_nT^n \) 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 \([34]\).

![FIG. 2. Superfluid density \( \rho_s \) vs. \( (T/T_c)^2 \), calculated assuming \( \lambda(0) = 1000, 1550 \) and 2000 Å. Dotted lines indicate pure quadratic power law. Dash-dotted line shows isotropic s-wave behavior.](image)

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 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 weak-
est candidate for a nodal order parameter. Fig. 3 shows 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.

![FIG. 3. $\rho_s$ in three PCCO single crystals assuming $\lambda(0) = 2500 \, \AA$ (data offset for clarity). Dotted lines show $T^2$ fits at low temperatures. Also shown data for Nb and calculated isotropic s-wave curve.](image)

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 [26]. 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 $T_{\text{nonlocal}} \approx 0.5 \, \text{K}$ to $2.5 \, \text{K}$ within our current knowledge of superconducting parameters. Since we observe a quadratic temperature dependence up to $8\rightarrow10 \, \text{K}$ 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 $H\parallel c$ 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 $\rho_s(T)$ [35]. In the “dirty $d$-wave” scenario, $\rho_s(T)$ will cross over from a linear to quadratic temperature dependence below $T^* \approx 6 \ln 2 2\gamma/\pi$, where $\gamma \approx 0.63\sqrt{\pi\Delta(0)}$ and $\Gamma$ is a scattering rate parameter, proportional to the impurity concentration [2]. The slope $d\lambda/dT^2|_{T\rightarrow0} \approx \pi\lambda(0)/(6\gamma\Delta(0))$. Casting this result in dimensionless form gives: $\Gamma/T_c \approx 0.28/[-d\rho_s/d(T/T_c)^2]$. In Fig. 3 we plot $T_c$ versus $\Gamma/T_c$ 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. In general, the trend shows $T_c$ suppression with increased scattering rate as expected for a d-wave state with impurity scattering [2]. $\Gamma/T_c$ is at least 10 times larger than the scattering rate observed in clean YBCO [17].

![FIG. 4. $T_c$ versus scattering parameter $\Gamma/T_c$ determined using 5 PCCO crystals. Filled symbols show $T_{c}\text{onset}$ defined as the onset of diamagnetism. Open symbols show $T_{c}\text{mid}$ defined as the inflection point on $\Delta\lambda(T)$.](image)

We now discuss measurements of $\lambda(T)$ in NCCO. This compound has been studied much more thoroughly than PCCO and was cited as the 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 $\lambda_L$ is the London penetration depth, $C$ is a Curie-Weiss constant, and $\Theta$ is the characteristic temperature for antiferromagnetic interaction [17]. To fit the data, we take $\Theta = 1.2 \, \text{K}$ from neutron scattering [14] and specific heat [35] measurements. For $C$ we have chosen two representative values $C = 0.3$ and 0.05, calculated 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 $T \approx 4 \, \text{K}$ there is a pronounced upturn, which we attribute to the paramagnetic contribution of Nd$^{3+}$ ions. The upper solid line in the inset to Fig. 5 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 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 $\Theta$ 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 value of $\Theta$ from 1.2 to 2 also had a small effect on the fit parameters. The value of $\Delta(0)$/Tc 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 non-magnetic PCCO, $\rho_s$ 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 $\Delta_{min}(0)/T_c = 0.32$.

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