

## Possible pseudogap behavior of electron-doped high-temperature superconductors

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We have measured the low-energy quasiparticle excitation spectrum of the electron doped high-temperature superconductors (HTS)  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$  and  $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$  as a function of temperature and applied magnetic field using tunneling spectroscopy. At zero magnetic field, for these optimum doped samples no excitation gap is observed in the tunneling spectra above the transition temperature  $T_c$ . In contrast, below  $T_c$  for applied magnetic fields well above the resistively determined upper critical field, a clear excitation gap at the Fermi level is found which is comparable to the superconducting energy gap below  $T_c$ . Possible interpretations of this observation are the existence of a normal-state pseudogap in the electron doped HTS or the existence of a spatially nonuniform superconducting state.

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The existence of a pseudogap in hole doped high-temperature superconductors (HTS) has been established over the recent years. The physical origin of the pseudogap state, however, is still one of the most debated topics for HTS. For a recent experimental review see, e.g., Ref. 1. In different types of experiments including tunneling spectroscopy it has been found that the pseudogap feature with the superconducting energy gap merge smoothly into each other at the critical temperature  $T_c$ .<sup>2-6</sup> Even more, from angle-resolved photoemission experiments it has been suggested that the pseudogap has the same  $d_{x^2-y^2}$ -symmetry as the superconducting gap in the hole doped HTS.<sup>2,3</sup> It has also been observed that the temperature  $T^*$  associated with the appearance of the pseudogap state roughly becomes equal to  $T_c$  around optimum doping or in the slightly overdoped regime, but is considerably larger than  $T_c$  in the underdoped regime. The evident question arising from the experimental observations is whether or not there is a relation between the physical origin of the superconducting gap and the pseudogap. Such a scenario has been proposed within theories involving so-called preformed pairs or at least dynamical pair correlations above  $T_c$ .<sup>7</sup>

With respect to the different HTS materials, the hole doped system  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  seems to be a special case. For this material, the behavior of the pseudogap has been reported to be different compared to the other hole doped HTS, e.g., the size of the pseudogap might be much larger than the superconducting gap.<sup>8</sup> However, the experimental situation is not well settled and more experiments are needed to further clarify this point. For the electron doped HTS of the class  $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$  ( $\text{Ln}=\text{Nd}, \text{Pr}$ ) with  $T'$  structure, up to now no low-energy spectroscopic experiments probing the pseudogap state have been reported. There is no doubt that experiments on electron doped HTS are important and highly desired with regard to the question whether hole and electron

doped HTS have the same underlying mechanisms of superconductivity and the pseudogap state. Furthermore, controversial experimental results on the symmetry of the superconducting order parameter in the electron doped HTS have been published recently.<sup>9-12</sup> That is, both the symmetry of the order parameter and the question whether there is a normal state pseudogap are under discussion for electron doped HTS.

In this communication, we report on the measurement of the tunneling spectra in superconductor-insulator-superconductor junctions based on bicrystal grain boundary junctions (GBJ's). The temperature and magnetic-field dependence of the tunneling spectra has been studied up to 16 T for the optimum electron doped HTS  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$  (NCCO) and  $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$  (PCCO). While above  $T_c(B=0)$  no pseudogap feature could be observed, below  $T_c(B=0)$  a pseudogap around the Fermi level is clearly present for magnetic fields larger than the resistively determined critical field  $B_{c2}^p$ . This suggests that similar to the hole doped HTS, there is a pseudogap state also for the electron doped HTS. However, the presence of a nonuniform superconducting state may also be consistent with our observations.

The NCCO- and PCCO-GBJ's have been fabricated by the deposition of 200 nm thick,  $c$  axis oriented NCCO- and PCCO-films on  $\text{SrTiO}_3$  bicrystal substrates using molecular beam epitaxy (MBE). Only symmetric, [001] tilt bicrystals with misorientation angles of  $24^\circ$  and  $36^\circ$  have been used. The thin-film deposition has been described in detailed by Naito and Sato.<sup>13</sup> For bicrystal GBJ's with a junction area of about  $10^{-8}$   $\text{cm}^2$  a normal resistance ranging between 0.1 and 5  $\text{k}\Omega$  is obtained.<sup>14</sup> Josephson behavior in NCCO-GBJ's has been demonstrated recently by Kleefisch *et al.*<sup>14</sup> We stress that the observation of Josephson behavior for both NCCO and PCCO together with the low in-plane resistivity

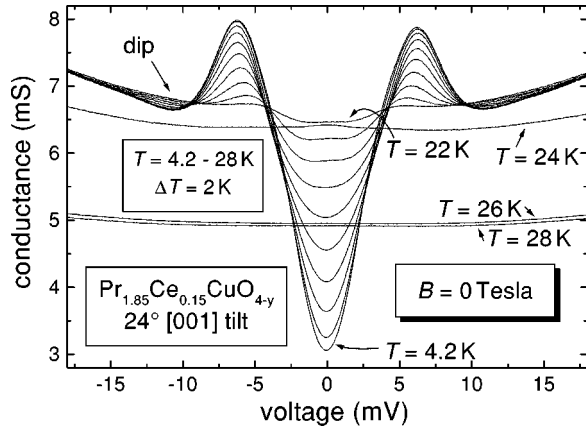


FIG. 1. Conductance vs voltage of a 24° [001] tilt PCCO-GBJ in zero applied magnetic field measured at different temperatures.

( $\rho_{ab} < 50 \mu\Omega\text{cm}$  at 25 K) of the films,  $T_c$  values of about 24 K, and the X-ray data demonstrate that our thin-film samples are optimum doped, well oxygen reduced, and single phase. This is important with respect to the possibility of an inhomogeneous dopant or oxygen distribution, or the formation of different phases. We note that such inhomogeneities are more difficult to be ruled out for large bulk single crystals.

In Fig. 1 quasiparticle tunneling spectra of a PCCO-GBJ are shown for temperatures between 4.2 and 28 K in zero magnetic field. Very similar spectra are obtained for NCCO. The superconducting gap clearly shows up in the spectra resulting in a large density of states peak at  $2\Delta$  (6.2 meV for PCCO and 5.8 meV for NCCO at 4.2 K). We note that the peak value itself corresponds to  $2\Delta$  only for a perfectly isotropic  $s$ -wave symmetry of the superconducting order parameter. Fitting the spectra to more anisotropic gap structures, larger values for  $\Delta$  up to 4 meV are obtained depending on the degree of anisotropy. Around  $V = \pm 10$  meV a dip structure is observed in the spectra that also has been seen in  $c$  axis tunneling in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ .<sup>5</sup> So far it is not clear whether this dip structure indicates strong coupling of the quasiparticles to collective excitations (as, e.g., phonons). Figure 1 shows that the states in the superconducting gap are filled up with increasing temperature. While for NCCO almost no change of the peak position is observed with increasing temperature, for PCCO there is a slight reduction. However, this reduction is much smaller than expected for  $\Delta(T)$  according to the BCS theory. The gap structure disappears at 24 K which corresponds to the  $T_c$  of the sample. Figure 1 also shows a temperature-independent background conductance of the GBJ that is parabolic in the low-energy regime, becomes linear for voltages above 20–30 mV, and stays about linear up to several 100 mV (not shown in Fig. 1).

Another way to probe the normal-state properties of a superconducting sample is to apply a magnetic field that is larger than its upper critical field. Following the experimental approach of Refs. 15 and 16, we have measured the magnetic-field dependence of the resistive transition of a PCCO epitaxial thin film with the magnetic field applied parallel to the  $c$  axis. As shown in Fig. 2, in a magnetic field of 1 T, the superconducting onset temperature is reduced and

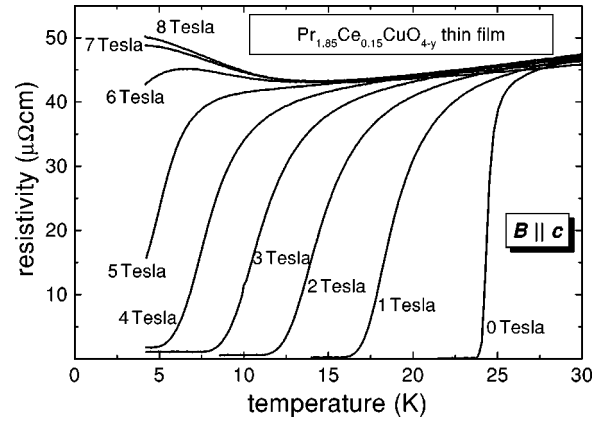


FIG. 2. Resistive transition of a  $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$  thin film sample at different applied magnetic fields.

the transition width is increased. On further increasing the applied field,  $\rho_{ab}(B, T)$  further shifts to lower temperatures, however, no further broadening of the superconducting transition is observed as it is the case, e.g., for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . From the data in Fig. 2 one can derive an upper critical field which is referred to as the resistive critical field  $B_{c2}^p(T)$ . The size of  $B_{c2}^p(T)$  depends on the chosen resistivity criterion. The functional form of  $B_{c2}^p(T)$ , however, seems to remain the same within our experimental resolution (see discussion below).

Figure 3 shows the quasiparticle tunneling spectra for NCCO measured at 2.2 K for magnetic fields between 0 and 16 T applied parallel to the  $c$  axis. The main effect of the applied field is the suppression of the density of states peaks at the superconducting gap feature and the filling of the gap at smaller voltages. Note that the position of the peaks does not change with varying applied magnetic fields, however, the peak amplitude decreases with increasing field and disappears at  $B_{c2}^p$ , which is about 5.6 T at 2.2 K. A key experimental finding is the fact that the gap feature itself remains clearly present even for the largest applied field of 16 T. This shows the *existence of a gapped state for  $B > B_{c2}^p$* .

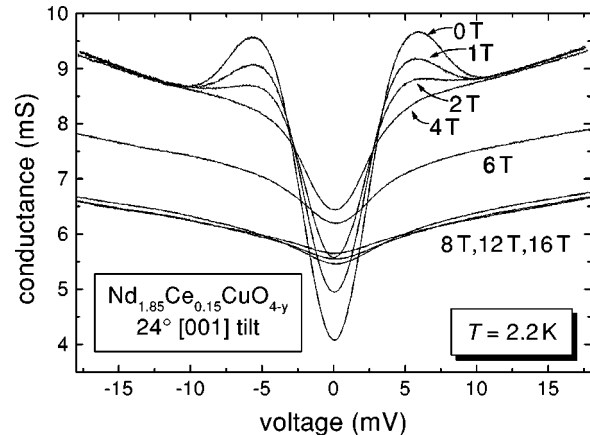


FIG. 3. Conductance vs voltage curves of a symmetric 24° [001] tilt NCCO-GBJ measured at 2.2 K in different applied magnetic fields applied parallel to the  $c$  axis.

While at 2.2 K the magnetic field needed to close the pseudogap feature is beyond the maximum field of 16 T available in our experiments, this is not the case for  $T > 7$  K. In this  $T$  regime, we can define a pseudogap critical field  $B_{c2}^{pg}$  that is sufficient to close the pseudogap feature. In Fig. 4 we show the temperature dependence of both  $B_{c2}^p$  and  $B_{c2}^{pg}$ . Although there is significant scatter in our data due to broadening, it is evident that  $B_{c2}^{pg}$  is by a factor of about 4 larger than  $B_{c2}^p$ . This observation holds for both NCCO and PCCO indicating that there is no major difference among these electron doped materials arising, e.g., from the magnetic moments of the  $\text{Nd}^{3+}$  ions in NCCO.<sup>11</sup> It is interesting to note that the functional form of the temperature dependence of both critical fields deviates strongly from a BCS-type temperature dependence of the upper critical field having negative curvature. The unusual positive curvature of  $B_{c2}^p(T)$  in Fig. 4 for NCCO has also been reported in Refs. 16 and 17, and, furthermore, has been observed in the hole doped HTS  $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ .<sup>15</sup> Recent measurements of  $\text{Bi}_2\text{Sr}_2\text{CuO}_x$  have shown that the curvature depends on the chosen resistivity criterion, becoming almost linear for a high resistivity criterion as expected for conventional type-II superconductors.<sup>18</sup> For our case, the curvature seems not to depend on the chosen criterion, however, for large fields and high resistivity criteria the evaluation of  $B_{c2}^p(T)$  becomes difficult due to the broadened  $\rho(T)$ .

While for the unusual behavior of  $B_{c2}^p(T)$  intrinsic origins have been proposed in the context of a quantum critical point at  $T=0$  (Ref. 19) and also within a bipolaron theory,<sup>20</sup> recently Geshkenbein *et al.* have suggested that inhomogeneous superconducting properties (as for example due to an inhomogeneous oxygen or dopant distribution) can cause the observed positive curvature of  $B_{c2}^p(T)$ .<sup>21</sup> In this case one has to assume regions with increased local  $T_c$  compared to the bulk  $T_c$ . Since in our case we are dealing with homogeneously reduced thin films close to the optimum doping level, an explanation based on inhomogeneous oxygen or dopant distribution is neither likely nor expected to change  $T_c$  considerably. However, intrinsically nonuniform superconductivity due to, e.g., phase separation cannot be ruled out. Any further discussion of these issues is beyond the scope of this communication.

We now address possible origins of the observed quasiparticle excitation gap structure observed below  $T_c$  for  $B_{c2}^p(T) < B < B_{c2}^{pg}(T)$ . Of course, it is tempting to assume that for electron doped cuprates there is a pseudogap feature with similar properties, as has been observed for the hole doped HTS. Then, according to our data the pseudogap in the electron doped HTS merges smoothly into the superconducting energy gap at  $B_{c2}^p$  in analogy to the experimental observation in Refs. 4–6 in that the pseudogap in the hole doped HTS merges into the superconducting gap at  $T_c$ . Moreover, in both cases the density of states peak in the tunneling spectra disappears at the transition from superconducting into the pseudogap state. We note that a recent  $c$ -axis tunneling study on  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  does not support the merging of the superconducting gap and the pseudogap.<sup>22</sup> A spatially non-uniform superconducting state with regions having locally

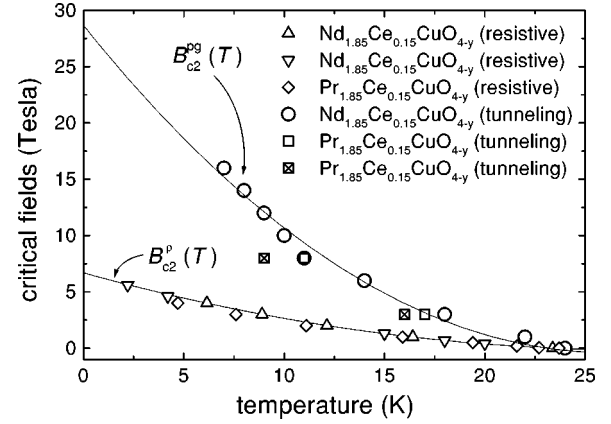


FIG. 4. Temperature dependence of the resistive critical field  $B_{c2}^p$  (full symbols) and the pseudogap critical field  $B_{c2}^{pg}$  (open symbols) for different samples of the electron doped HTS, NCCO, and PCCO. The solid lines are guides to the eye.

higher  $B_{c2}$  than the bulk could also produce a gaplike behavior in quasiparticle tunneling. However, as discussed above it is unclear how such regions can form within the optimum electron and oxygen doped compound.

We next discuss possible physical interpretations of the critical field  $B_{c2}^{pg}$ . Let us first assume that  $B_{c2}^{pg}$  is close to the thermodynamic critical field  $B_{c2}$ . Then, extrapolating  $B_{c2}^{pg}(T)$  to  $T=0$  yields  $B_{c2}(T=0) \approx 30$  T. Using the relation  $\xi_{ab}(0) = \sqrt{\Phi_0/2\pi B_{c2}(0)}$ , one derives  $\xi_{ab}(0) \approx 30$  Å. This value is similar to that obtained, e.g., for the hole doped HTS  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  but is significantly smaller than the usual value of about 70 Å in NCCO.<sup>17</sup> A smaller value of  $\xi_{ab}(0)$  would increase the importance of fluctuation effects in the electron doped HTS.<sup>7</sup> However, as can be seen from Fig. 2, in the resistivity vs temperature curves, the fluctuation regime is small and fields slightly above  $B_{c2}^p$  are sufficient to drive the films onto a weakly field-dependent semiconducting  $\rho_{ab}(T)$  curve. Moreover, the fluctuation analysis in Ref. 16 suggests that  $B_{c2}^p$  is not identical with the thermodynamic critical field  $B_{c2}$ , but cannot account for the difference by a factor of around 4 between  $B_{c2}^p$  and  $B_{c2}^{pg}$ . Last, we note that recently a very small value of  $\xi_{ab} \approx 6-9$  Å has been calculated assuming a spin-fluctuation pairing mechanism for both hole and electron doped HTS (Ref. 23) corresponding to an even higher value of  $B_{c2}$ .

Finally, at present there is no prediction for the magnetic-field dependence of the pseudogap even in the hole doped case. Assuming that the pseudogap is caused by the existence of so-called preformed pairs, the pseudogap state should be destroyed in magnetic fields exceeding the Clogston paramagnetic limit<sup>24</sup>  $B_p = \Delta/\sqrt{2}\mu_B$ . Taking into account corrections for a possible  $d$ -wave symmetry [ $B_p^d \approx 0.52\Delta/\mu_B$  (Ref. 25)], one obtains  $B_p \approx 30-40$  T using  $\Delta \approx 3.5$  meV obtained from our tunneling measurements. This value coincides well with  $B_{c2}^{pg}(T=0)$ . However, one would then also expect  $B_{c2}^{pg}(T) \propto \Delta(T)$  what is not supported by our data. In order to further clarify the experimental situation as well as to bring more insight into the nature of the superconducting and, in particular, the possible pseudogap

state in the electron doped HTS, more measurements at lower temperatures, higher fields, and for different electron doping levels, especially for the under(electron)doped case, are required.

In conclusion, tunneling spectroscopy performed on bicrystal GBJ's has revealed a pseudogap feature in the low-energy quasiparticle excitation spectrum of the electron doped HTS, NCCO, and PCCO. The pseudogap feature evolves from the superconducting gap in applied magnetic

fields above the resistive critical field  $B_{c2}^p$  and vanishes at a four-times-higher field  $B_{c2}^g$  which is close to the Clogston limit. These experimental observations suggest the existence of a pseudogap state also in the electron doped HTS. Further clarification of the pseudogap evidence for electron doped HTS is highly desired for a more general understanding of the physical origin of the pseudogap in the HTS.

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