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Phase Diagram of the Electron-Doped $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ Cuprate Superconductor from Andreev Bound States at Grain Boundary Junctions

M. Wagenknecht,^{*} D. Koelle, and R. Kleiner

Physikalisches Institut—Experimentalphysik II and Center for Collective Quantum Phenomena, Universität Tübingen, Auf der Morgenstelle 14, D-72076 Tübingen, Germany

S. Graser and N. Schopohl

Institut für Theoretische Physik, Universität Tübingen, Auf der Morgenstelle 14, D-72076 Tübingen, Germany

B. Chesca

Department of Physics, Loughborough University, Loughborough, Leics LE11 3TU, United Kingdom

A. Tsukada

NTT Basic Research Laboratories, 3-1 Morinosato Wakamiya, Atsugi-shi, Kanagawa 243, Japan

S. T. B. Goennenwein and R. Gross

Walther-Meissner-Institut, Bayerische Akademie der Wissenschaften, Walther-Meissner Strasse 8, D-85748 Garching, Germany
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We use quasiparticle tunneling across $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ grain boundary junctions to probe the superconducting state and its disappearance with increasing temperature and magnetic field. A zero bias conductance peak due to zero energy surface Andreev bound states is a clear signature of the phase coherence of the superconducting state. Hence, such a peak must disappear at or below the upper critical field $B_{c2}(T)$. For $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ this approach sets a lower bound for $B_{c2}(0) \approx 25$ T which is substantially higher than reported previously. The method of probing the superconducting state via Andreev bound states should also be applicable to other cuprate superconductors.

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Determining the magnetic field-temperature (B - T) phase diagram of high- T_c cuprates has been the focus of interest since the discovery of these materials. In contrast to conventional type II superconductors, where the B - T phase diagram basically consists of the Meissner phase, the Shubnikov phase and the normal state, the phase diagram of high- T_c cuprates is extremely rich, exhibiting a variety of vortex phases [1] and also a pseudogap region [2,3]. The transition between the superconducting state and the normal state, and thus the relation between the superconducting and the pseudogap states, is hard to determine, not only due to the large values of the upper critical field B_{c2} in the case of hole-doped cuprates, but also because of the presence of vortex liquid phases as well as strong fluctuation effects, leading to nonzero resistance well below B_{c2} . For the electron-doped cuprates $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ (PCCO) and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ resistive measurements [4] or the vortex Nernst signal [5–7] revealed $B_{c2}(0)$ values in the range of 7–10 T. For $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ (LCCO) an analysis of the vortex pinning strength yielded $B_{c2}(0) \approx 9$ T [8]. However, the various methods applied to determine B_{c2} often yield inconsistent results; see, e.g., the discussion in [4]. In this Letter we show that an analysis of Andreev bound states (ABS) causing a zero bias conductance peak (ZBCP) in the conductance spectra of cuprate grain boundary junctions (GBJs) yields a new lower bound for B_{c2}

which is—for the LCCO thin films investigated here—at least a factor of 2.5 above previous estimates.

ABS result from the constructive interference of Andreev reflected electron- and holelike quasiparticles [9]. If the quasiparticles experience a sign change of the superconducting order parameter upon reflection, ABS appear at the Fermi energy, giving rise to the ZBCP [10]. ABS-caused ZBCPs have been observed in hole-doped [11–15] and electron-doped [16–19] cuprates, where the sign change is due to the $d_{x^2-y^2}$ order parameter symmetry [20]. This type of ZBCP can be observed with GBJs [14,19] and with normal metal-superconductor junctions [11,12,14–18] or junctions between a conventional and a d -wave superconductor [21].

A ZBCP caused by ABS [22] relies on the phase coherence of the elementary excitations above the Cooper pairing ground state. It thus should vanish when the phase coherence is lost, i.e., at the transition between the superconducting state and the normal state. Such ZBCPs thus allow us to determine B_{c2} , or at least to give a reasonable lower bound, provided that the ZBCPs do not vanish far below B_{c2} , e.g., due to the formation of a vortex liquid or other effects like a (field induced) shift of ABS to larger energy. As we will see below, in the geometry used in our experiments an unsplit ZBCP is visible above the irreversibility line, allowing its use as a probe of the super-

conducting state. Note that the formation of ABS requires phase coherent regions only a few times the BCS coherence length in size. Thus such ZBCPs probe superconductivity on microscopic scales.

The 900 nm thin films for our study were deposited by molecular beam epitaxy [25] on SrTiO₃ symmetric ($\alpha_1 = -\alpha_2$, see inset of Fig. 2) [001]-tilt bicrystal substrates with a misorientation angle of 24° and 30°. All films had a Ce doping of $x \sim 0.08$ (slightly underdoped, $T_c \approx 29$ K). The samples were patterned by photolithography and Ar ion milling with junction widths ranging from 40 to 400 μm [26]. Transport data were collected with a current bias four point probe and magnetic fields applied parallel to the thin film c axis. $dI(V)/dV$ characteristics were measured with a lock-in amplifier (modulation frequency 1–5 kHz, modulation current $I_{ac} = 1\text{--}10$ μA) and subsequently calibrated with the numerical derivative of simultaneously recorded $I(V)$ curves. Unless indicated otherwise, the data shown below are all for the same 24° GBJ.

Figure 1 shows the resistivity $\rho(T)$ of a bridge structure not crossing the grain boundary, for $0 \text{ T} \leq B \leq 10 \text{ T}$. As for thin films of PCCO [27] and LCCO [28], the onset of T_c decreases with increasing B and the transition width is broadened. For $B > 6 \text{ T}$ the resistance remains nonzero for T down to 5 K, and for larger fields we observe an upturn in $\rho(T)$, as already reported previously [27,29]. We determine “transition temperatures” where the resistance of the (extrapolated) linear part of $\rho(T)$ [cf. dashed line in Fig. 1] has dropped to, respectively, 10%, 50%, and 90% of its normal state value, given by the intersection of the dashed line with the parabolic fit for $\rho(T)$ above 35 K. The corresponding transition fields B_{10} , B_{50} , and B_{90} , are shown further below in the B - T diagram of Fig. 4. Although the resistive transition broadens significantly,

FIG. 1 (color online). $\rho(T)$ of a LCCO thin film for $0 \text{ T} \leq B \leq 10 \text{ T}$ (in steps of 1 T). Dashed lines and full circles on the 6 T curve indicate determination of temperatures where the resistance has dropped to, respectively, 10%, 50%, and 90% of its normal state value (gray line). These values define the critical fields B_{10} , B_{50} , and B_{90} . The inset shows $\rho(T)$ at $B = 0$ up to 200 K with a parabolic fit (gray line).

these fields do not differ strongly at a given temperature and tend to extrapolate to a zero temperature value around 7 T, suggesting that $B_{c2}(0)$ is of this order. However, as we will discuss below, ZBCPs can be seen in much higher fields, suggesting, e.g., superconductivity below 12 K at 16 T.

Figure 2(a) shows quasiparticle tunneling spectra for a 24° GBJ, at 5 K for B up to 16 T. At $B = 0$ (i.e., in the residual field of the cryostat which is a few G), a clear gap structure, i.e., a suppression in the quasiparticle density of states, is observed, with symmetric coherence peaks at voltages $V_{\text{gap}} = \pm 9 \text{ mV}$. There is a small dip at voltages near $\pm 7 \text{ mV}$ which disappears at higher fields (at $B = 0$ the Josephson current is not yet completely suppressed; the dip may, e.g., be associated with cavity resonances pumped by ac Josephson currents). With increasing B the coherence peaks decrease and are strongly suppressed for $B > 6 \text{ T}$. For voltages well above V_{gap} the conductance increases linearly with voltage, cf. upper inset in (b), and is almost independent of B up to 6 T [30]. For $B > 6 \text{ T}$ the differential conductance strongly decreases due to the onset of resistance in the film adding voltage in series to the grain boundary. We note that (a) the film behaves Ohmic well above its resistive transition and (b) the conductance of the GBJ is essentially field independent for a bias above the coherence peaks. Thus, to a good approximation, one can determine (and subtract) the film resistance from the raw data via the additional voltage drop $R_{\text{film}}I$ occurring in the $I(V)$ curves at high fields and large bias currents. The rescaled dI/dV vs rescaled V in Fig. 2(b) shows that the conductance in the subgap region increases monotonically with increasing field. The integral over the tunnel conductance from -15 to 15 mV [cf. lower left inset in Fig. 2(b)] is, within experimental accuracy, field independent; i.e., the density of states is conserved.

The quasiparticle tunneling spectra of our samples also show a ZBCP, consistent with optimally doped LCCO GBJs [19]. At $T = 5 \text{ K}$ the ZBCP persists up to the highest fields achievable with our setup. The ZBCP can already be seen clearly in the uncorrected data, cf. inset of Fig. 2(a). We saw similar ZBCPs in 15 out of 19 samples both on 24° and 30° substrates.

Figure 3 shows the evolution of the ZBCP as a function of T at $B = 16 \text{ T}$ (a), and as a function of B at $T = 13 \text{ K}$ (b). Data are shown by thick black lines. The thin lines represent parabolic fits to the background quasiparticle conductance at low voltages. At $B = 16 \text{ T}$ the ZBCP disappears between 11 and 12 K, while at $T = 13 \text{ K}$ it disappears between 13 and 14 T [32]. As the ZBCP disappears reproducibly for a given T or B while increasing B or T , respectively, we can follow the disappearance of the ZBCP in a B - T phase diagram, cf. Fig. 4. Full black symbols show the “critical” field B_{ZBCP} where the ZBCP area A_{ZBCP} has reached zero for two different samples (squares: 30° GBJ, circles: 24° GBJ). We determined A_{ZBCP} by integrating the difference of the measured quasiparticle spectra and the

FIG. 2 (color online). Quasiparticle conductance spectra of a 24° GBJ at $T = 5$ K for $0 \text{ T} \leq B \leq 16 \text{ T}$ in steps of 2 T. Graph (a) shows conductance as measured. In (b) the voltage across the leads appearing above 6 T has been subtracted. The inset in (a) shows an enlargement of the low bias region at 16 T. The upper inset in (b) shows the zero field conductance on a larger voltage scale at $T = 5$ K (black line) and at $T = 32$ K (gray line), where the ZBCP has disappeared. The lower left inset shows the integral over the conductance curves taken for voltages between ± 15 mV. The lower right inset in (b) illustrates the geometry of the bicrystal GBJ. Vortices are indicated by circles, screening currents by arrows.

parabolic background conductance [cf. Fig. 3] in the range ± 3 mV. As $A_{\text{ZBCP}}(B)|_{T=\text{const}}$ and $A_{\text{ZBCP}}(T)|_{B=\text{const}}$ decreases nearly linearly with increasing B and T [33], the intersection of the linear fits with the $A_{\text{ZBCP}} = 0$ axis defines B_{ZBCP} (with vertical and horizontal error bars, respectively, in Fig. 4). This procedure also allows us to determine B_{ZBCP} for $B > 16$ T from $A_{\text{ZBCP}}(B)|_{T=\text{const}}$ (see inset of Fig. 4 and gray circles in main graph). B_{ZBCP} increases monotonically with decreasing T , extrapolating to $B_{\text{ZBCP}}(T = 0) \approx 25$ T. The black and gray lines show $B_{c2}(T)$, obtained from microscopic calculations [with $T_c = 29$ K and $B_{c2}(0) = 25$ T], assuming either a 2D Fermi cylinder (black line) [34] or a 3D Fermi sphere (gray line) [35]. These lines may be considered as a lower bound for the true B_{c2} of our samples. Note that $B_{c2}(0) = 25$ T is at least a factor of 3.5 larger than the zero temperature extrapolation of B_{90} . One could argue that the upper criti-

FIG. 3 (color online). Quasiparticle conductance, corrected for the voltage across the leads, of a 24° GBJ near zero bias showing the disappearance of the ZBCP (a) at constant field $B = 16$ T for different T and (b) at constant temperature $T = 13$ K for different B . Thin lines are parabolic fits to the quasiparticle conductance outside the ZBCP.

cal field at the grain boundary is larger than its bulk value, e.g., due to local disorder or surface effects. Indeed, at a superconducting surface to free space the upper critical field can be 70% higher than in the bulk. However, the boundary conditions of the superconducting wave function at a grain boundary are much less restrictive, so that we do not expect a strong increase of the upper critical field over its bulk value [36].

FIG. 4. Magnetic field vs temperature phase diagram showing the fields B_{10} (open squares), B_{50} (open diamonds), and B_{90} (open triangles), as determined from $\rho(T)$ curves of Fig. 1, together with the field B_{ZBCP} where the ZBCP in the quasiparticle tunnel spectrum disappears. Black (gray) circles: 24° GBJ, measured (extrapolated) values; full squares: 30° GBJ. The black and the gray lines correspond to $B_{c2}(T)$, calculated for a 2D Fermi cylinder and a 3D Fermi sphere, respectively. The inset shows the ZBCP area vs B for different temperatures. Lines are linear fits, which, by extrapolation to zero ZBCP area, define values of B_{ZBCP} for $B > 16$ T.

Further, seeing that, say, at a field of 10 T, superconductivity sets in below 18 K or so, one could ask whether there is some feature on the corresponding ρ vs T curve in Fig. 1. Indeed, the low temperature increase of ρ seems to slow down below this temperature. A similar effect can also be seen in the other high field resistance curves, again indicating that the claimed high field superconductivity is not restricted to the vicinity of the grain boundary.

We should also discuss why we see a uniform ZBCP at all at large fields, without evidence for a splitting. In both the Meissner state and the vortex state a splitting would occur in the presence of strong screening currents near the grain boundary [37]. In the case of a symmetric *static* vortex configuration, the screening currents that flow along the grain boundary are of equal strengths but opposite direction, canceling the effect [cf. arrows in lower right inset in Fig. 2(b)]. In the case of a *fluctuating* vortex liquid, which is likely to be present in the high field region, the screening currents on the two sides of the GBJ will fluctuate, but are likely to have zero average. Thus again the energy shifts of the ABS (forming fast compared to the time scale of vortex fluctuations) will be washed out during the time of measurement, naturally explaining the experimental observation.

Returning to the quasiparticle tunneling spectra as shown in Fig. 2, we note that the coherence peaks are suppressed already at 50% of B_{c2} or so. This observation is consistent with calculations based on the quasiclassical Eilenberger equations of the density of states in the vortex state, cf. Fig. 5 of Ref. [38] where, at $0.5B_{c2}$ the coherence peaks are hardly visible.

In conclusion, we have shown that in the electron-doped cuprate $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ the superconducting state persists to substantially higher magnetic fields than reported previously. Particularly, a zero temperature extrapolation suggests that $B_{c2}(0)$ is at least 25 T. Extending superconductivity to such high fields shrinks the region where a pseudogap phase may exist. We have explored the B - T phase diagram via zero energy Andreev bound states. This method should be applicable to any superconductor where the superconducting order parameter changes sign, providing an effective additional tool to explore the superconducting state.

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*wagenknecht@uni-tuebingen.de

- [1] G. Blatter *et al.*, Rev. Mod. Phys. **66**, 1125 (1994).
- [2] A. Damascelli, Z. Hussain, and Z.-X. Shen, Rev. Mod. Phys. **75**, 473 (2003).
- [3] Ø. Fischer *et al.*, Rev. Mod. Phys. **79**, 353 (2007).
- [4] P. Fournier and R.L. Greene, Phys. Rev. B **68**, 094507 (2003).
- [5] F. Gollnik and M. Naito, Phys. Rev. B **58**, 11734 (1998).
- [6] H. Balci *et al.*, Phys. Rev. B **68**, 054520 (2003).
- [7] Y. Wang *et al.*, Science **299**, 86 (2003).
- [8] Y. Zuev *et al.*, Phys. Status Solidi (b) **236**, 412 (2003).
- [9] G. Deutscher, Rev. Mod. Phys. **77**, 109 (2005).
- [10] S. Kashiwaya and Y. Tanaka, Rep. Prog. Phys. **63**, 1641 (2000).
- [11] J. W. Ekin *et al.*, Phys. Rev. B **56**, 13746 (1997).
- [12] M. Covington *et al.*, Phys. Rev. Lett. **79**, 277 (1997).
- [13] L. Alff *et al.*, Phys. Rev. B **55**, R14757 (1997).
- [14] L. Alff *et al.*, Phys. Rev. B **58**, 11197 (1998).
- [15] J. Y. T. Wei *et al.*, Phys. Rev. Lett. **81**, 2542 (1998).
- [16] F. Hayashi *et al.*, J. Phys. Soc. Jpn. **67**, 3234 (1998).
- [17] A. Mourachkine, Europhys. Lett. **50**, 663 (2000).
- [18] A. Biswas *et al.*, Phys. Rev. Lett. **88**, 207004 (2002).
- [19] B. Chesca *et al.*, Phys. Rev. B **71**, 104504 (2005).
- [20] C. C. Tsuei and J. R. Kirtley, Rev. Mod. Phys. **72**, 969 (2000).
- [21] B. Chesca *et al.*, Phys. Rev. B **73**, 014529 (2006).
- [22] ZBCPs in the quasiparticle tunnel spectrum of superconductors can have other reasons than the formation of ABS, most prominent being the scattering of quasiparticles by magnetic impurities in the tunnel barrier [23,24]. Such competing mechanisms can be identified, however, e.g., by analyzing the temperature and magnetic field dependence of the ZBCP.
- [23] J. Appelbaum, Phys. Rev. Lett. **17**, 91 (1966).
- [24] P. W. Anderson, Phys. Rev. Lett. **17**, 95 (1966).
- [25] M. Naito and M. Hepp, Jpn. J. Appl. Phys. **39**, L485 (2000).
- [26] In fact, we used a SQUID design to investigate both Cooper pair tunneling at low magnetic fields (μT range) and quasiparticle tunneling at high fields (T range). For the measurements in high fields presented here Cooper pair tunneling plays no role.
- [27] S. Kleefisch *et al.*, Phys. Rev. B **63**, 100507(R) (2001).
- [28] A. Sawa *et al.*, Phys. Rev. B **66**, 014531 (2002).
- [29] P. Fournier *et al.*, Phys. Rev. Lett. **81**, 4720 (1998).
- [30] A similar linear increase of the background conductance at higher voltages also has been seen for other electron- or hole-doped cuprates, e.g., in [27,31].
- [31] Y. Dagan, M. M. Qazilbash, and R. L. Greene, Phys. Rev. Lett. **94**, 187003 (2005).
- [32] The disappearance of the ZBCP can also be seen on the raw data, essentially yielding the same value of B_{ZBCP} without subtracting the film resistance. For fields where the ZBCP has disappeared the corrected quasiparticle conductance looks parabolic at low bias and turns linear at larger bias without a clear sign of an additional suppression at low voltages due to a pseudogap state.
- [33] This linear decrease was observed for the high field range. For lower fields, A_{ZBCP} decreases nonlinearly, as it is expected for a ZBCP caused by ABS, cf. [19].
- [34] T. Dahm and N. Schopohl, Phys. Rev. Lett. **91**, 017001 (2003).
- [35] E. Helfand and N. R. Werthamer, Phys. Rev. **147**, 288 (1966).
- [36] R. G. Boyd, Phys. Rev. **153**, 444 (1967).
- [37] S. Graser *et al.*, Phys. Rev. Lett. **93**, 247001 (2004).
- [38] T. Dahm *et al.*, Phys. Rev. B **66**, 144515 (2002).