Anomalous Low Temperature Behavior of Superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-y}$

L. Alff,[1] S. Meyer,[1] S. Kleefisch,[1] U. Schoop,[1] A. Marx,[1] H. Sato,[2] M. Naito,[2] and R. Gross[1]
[1]*II. Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, D-50937 Köln, Germany*
[2]*NTT Basic Research Laboratories, 3-1 Morinosato Wakamiya, Atsugi-shi, Kanagawa 243, Japan*
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We have measured the temperature dependence of the in-plane London penetration depth $\lambda_{ab}(T)$ and the maximum Josephson current $I_c(T)$ using bicrystal grain boundary Josephson junctions of the electron-doped cuprate superconductor $Nd_{1.85}Ce_{0.15}CuO_{4-y}$. In contrast to the usual monotonous decrease (increase) of $\lambda_{ab}(T)$ [$I_c(T)$] with decreasing temperature, $\lambda_{ab}(T)$ and $I_c(T)$ are found to increase and decrease, respectively, with decreasing temperature below 4 K. We attribute this anomalous behavior to the presence of the Nd^{3+} paramagnetic moments. Correcting the measured $\lambda_{ab}(T)$ dependence for the temperature dependent susceptibility due to the Nd moments, an exponential dependence is obtained indicating isotropic s-wave pairing.

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The vast majority of experiments on the cuprate superconductors are performed on hole-doped materials. Much less attention has been paid to the system $Ln_{2-x}Ce_xCuO_{4-y}$ (with Ln = Pr, Nd, Sm, and Eu) [1] which represents an electron-doped material. Both hole- and electron-doped cuprates have in common the copper oxygen planes as the central building blocks of the high temperature superconductors (HTS) suggesting similar superconducting properties. However, as can already be seen from the differences of the generic phase diagram on the electron- and hole-doped side, the physics of electron- and hole-doped HTS is different. In particular, the order parameter (OP) symmetry of the electron-doped cuprates is most likely of the s-wave type [2–5], in contrast to the d-wave OP symmetry in the hole-doped HTS. To clarify the specific differences and similarities between the electron- and hole-doped HTS a more detailed experimental study of the electron-doped HTS is required.

Among the electron-doped materials, up to now $Nd_{2-x}Ce_xCuO_{4-y}$ has been the most intensively investigated material. This system is also remarkable because of the significant influence of the magnetic moment of the Nd^{3+} ions, whereas in $Pr_{2-x}Ce_xCuO_{4-y}$ the Pr^{3+} ion has a singlet nonmagnetic crystalline electric field ground state. It is well known that the specific heat C_p of $Nd_{2-x}Ce_xCuO_{4-y}$ shows a Schottky anomaly at low temperatures and low Ce doping levels. This anomaly is attributed to the splitting of the Nd-4f ground-state doublet due to interactions between the Nd moments and the ordered Cu moments [6]. Surprisingly, a C_p anomaly also was found for $x = 0.15$, even though no Cu ordering is observed for a Ce concentration above $x \approx 0.14$ [7]. Compared to the Schottky anomaly at low Ce doping levels this anomaly is shifted to lower temperatures and is considerably broadened. Furthermore, the observed large value of the linear specific heat coefficient γ at temperatures below 1 K is still controversially discussed in terms of a novel type of heavy-fermion behavior [8] and, alternatively, in terms of magnetic Nd excitations [9,10]. Nevertheless, it seems reasonable to assume that at high Ce doping levels the Nd-Cu exchange is strongly reduced and Nd-Nd interactions become more important inducing antiferromagnetic coupling along the c direction [9].

In this Letter, we report on the investigation of the influence of the Nd magnetic moments on the superconducting properties of the fully oxygen reduced compound $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (NCCO) with $x = 0.15$ having a maximum critical temperature $T_c \approx 24$ K. We measured the T dependence of the in-plane London penetration depth λ_{ab}, of the maximum Josephson current I_c, as well as of the energy gap Δ using bicrystal grain boundary Josephson junctions (GBJs). The advantage of the use of GBJs is that all three measurements can be done using the same sample thereby eliminating effects of different sample quality in the measurement of the different quantities. In order to clearly establish the effect of the Nd moments on the measured quantities comparative experiments have been performed on $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ (PCCO). The basic result of our measurements is that for NCCO both $\lambda_{ab}(T)$ and $I_c(T)$ show pronounced anomalies below about 4 K, whereas such anomalies are absent for PCCO. The $\lambda_{ab}(T)$ data of both NCCO, after being corrected for the influence of the Nd moments, and PCCO are consistent with an isotropic s-wave OP. For $4\text{ K} < T < T_c$ the superconducting properties of NCCO and PCCO are similar suggesting that at low T the influence of the Nd^{3+} moments causes the difference between the two materials. The observation that $\Delta(T)$ derived from tunneling spectra is almost identical for both materials between 2 K and T_c indicates that the Nd moments are not coupled to the superconducting electron system by conduction mediated processes. More likely, the Nd-Nd interactions affect the superconducting properties of NCCO only through relatively weak dipolar terms as has already been discussed, e.g., in the case of the hole-doped system $GdBa_2Cu_3O_{7-\delta}$ [11]. The observation of a decreasing I_c with decreasing T in NCCO Josephson

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junctions is a completely new effect that is believed to be also associated with the Nd magnetic moments.

The NCCO and PCCO GBJs were fabricated by the deposition of c-axis oriented NCCO and PCCO thin films on $SrTiO_3$ bicrystal substrates with misorientation angles of 7°, 10°, and 24° using molecular beam epitaxy. A detailed description of the fabrication process was given by Naito *et al.* [12]. Josephson behavior in NCCO GBJs has been demonstrated by Kleefisch *et al.* [13]. We stress that the demonstration of the Josephson effect for both NCCO and PCCO, the low resistivity values (below 50 $\mu\Omega$ cm at 25 K), and the T_c value of about 24 K demonstrate that the thin film samples are optimum doped, well oxygen reduced, and single phase. This is important with respect to the possibility of inhomogeneous dopant distribution or the formation of different phases which is more difficult to control for large bulk single crystals.

The maximum Josephson current I_c of the GBJs was determined by a standard four probe technique in a magnetically shielded environment. The measurement of $\Delta\lambda_{ab}$ is based on the measurement of I_c as a function of an applied magnetic field $H \| c$. GBJs formed in different HTS have been successfully used to determine the relative change

$$\frac{\Delta\lambda_{ab}(T)}{\lambda_{ab}(T=0)} = \frac{\lambda_{ab}(T) - \lambda_{ab}(T=0)}{\lambda_{ab}(T=0)}$$

of the in-plane London penetration depth λ_{ab} with the high precision of below 1 Å. In this technique the shift of the sidelobes of the $I_c(H)$ pattern of small Josephson junctions is measured as a function of T. Details of this measurement technique have been described elsewhere [14].

In Fig. 1 the relative change of λ_{ab} is plotted versus temperature. For PCCO, $\lambda_{ab}(T)$ behaves exponentially at low T following $\Delta\lambda_{ab}(T) \propto \sqrt{\Delta/T}\exp^{-\Delta/k_BT}$ as expected for a BCS-type isotropic s-wave superconductor [15]. In contrast, for a d-wave superconductor, the nodes in the OP cause a linear behavior $\Delta\lambda_{ab}(T) \propto T/\Delta$ [16]. This linear behavior has been observed for hole-doped HTS using the method described above [14]. A d-wave behavior clearly is not consistent with the $\Delta\lambda_{ab}(T)$ data measured for PCCO. We note that irrespective of the detailed OP symmetry, a *monotonous* $\Delta\lambda_{ab}(T)$ dependence is expected in clear contrast with the result obtained for NCCO below about 4 K.

In Fig. 2, $J_c(T)$ is plotted for NCCO and PCCO GBJs. Whereas a monotonous increase of $I_c(T)$ with decreasing T is found for PCCO, for NCCO I_c is found to decrease again at low T. A monotonous $I_c(T)$ dependence as found for PCCO GBJs is also observed for GBJs fabricated from the hole-doped HTS.

In order to interpret our NCCO data, at first sight it is tempting to assume a reduction of the superconducting OP with decreasing T due to enhanced pair beaking by magnetic scattering, e.g., similar to the ternary molybdenum chalcogenides (Chevrel phases) [17]. Then, a reduced superfluid density n_s could be the origin of the observed anomalies because of $J_c \propto n_s$ and $\lambda_{ab}(T) \propto 1/\sqrt{n_s}$. However, in tunneling measurements performed on the same samples no significant change of the gap value is observed at low T both for NCCO and PCCO. Moreover, the tunneling conductance G at zero bias still decreases when T is lowered from 4 to 2 K as shown in Fig. 3. These experimental facts give strong evidence against the assumption of reduced n_s or Δ as the origin of the observed anomalies.

Next we briefly discuss whether the observed anomalies in $\lambda_{ab}(T)$ and $I_c(T)$ can be caused by a d-wave OP. It has been both theoretically predicted and experimentally observed that $\lambda_{ab}(T)$ can increase with decreasing T due to so-called anti-Meissner currents related to Andreev bound states [18,19]. However, assuming $d_{x^2-y^2}$ symmetry of the OP the maximum spectral weight of such bound states is expected for interfaces close to the (110) orientation. As a consequence this effect has been observed only in large angle grain boundaries [18], whereas the T dependence of $\Delta\lambda_{ab}(T)$ for small misorientation angles ($\theta \lesssim 24°$) was found to behave linearly as expected for a d-wave OP [14]. Furthermore, the YBCO GBJs showing

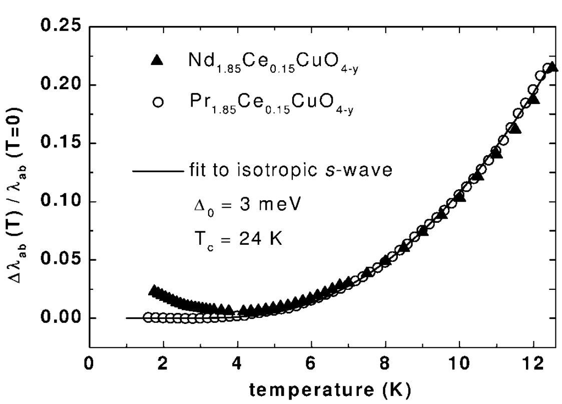

FIG. 1. Relative change $\Delta\lambda_{ab}$ of the London penetration depth in NCCO and PCCO as a function of temperature measured for a symmetrical, 10° [001] tilt GBJ.

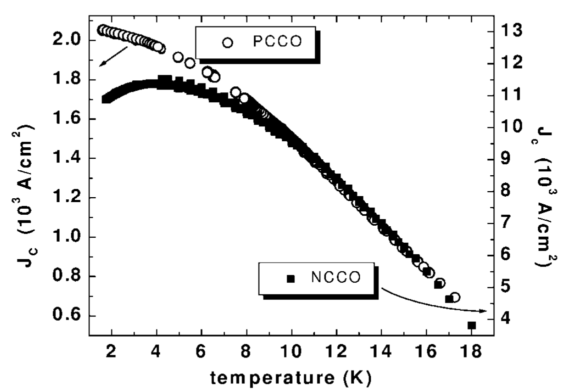

FIG. 2. Critical Josephson current density J_c vs temperature for symmetrical, 10° [001] tilt NCCO and PCCO GBJs.

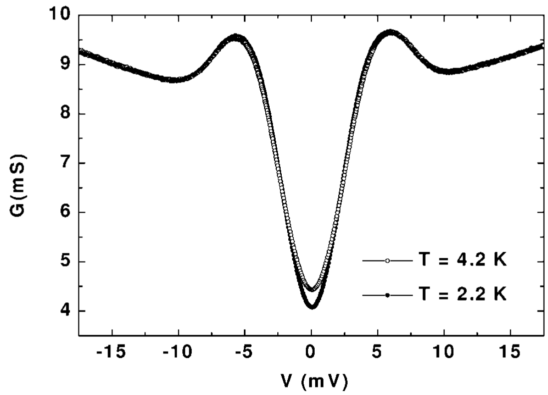

FIG. 3. Tunneling conductance vs voltage of a symmetrical, 24° [001] tilt NCCO GBJ at 4.2 and 2.2 K.

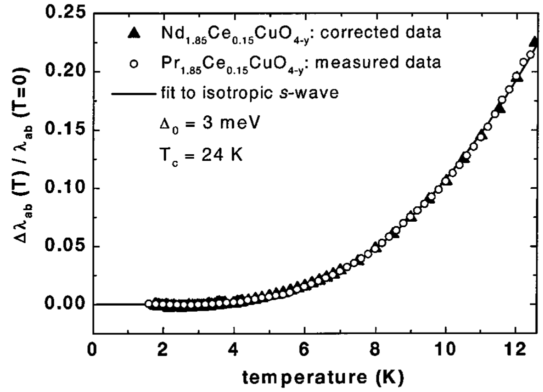

FIG. 4. $\Delta\lambda_{ab}(T)/\lambda_{ab}(0)$ for NCCO and PCCO. The NCCO data are corrected as described in the text.

this kind of anomaly in $\lambda_{ab}(T)$ also show a $I_c(H)$ pattern that strongly deviates from a Fraunhofer pattern and has the maximum I_c value shifted to $H \neq 0$. This indicates the presence of negative currents due to the d-wave symmetry of the OP in the electrodes [20]. In contrast, the $I_c(H)$ patterns of NCCO and PCCO GBJs are close to a regular Fraunhofer diffraction pattern expected for an ideal Josephson junction [13]. Finally, the tunneling spectra measured for NCCO do not show any zero bias anomaly giving strong evidence for the absence of a sign change in the superconducting pair potential [5,18,21]. These experimental facts exclude both a $d_{x^2-y^2}$ and d_{xy} symmetry of the OP for NCCO and PCCO.

We now discuss the influence of the Nd magnetic moments on the measured T dependence of the London penetration depth of NCCO. The anomaly in the $\Delta\lambda_{ab}(T)$ dependence of NCCO can be understood by taking into account the effective magnetic moment of the Nd^{3+} ions as recently proposed by Cooper [22]. The measured paramagnetic susceptibility χ of NCCO with the magnetic field applied parallel to the c axis fits to a Curie-Weiss law $\chi(T) = \chi_0 + C/(T + \Theta)$, where C is the Curie constant and Θ the Curie-Weiss temperature [23]. This results in a magnetic permeability $\mu(T) = 1 + 4\pi\chi(T) \approx 1 + \text{const}/(T + \Theta)$. In our analysis we assume that this dependence holds down to $T \approx 2$ K with $C \approx 0.2$ emu K/mol Nd (corresponding to an effective moment of about $1.2\mu_B$ per Nd^{3+} ion). The effect of the strong T dependence of the magnetic susceptibility on $\lambda_{ab}(T)$ is as follows: On the one hand, the solution of London's equation shows that the measured penetration depth has to be multiplied by the additional factor $\sqrt{\mu(T)}$ in order to reveal the London penetration depth mirroring the superfluid density n_s. On the other hand, for the maximum Josephson current the flux density $\mathbf{B} = \mu(T)\mu_0\mathbf{H}$ threading the GBJ is relevant. Hence, in total, for our experimental method the measured penetration depth has to be divided by $\sqrt{\mu(T)}$ to reveal the intrinsic penetration depth reflecting n_s. As can be seen from Fig. 4, the anomaly in $\lambda_{ab}(T)$ can be entirely attributed to the influence of the T dependent permeability due to the Nd moments. After correcting the NCCO data they coincide with the PCCO data supporting the validity of the data correction. The intrinsic penetration depth derived in this way can be well fitted to the exponential T dependence of an isotropic s-wave superconductor. Assuming a d-wave OP no reasonable fit could be obtained. We note that this result is in clear contrast to the recent conclusion of Cooper who suggested that $\lambda_{ab}(T)$ of NCCO might be consistent with a d-wave OP after data correction. In contrast, our data for both NCCO and PCCO are clearly consistent with an isotropic s-wave symmetry of the OP. We further note that there is still a discrepancy between tunneling measurements suggesting an *an*isotropic s-wave OP for NCCO [18,21] and the present $\Delta\lambda_{ab}(T)$ measurements indicating an almost isotropic s-wave OP for both NCCO and PCCO. However, both measurements are clearly *not* consistent with a d-wave OP in the electron-doped HTS.

We finally discuss the anomalous behavior of $I_c(T)$ for NCCO GBJs. As shown in Fig. 2, I_c is reduced by about 15% at 2 K as compared to the value extrapolated from the $I_c(T)$ dependence at higher T. An equivalent reduction would be obtained by applying a magnetic field of about 0.2 G. Since the anomalous $I_c(T)$ dependence is absent for the PCCO GBJs, it is natural to attribute this effect also to the presence of the Nd magnetic moments. However, at present we have no conclusive theoretical understanding of the origin of the $I_c(T)$ anomaly. From neutron scattering experiments in NCCO with high Ce doping levels it has been concluded that a short-range order of the diluted Nd moments is gradually established over a large temperature range with no clearly defined Néel temperature [9]. Unfortunately, until now it is unclear whether the NCCO samples used for neutron scattering were fully oxygen reduced and whether a possible Nd ordering can create a small effective magnetic field reducing I_c. Another possibility is the creation of an effective field at the grain boundary interface due to disorder. To clarify the detailed origin of the anomalous $I_c(T)$ dependence, experiments directly probing the magnetic interactions in the optimum superconducting compound are desirable. Also, the possible presence of magnetic flux in the grain boundary region might be checked by comparative scanning SQUID measurements on NCCO and PCCO GBJs. We finally note that our measurement cannot exclude the possibility of a coupling of the Nd spin system to the conduction electrons at still lower temperatures ($T < 1$ K) [8]. We also would like to point out that anomalous $\Delta\lambda_{ab}(T)$ and $I_c(T)$ dependencies are expected for magnetic rare-earth substituted hole-doped HTS [24]. However, in contrast to NCCO the corrected $\Delta\lambda_{ab}(T)$ data are expected to be consistent with a $d_{x^2-y^2}$-wave symmetry of the OP.

As a consequence of the anomalous low T behavior of NCCO it is evident that $Nd_{2-x}Ce_xCuO_{4-y}$ is not well suited for a detailed comparison of the superconducting properties of electron-doped to the corresponding hole-doped cuprate superconductors. This is, in particular, important for measurements of $\lambda_{ab}(T)$ and conclusions drawn from such measurements with respect to the symmetry of the OP. In this context some recent measurements have to be reinterpreted. For comparative measurements of the penetration depth of hole- and electron-doped HTS at $T < 4$ K, the Pr doped compound certainly is the better choice. However, there is no problem with the results of tunneling measurements. It has been shown that there is no qualitative difference in the tunneling spectra between NCCO and PCCO for $2\text{ K} < T < T_c$ [5,18].

In conclusion, we have observed an anomalous low temperature dependence of the in-plane London penetration depth and the maximum Josephson current of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ GBJs. The absence of the anomalous behavior in $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ GBJs strongly suggests that the anomalies observed for NCCO are caused by the Nd^{3+} magnetic moments. The anomalous $\lambda_{ab}(T)$ dependence is in good agreement with theoretical predictions based on a Curie-Weiss-type temperature dependence of the magnetic susceptibility of NCCO affecting the measurement of $\lambda_{ab}(T)$. A possible d-wave order parameter symmetry in NCCO that also could account for an anomalous behavior can be excluded. In contrast, our $\lambda_{ab}(T)$ data are consistent with an isotropic s-wave order parameter for both investigated electron-doped HTS.

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