Microwave Electrodynamics of the Electron-Doped Cuprate Superconductors $Pr_{2-x}Ce_xCuO_{4-y}$ and $Nd_{2-x}Ce_xCuO_{4-y}$

J. David Kokales, Patrick Fournier, Lucia V. Mercaldo, Vladimir V. Talanov, Richard L. Greene, and Steven M. Anlage

Center for Superconductivity Research, Department of Physics,
University of Maryland, College Park, MD 20742-4111

The pairing-state symmetry of the electron-doped cuprate superconductors is thought to be s-wave in nature, in contrast with their hole-doped counterparts which exhibit a d-wave symmetry. We re-examine this issue based on recent improvements in our electron-doped materials and our measurement techniques. We report microwave cavity perturbation measurements of the temperature dependence of the penetration depth of $Pr_{2-x}Ce_xCuO_{4-y}$ and $Nd_{2-x}Ce_xCuO_{4-y}$ crystals. Our data suggest that these materials do not have a large, or standard, s-wave gap in their excitation spectrum.

1. Introduction

Existing experimental evidence suggests that the pairing-state symmetry in the electron-doped cuprate superconductors is s-wave in nature, in contrast to the d-wave symmetry observed in the hole-doped cuprates. There is no compelling theoretical reason for this difference. The strongest evidence for s-wave symmetry comes from measurements of the penetration depth [1]. However, it is possible that the paramagnetism of the Nd rare-earth ion in $Nd_{2-x}Ce_xCuO_{4-y}$(NCCO) may have influenced the determination of the symmetry [2] from temperature-dependent penetration depth measurements [1].

In order to more definitively determine the pairing-state symmetry of the electron-doped cuprates, we have again studied the low-temperature behavior of the penetration depth, $\lambda(T)$. The functional form of $\lambda(T)$ is determined by the low-energy excitations of the system, and thus indirectly determines the pairing-state symmetry of these materials. In addition, we are now able to observe the behavior of $\lambda(T)$ to a lower temperature than was done previously [1]. This, along with the possible role of paramagnetism in previous measurements, makes it prudent to study an electron-doped system which is not strongly paramagnetic, such as the cuprate superconductor $Pr_{2-x}Ce_xCuO_{4-y}$ (PCCO).

The samples studied were crystals grown using a directional solidification technique and have been characterized in previous studies [1,3,4]. Typically, these samples exhibited a transition temperature of 19 K for PCCO and 24 K for NCCO with a transition width in the surface resistance of less than 3 K and residual normal state resistivity values of about 60 $\mu\Omega$-cm. A typical sample size was 1mm x 1mm x 30μm. The phase diagram for the electron-doped cuprates [5] shows that a cerium dopant concentration of x=0.15 is optimal. Based upon the resistivity, T_c, and transition width, we believe that our samples are at the optimal doping level.

2. Experimental Method

The in-plane penetration depth, $\lambda_{ab}(T)$, as well as the surface resistance, $R_S(T)$, were measured using a superconducting niobium microwave resonant cylindrical cavity operating at 9.6 GHz in which the TE_{011} mode is stimulated. In this mode, H_{rf} is maximum and E_{rf} zero at the center of the cavity, where the sample is placed on a hot finger with its c-axis aligned parallel to H_{rf}. This induces screening currents in the copper-oxide planes of the crystal. The sample temperature was varied from approximately 1.8 K to

above T_c. As $\lambda(T)$ changes with temperature, the resonant frequency, f(T), and quality factor, Q(T), of the cavity change. By measuring these shifts in f(T) and Q(T), quantities such as the temperature dependence of $\Delta\lambda(T)$ and $R_s(T)$ can be deduced. Further details of this technique are given elsewhere [4].

Our measurement of $\Delta\lambda(T)$ can be corrupted by a paramagnetic contribution, $\mu_r(T)$, from the sample. This comes from its effect on the measured frequency, $f(T) \propto \lambda(T)\sqrt{\mu_r(T)}$ [2]. This paramagnetic influence is not present in YBCO, but has been seen in other $REBa_2Cu_3O_7$ compounds [6].

There are some important improvements to this technique, reported here for the first time, which influence our determination of the pairing-state symmetry. In the past [1], four issues were of major concern regarding the microwave resonant cavity technique. These involved the base temperature, reproducibility of the data, the effects of changing liquid helium hydrostatic pressure on the dimensions of the resonator, and the orientation of the sample with respect to H_{rf}.

In our present design, we are able to reach a base temperature of approximately 1.8 K without the use of an exchange gas, which can corrupt the data. This has been accomplished by pumping on the helium bath and providing a stronger thermal link between the sample and the bath. This allows us to explore sample properties in a region of temperature in which the distinction between the different possible pairing-state symmetries is most apparent, and any paramagnetic influence would be most evident.

A further improvement was realized by permanently mounting the sample rod to the base of the apparatus. It is necessary to introduce the sample to the proper position within the resonant cavity where E_{rf} is minimal, and H_{rf} is maximum and aligned in a known direction, along the axis of the cylindrical cavity. Furthermore, having the sample rod permanently secured ensures that the sample will be introduced to the same location within the cavity every time. This is critical in order for measurements to be reproducible.

Also, we have addressed the issue of the helium hydrostatic pressure. As the level of the

liquid helium drops over the course of an experimental run, the pressure it exerts on the cavity decreases, causing the cavity to expand slightly. This results in a constant drop in resonant frequency with time. In order to minimize this effect, it is necessary to isolate the cavity from the helium bath. To achieve this, we surround the resonant cavity with a vacuum jacket. Thermal links were maintained by direct surface-to-surface contact between the cavity and this outer cylinder at certain points. The result of this improvement was to reduce any drift in frequency due to changes in the helium hydrostatic pressure to less than the random noise present in the data.

Finally, the orientation of the sample in the cavity is different from previous experiments [1]. H_{rf} is now applied parallel to the c-axis of the sample, whereas in the past, it was parallel to the a-b plane of the crystal. This change has two effects. First, the rare-earth paramagnetism is stronger when H_{rf} is applied in the plane [7]. Thus, by changing the orientation we were able to significantly reduce the paramagnetic influence on our measurements. Secondly, the former orientation induced c-axis currents in the sample. This led to the simultaneous measurement of $\lambda_{ab}(T)$ and $\lambda_c(T)$, making it difficult to analyze the inplane penetration depth without c-axis contributions. However, with H_{rf} now applied parallel to the c-axis, only a-b plane currents are induced. This allows for a direct measurement of $\lambda_{ab}(T)$.

3. Results

The surface resistance as a function of T/T_c is presented in figure 1 for one PCCO and one NCCO crystal studied. Note that both samples display a single transition at T_c, and show the same behavior until the PCCO crystal's surface resistance saturates at the residual resistance value. The homogeneity of the crystals is attested to by the nature of the transition, and the width of the transition, about 0.15 T_c, is typical for our samples. This, along with their reasonable values of T_c, indicates that the doping is near optimal levels. Thus, the low temperature behavior of the $\Delta\lambda(T)$ for these samples should be representative of the electron-doped cuprate supercon-
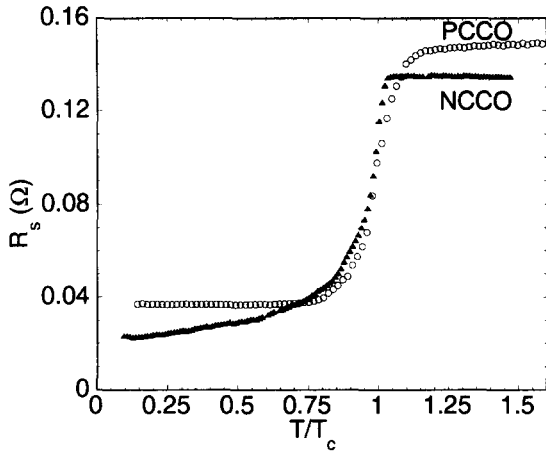
Figure 1. Surface resistance, $R_S(T/T_c)$, for PCCO (open circles) and NCCO (closed triangles) crystals, measured at 9.6 GHz, as a function of T/T_c.

Figure 2. $\Delta\lambda(T/T_c)$ as a function of T/T_c for crystals of PCCO (open circles), NCCO (closed triangles), and the asymptotic BCS s-wave model with $\lambda(0)=1500$ Å and $2\Delta/k_bT_c=3.50$ (dashed line). The solid lines are asymptotic BCS s-wave fits of the form $\Delta\lambda(T) = \lambda(0)(\pi\Delta(0)/2k_BT)^{1/2}e^{-\Delta(0)/k_BT}$ Note: PCCO data is offset and NCCO data is fit for $T>0.16T_c$.

ductors, with minimal extrinsic influences. This is in contrast to the behavior of other crystals which displayed much broader transitions as well as step-like features in $R_S(T)$, indicative of additional superconducting transitions. These crystals also showed multiple transitions in the c-axis resistivity, were judged to be inhomogeneous, and subsequently rejected.

The low temperature behavior of $\Delta\lambda(T)$ has been used as an indication of the pairing symmetry [1,4]. In the case of BCS s-wave symmetry, $\Delta\lambda(T)$ is expected to behave exponentially, the exact behavior dependent upon the zero-temperature penetration depth, $\lambda(0)$, and the energy gap, $\Delta(0)$. The asymptotic BCS s-wave form is: $\Delta\lambda(T) = \lambda(0)(\pi\Delta(0)/2k_BT)^{1/2}e^{-\Delta(0)/k_BT}$ for $T\ll T_c/2$.

In figure 2 we show $\Delta\lambda(T)$ for an NCCO and PCCO crystal up to $T_c/3$, as well as the asymptotic BCS s-wave model using $\lambda(0) = 1500$ Å and $2\Delta(0)/k_BT_c = 3.50$. The data for the electron-doped crystals clearly differs from the expected asymptotic BCS s-wave behavior, with neither
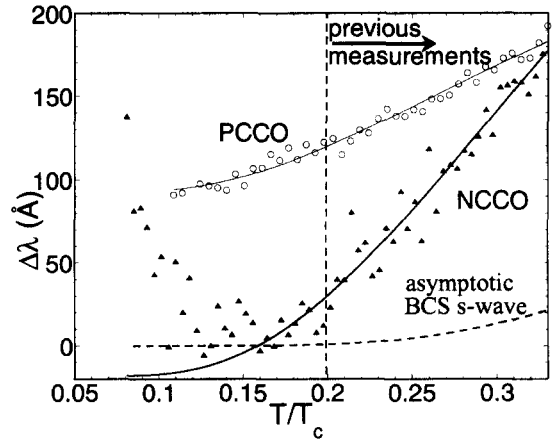
sample exhibiting the nearly constant $\lambda(T)$ expected below $0.2T_c$. Nevertheless, we can force the data to fit the asymptotic s-wave BCS form by allowing both $\lambda(0)$ and $\Delta(0)$ to vary. For the PCCO crystal we found $\lambda(0) = 390$ Å and $2\Delta(0)/k_BT_c = 1.37$. Similarly, the NCCO crystal yields $\lambda(0) = 1150$ Å and $2\Delta(0)/k_BT_c = 1.61$. In both cases we find small gap values, much less than the 3.5 expected from BCS theory, and much smaller than previously reported in NCCO [1,4,8,9].

Also of note in figure 2 is the upturn in the NCCO $\Delta\lambda(T)$ data at low temperatures. We believe that this upturn is due to the paramagnetism of the Nd^{3+} ions [6,10,11]. It is important to realize that previous studies [1] only obtained data for temperatures above the vertical dashed line in figure 2, and in an orientation which included a stronger paramagnetic contribution to the frequency shift [2,7]. The paramagnetic up-

turn in NCCO was not observed in the earlier work because critical low temperature data was not collected. This may explain why these previous studies found NCCO to be an s-wave superconductor. In the fit considered above, we naively accounted for the paramagnetism in NCCO by excluding data below 0.16 T_c from our analysis. At temperatures above 0.16 T_c, we believe the paramagnetic influence is less than in previous studies due to the difference in orientation of the sample. A similar paramagnetic upturn is not observed in the PCCO data due to the much weaker paramagnetism in this compound [7]. Thus, the PCCO data should more closely reflect the intrinsic behavior of $\lambda(T)$. A more detailed analysis of this data, and data on thin films, is forthcoming in which we conclude that our data fits best to a dirty d-wave model [12].

4. Discussion

Alff *et al.* recently obtained $\Delta\lambda(T)/\lambda(0)$ data on NCCO and PCCO grain boundary junctions in thin films [10]. They concluded that their data was consistent with an s-wave scenario. They applied the same paramagnetic correction to their NCCO data which Cooper used to arrive at a d-wave explanation [2]. This is evidence of how sensitive the final determination of the pairing-state symmetry is to the choice of parameters for the Curie-Weiss law. Although not shown here, we can also force our $\Delta\lambda(T)$ data for a number of PCCO crystals to fit to an s-wave form. In general however, this requires using unphysically small $\Delta(0)$ values, $2\Delta(0)/k_B T_c < 2$ [12]. Alff *et al.* reported a value for $2\Delta(0)/k_B T_c$ of about 2.9, which is less than the BCS value of 3.5. We believe that the $\Delta(0)$ and $\lambda(0)$ fit values exclude a standard BCS s-wave explanation.

However, there are some s-wave scenarios which might be viable. Gapless superconductivity could lead to T^2 behavior for $\Delta\lambda(T)$ at low temperatures. Also, the presence of magnetic impurities could potentially reduce the size of the activation gap. This could explain the small values for $\Delta(0)$ we obtain when fitting to an s-wave functional form. Nevertheless, the data is not consistent with a large-gap isotropic BCS s-wave behavior.

5. Conclusion

We have employed a microwave resonant cavity system to measure $\lambda(T)$ and $R_S(T)$ for NCCO and PCCO crystals down to 1.2 K. This data supports the conjecture that rare-earth paramagnetism affects the observed $\lambda(T)$ behavior in NCCO. By analyzing the functional form of the $\lambda(T)$ temperature dependence, we conclude that the pairing symmetry of the electron-doped cuprate superconductors is neither a standard, nor a large-gap s-wave, and that other pairing symmetries should be considered.

REFERENCES

1. D. H. Wu *et al.*, Phys. Rev. Lett. **70**, 85 (1993).
2. J. R. Cooper, Phys. Rev. B **54**, R3753 (1996).
3. J. L. Peng, Z. Y. Li, and R. L. Greene, Physica C **177**, 79 (1991).
4. S. M. Anlage *et al.*, Phys. Rev. B **50**, 523 (1994).
5. E. Maiser *et al.*, Physica C **297**, 15 (1998).
6. L. V. Mercaldo, V. V. Talanov, and S. M. Anlage, to be published in Physica C, cond-mat/9912418; see also R. J. Ormeno, C. E. Gough, and G. Yang, submitted to Phys. Rev. B, cond-mat/0001379.
7. Y. Dalichaouch, M. C. de Andrade, and M. B. Maple, Physica C **218**, 309 (1993).
8. C. W. Schneider *et al.*, Physica C **233**, 77 (1994).
9. A. Andreone *et al.*, Phys. Rev. B **49**, 6392 (1994).
10. L. Alff *et al.*, Phys. Rev. Lett. **83**, 2644 (1999).
11. R. Prozorov *et al.*, to be published in Physica C, cond-mat/9912001; R. Prozorov *et al.*, submitted to Phys. Rev. Lett., cond-mat/0002301.
12. J. D. Kokales *et al.*, submitted to Phys. Rev. Lett., cond-mat/0002300.