

# Electron Doped Cuprates

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High temperature superconductivity in the copper-oxide ceramics obtains upon hole or electron doping the parent Mott insulating material. While the pairing symmetry of the order parameter in the hole-doped materials is well accepted to be of the  $d_{x^2-y^2}$ -type, the situation is far from settled in the electron-doped materials. This paper will analyze the evidence for a complex order in the electron doped materials and explore the possibility that a quantum phase transition exists at a critical doping. In addition, the "odd" occurrence of  $T^2$  electrical resistivity of the normal state of the electron-doped cuprates will be examined.

## Introduction

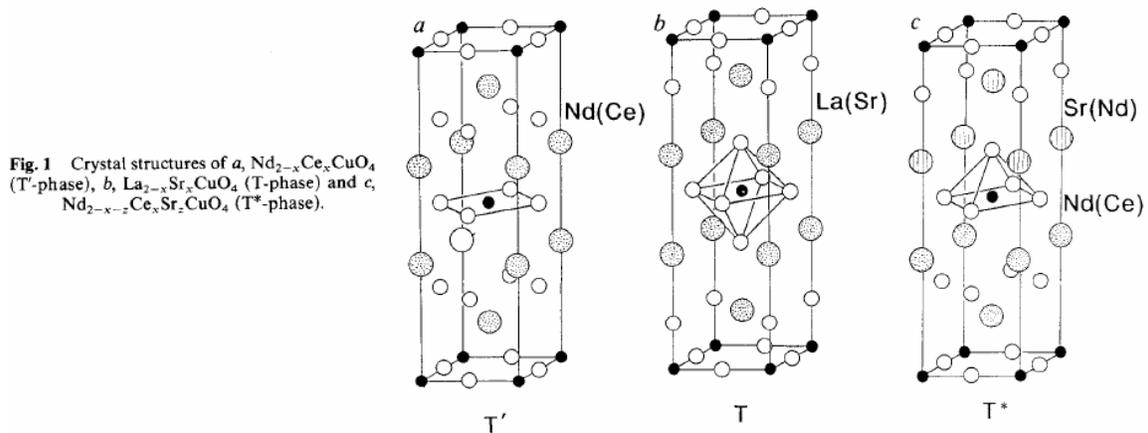
20 years ago J. Bednorz and K. Müller [1] discovered High-Tc superconductivity in hole-doped copper oxides (cuprates). Three years later Y. Tokura et al. [2] were the first to report a “superconducting copper oxide compound with electrons as the charge carriers”.

In spite of intense research on the High-Tc materials, the mechanism for superconductivity is still not yet understood. It is believed, that the copper-oxygen planes are the essential ingredient for superconductivity, which is obtained by hole- or electron-doping the parent mott-insulator. Additionally there is the hope, that the mechanism of high-Tc superconductivity has the same origin in hole- and electron-doped cuprates.

Therefore, the discovery of the electron superconductivity in cuprate compounds has significant implication for our understanding of the mechanism for High-Tc superconductivity. The investigation of these materials can test existing theories, and imposes significant constraints on new theories, that attempt to describe simultaneously all copper oxide superconductors.

## Crystal structure

The so called “electron-doped cuprates”  $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$  ( $\text{Ln} = \text{Nd, Pr, Sm, or Eu}$ ), possess the essential building block encountered in the cuprate family: the copper-oxygen planes. While the crystal structure of hole doped cuprates is found to be either of the T-phase-type (Cu-O octahedra) or T\*-phase type (Cu-O pyramids), the crystal structure of LnCCO is the T'-phase (See Fig. 1). The T'-phase is composed of sheets of Cu-O squares and has no apical oxygen atoms.

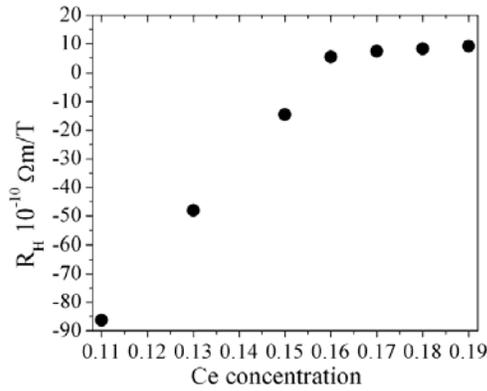


Because of this particular crystal structure, LnCCO can only be doped with electrons. The mobile electrons are introduced by replacing the trivalent lanthanide with  $\text{Ce}^{4+}$  and fill 3d holes on the copper atoms, thus converting some  $\text{Cu}^{2+}$  ions to  $\text{Cu}^+$  [3].

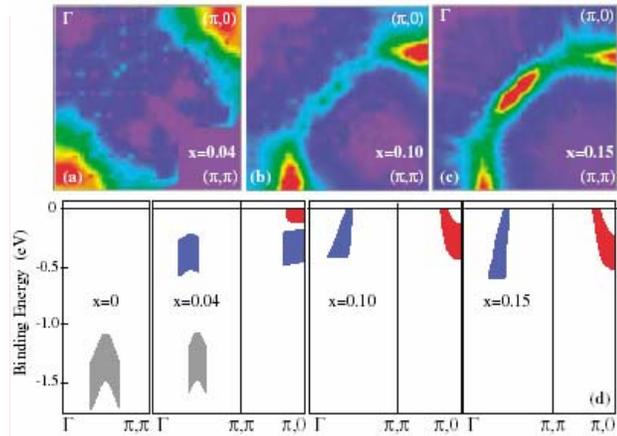
## Charge carriers and $T^2$ -resistivity

The nature of the charge carriers has been investigated in detail. It was initially believed, that the charge carriers are only electrons [2], [3] but improved experiment and samples claim to reveal both electrons and holes [4], [5], [6], [7].

Frequently the change of the sign of the hall coefficient [7] (Fig. 2) and the finding of an electron pocket, that evolves with doping into a large hole like Fermi surface in ARPES [8] (Fig. 3) are referred to prove the existence of the two charge carriers in n-doped cuprates.



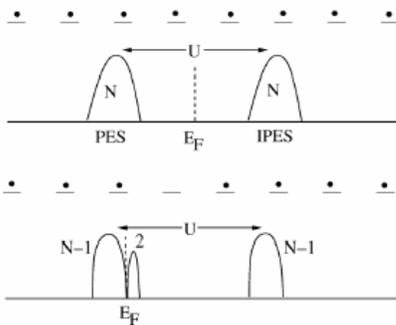
(Fig. 2)



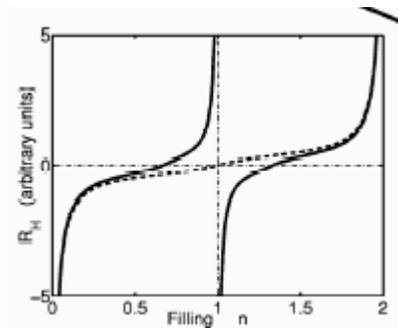
(Fig. 3)

But this is not enough to establish the existence of electrons and holes in n-doped cuprates!!!

The sign of the hall coefficient is directly linked to the sign of the charge carriers. For a closed electron like Fermi surface the hall coefficient is negative while for a hole like surface it is positive. Stanescu and P. Phillips [8] have shown that the change of the sign of the hall coefficient is a direct consequence of electron- or hole-doping a half filled mott-insulator. Upon hole-doping for example, the chemical potential moves through the lower Hubbard band (LHB) and spectral weight is removed from it (Fig. 4). When exactly half of the spectral weight is transferred locally particle-hole symmetry exists. Hence, the hall coefficient has to cross zero and change its sign.



(Fig. 4)

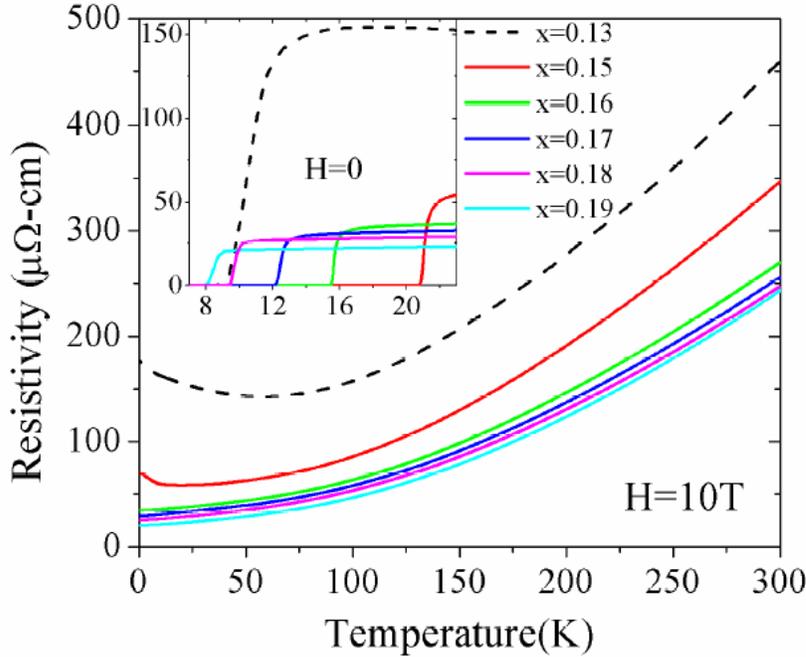


(Fig. 5)

For hole doping the lower bound for the doping can precisely be determined to  $n_h = 2/3$ . For electron doping the superior bound is  $n_{el} = 4/3$ . The change of sign in the hall coefficient is expected in n- and p-doped cuprates and experimentally verified in n-doped [6] and p-doped cuprates [9] and does not require by itself a two charge carrier explanation.

Additional transport data, more precisely, resistivity measurements, Nernst- and Seebeck-effect [4] and thermoelectric power [5] support the two charge carrier scenario. Comparing, for example, the Hall-angle  $\tan(\theta_H) = \rho_H/\rho$  with  $\tan(\theta_T) = E_{\text{Nernst}}/E_{\text{Seebeck}}$ , rules out a simple one conduction band scenario, which would predict  $\tan(\theta_H) = \tan(\theta_T)$ . Moreover Peng et al. [4] claim, that the superconducting samples ( $0.14 < x < 0.17$ ) are at the threshold where hole-conductivity starts to dominate. Therefore, holes seem to be an important ingredient for superconductivity.

The existence of two charge carriers can also explain the "odd" occurrence of  $T^2$  electrical resistivity [4] of the normal state (Fig. 6).



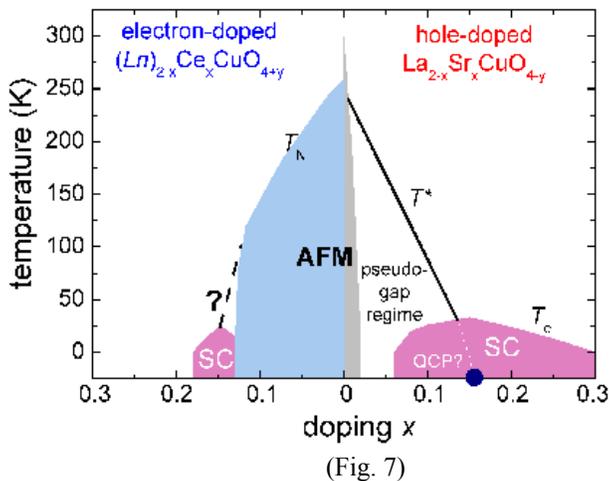
(Fig. 6)

It is commonly assumed that the  $T^2$  behavior is due to electron-hole-scattering [10]. But again the two charge carrier scenario is not the only explanation for that  $T^2$  behavior. For example electron-electron Umklapp-scattering also gives the  $T^2$ -law.

## Asymmetry of p- and n-doped cuprates

The  $T^2$  behavior and the existence of two types of carriers in electron doped cuprates are initially surprising because it differs from the well established linear  $T$  in hole-doped cuprates. But interestingly, several properties have been observed to be different in hole- and electron doped copper oxides:

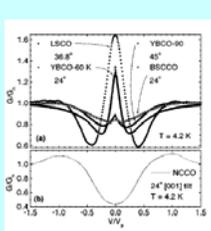
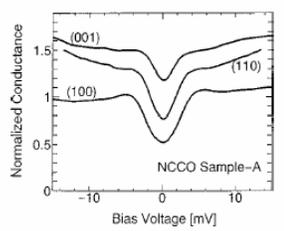
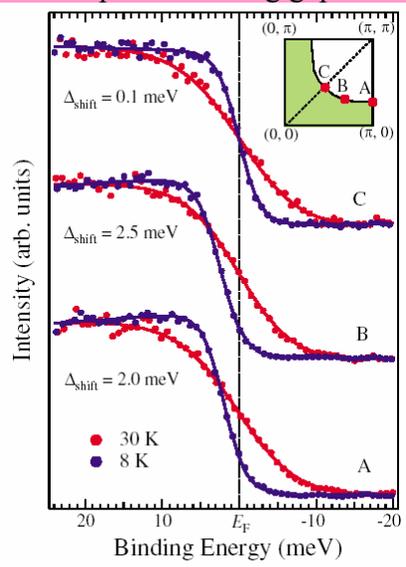
- As mentioned above the electrical resistivity of the normal state of electron-doped cuprates is known to follow a  $T^2$  behavior from  $T_c$  up to room temperature, while the hole-doped cuprates show linear resistivity.
- In n-doped cuprates, for the doping at which  $T_c$  is a maximum (optimal doping), the resistivity is metallic for both the ab-plane and c-axis. These particularly distinguish them from the p-doped cuprates, which show a non-metallic c-axis resistivity.
- $T_c$  is of the order 20 K [2] and therefore much smaller than in p-doped cuprates [1]
- The magnetic field  $H_{c2}$ , to suppress superconductivity in n-type cuprates, is about 10 Tesla [11]. Therefore the normal state of n-doped cuprates is easily accessible in experiments. In contrary,  $H_{c2} \geq 50$  Tesla in p-doped cuprates [12], and enormous magnets are needed to access the normal state.
- Another important issue is the nature of the superconducting state. While the pairing symmetry of the order parameter in the hole-doped materials is well established to be of the  $d_{x^2-y^2}$ -type [13], the situation is far from being settled in the electron-doped materials. The current situation will be presented in the following.



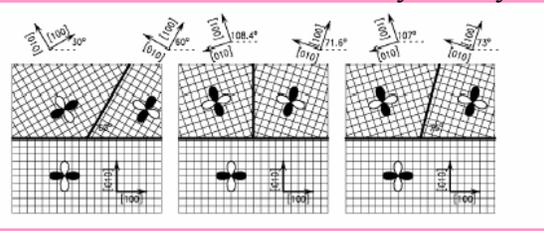
- Finally, the phase diagram of the cuprates reveals the asymmetry between n- and p-doping (Fig. 5). Hence, it is obvious, that every theory trying to describe High- $T_c$  superconductivity, has to possess a mechanism to break particle-hole symmetry!!!

## Gap symmetry

Early experiments on NCCO suggested, that the superconducting order parameter, the superconducting gap, has s-wave symmetry ([14]-[20]) like most conventional, low-Tc superconductors. However, later experiments, for example ARPES and Raman scattering ([21]-[27]), seemed to indicate d-wave symmetry in agreement with the hole-doped compounds. Chart 1 displays a summary of the experimental results.

<i>s- wave</i>	<i>d-wave</i>	
<ul style="list-style-type: none"> <li>• Penetration depth [14]-[17] The intrinsic penetration depth is best fitted to the exponential T-dependence of an isotropic s-wave superconductor. Especially the measured exponential flatness at low temperature suggests a gapped superconducting state.</li> </ul>	<ul style="list-style-type: none"> <li>• Penetration depth [21],[22] Cooper [28] suggested that the paramagnetic moment of the Nd could mask the power law dependence of the penetration depth, that is the indication of nodes in the order parameter. After correcting for that effect the authors find that the data is best fitted with a quadratic T-dependence. Further, the expected temperature dependence can change from T to T<sup>2</sup>, depending on the amount of impurity scattering which may be large in electron-doped cuprates (dirty d-wave” scenario). Linear T is consistent with nodes in the gap function.</li> </ul>	
<ul style="list-style-type: none"> <li>• Tunneling spectroscopy [18], [19] For d-wave symmetry, a pronounced zero bias conductance peak (ZBCP) has been predicted originating from midgap surface states or zero energy bound states (ZES) [18]. Quasiparticles incident and reflect from surfaces, propagate through the different order parameter fields, which leads to Andreev-reflection [29]. The constructive interference between incident and Andreev-reflected quasiparticles results in bound states. Stable ZES are formed if the scattering induces a sign-change of the order parameter, what is the case for d-wave symmetry but not for s-wave symmetry. Therefore the absence of the ZBCP in NCCO, which is clearly seen in different p-doped cuprates (Fig. 8 and 9), has been taken as strong evidence for s-wave pairing symmetry in n-doped cuprates.</li> </ul>	<ul style="list-style-type: none"> <li>• ARPES [23]-[25] A comparison of the leading edge midpoints between the superconducting and normal states reveals a small, but finite shift of 1.5-2 meV near the (π,0) position, but no observable shift along the zone diagonal near (π/2, π/2) (Fig. 11). This is interpreted as a direct observation of a nonmonotonic d_{x<sup>2</sup>-y<sup>2</sup>}-wave superconducting gap</li> </ul>	
 <p>(Fig. 8)</p>	 <p>(Fig. 9)</p>	 <p>(Fig. 11)</p>

• Tricrystal experiment [27]  
 A scanning SQUID microscope is used in a series of tricrystal experiments to produce definitive phase-sensitive evidence for d-wave pairing. The observation of the half-flux quantum effect serves as conclusive evidence for d-wave symmetry.



(Fig. 12)

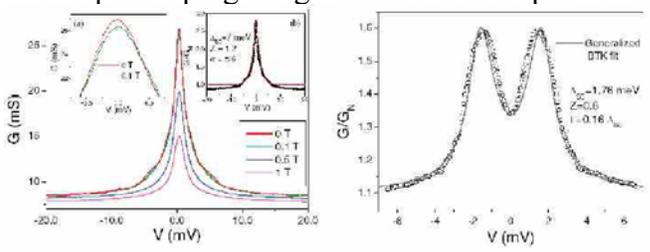
• Raman scattering [28]  
 The low temperature data for different scattering channels have been found to be consistent with a nonmonotonic  $d_{x^2-y^2}$ -type gap.

• Raman scattering [20]  
 In the early Raman data the measured  $B_{1g}$  and  $B_{2g}$  intensities do not differ by more than 5 to 10 wavenumbers. This indicates that the pair breaking is independent of direction in the FBZ. Hence, the early Raman measurements were interpreted as evidence for a nearly uniformly gapped Fermi surface consistent with an s-wave order parameter.

This obvious disagreement between the experiments, might be resolved by recent experiments [30-32], which indicate a transition from s- to d-wave symmetry:

• Penetration depth measurement [30]  
 Skinta et al. found that at low Ce doping level and low temperature  $\lambda^{-2}$  is quadratic in T but at higher doping shows activated behavior. The power law behavior in underdoped samples and exponential T dependence for optimally- and overdoped samples suggest a d- to s-wave pairing transition near optimal doping.

• Point contact tunneling [31]  
 Biswas et al. performed tunneling measurement for underdoped ( $x=0.13$ ) and overdoped ( $x=0.17$ ) PCCO samples. The measurement on the underdoped sample confirmed previous tunneling results [18], [19]. In contrary the over-doped samples show a pronounced zero bias conductance peak (Fig. 13), that implies a transition from d- to s-wave upon doping in agreement with the penetration depth data.



Underdoped sample with  $x=0.13$  Zero-bias peak characteristic for d-wave  
 Overdoped sample with  $x=0.17$  Double peak characteristic for s-wave (Fig. 13)

- Heat capacity [32]

Balci et al. performed heat capacity measurements on single PCCO crystals ( $x=0.15$ ) to probe the gap symmetry in the bulk of the superconductor. In a d-wave superconductor the dominant contribution to the specific heat in a magnetic field comes from the quasiparticle excitations close to the nodes of the order parameter. A linear magnetic field dependence is expected for the electronic heat capacity in an s-wave superconductor, whereas a non-linear field dependence ( $C_{el} \sim H^{1/2}$ ) is expected for a d-wave superconductor. The data shows a surprising change in the field dependence between non-linear at 4.5K to linear at 2K, and suggest a transition from s- to d-wave pairing with increasing temperature.

*This interpretation is particularly attractive since it has the potential of reconciling the results of many conflicting experiments. The SQUID, ARPES, and Raman [23]-[28] measurements, that suggested d-wave symmetry are almost exclusively performed above 4.2 K. On the other the hand penetration depth measurement that indicated s-wave symmetry [14]-[17] and point contact tunneling spectroscopy [18], [19] were performed below 2 K !!!*

- Theoretical explanation

The hot spot scenario of Khodel et al. [33] is an attempt to explain the experimental observations. The theory is based on a weak-coupling scenario in which the volume of the Fermi surface shrinks upon doping, and the possibility that antiferromagnetic spin fluctuation (ASF) peaked at the wave vector  $Q = (\pi, \pi)$  might account for d-wave superconductivity in the cuprates [34], [35].

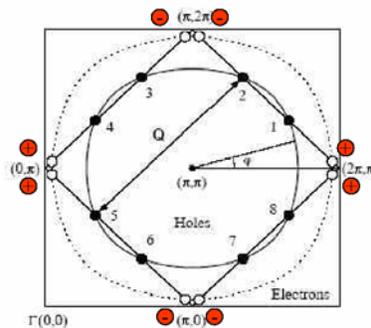
These fluctuations are observed in electron doped cuprates [36].

Hotspots are the points at the Fermi surface where the interaction via ASF is maximized, that is, the points where the Fermi surface cuts the magnetic Brillouin zone boundary (8 possible points). Assuming that the Fermi surface shrinks upon doping, the hotspots will be pulled together. To explain the transition from d-wave to another pairing symmetry two assumptions have to be made:

- $\Delta(p+Q) = -\Delta(p)$  (the interaction via ASF is repulsive in the singlet channel)
- the gap has the same sign within each pair of neighboring hotspots

**a) Hole doped case**

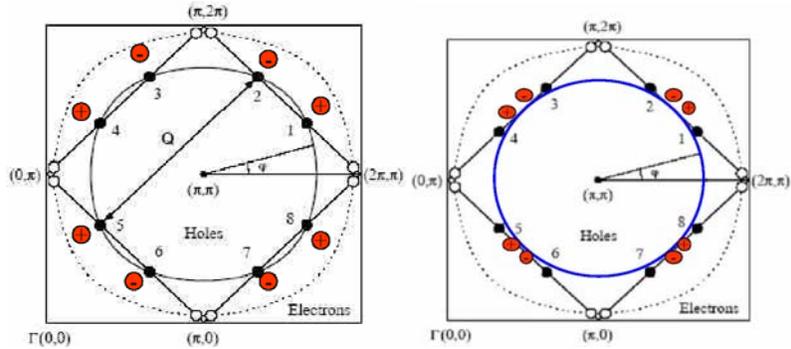
The large Fermi surface (dashed line in Fig.14) cuts the Brillouin zone close to the van Hove point  $(0, \pi)$ ,  $(\pi, 0)$ ,  $(2\pi, \pi)$  and  $(\pi, 2\pi)$ . The position of the hotspot represents the familiar  $d_{\{x^2-y^2\}}$ -symmetry of the pairing potential.



(Fig. 14) p-doped

### b) Electron doped case

The Fermi surface (solid line) is smaller and cuts with increasing doping closer towards the Brillouin zone diagonal. When the hot spots of opposite sign merge sufficiently, d-wave pairing is suppressed (Fig. 15b) and superconductivity of other pairing symmetries can emerge. Khodel et al, argue in favor of triplet p-wave pairing in disagreement with the experiments!!!



(Fig. 15a) low n-doped

(Fig. 15b) high n-doped

### Possibility of a quantum phase transition at a critical doping

To explain the phase diagram of the cuprates the idea of a quantum phase transition (QPT) between to competing phases near a critical doping has been introduced by several groups [37]-[41].

A QPT is a phase transition at zero temperature, where the physics is governed only by the quantum fluctuations demanded by Heisenberg's uncertainty principle. The transition takes place at the "quantum critical" value of some external parameter (in our case the doping).

At zero temperature both the spatial correlations  $\xi_s$  and temporal correlations  $\xi_t$  diverge and are related by  $\xi_t = \xi_s^z$ , where  $z$  is the dynamical exponent.

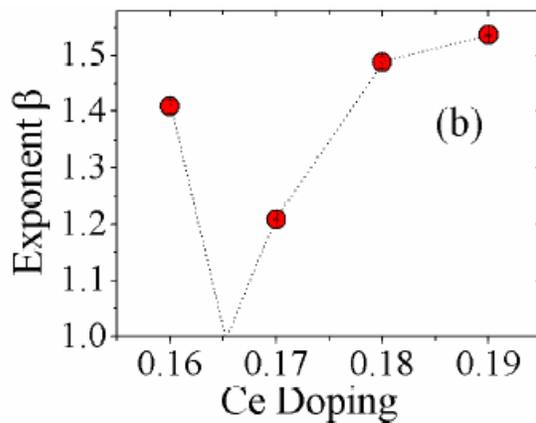
In the quantum critical region, the only energy scale is the temperature. Hence the scattering rate has to scale as  $1/\tau \sim T$ . If the current is carried by the quantum critical modes, then the resistivity is a linear function of temperature. This is why linear  $T$  is associated with quantum criticality.

Fournier et al. [42] were the first to report linear  $T$  resistivity from 10K down to 40mK in one of their over-doped PCCO films ( $x = 0.17$ ). But instead of linking this to a quantum critical scenario Fournier et al. interpreted this result as a strong evidence of electron-electron inelastic scattering in the normal state of the over-doped electron-doped cuprates.

Dagan et al. [43] performed detailed measurements of transport data (electrical resistivity and Hall coefficient) in electron doped cuprates, and interpreted their results as an evidence for a QPT at a critical doping near  $x = 0.165$ .

- Electrical-resistivity

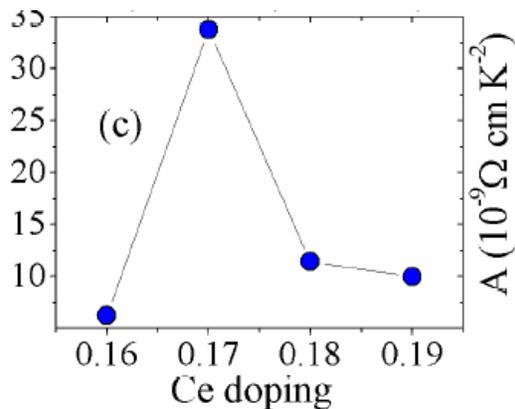
The resistivity was measured for different doping levels over a wide temperature-range. For very low and very high temperatures ( $T > 30\text{K}$ ) the  $T^2$  behavior was observed. In the intermediate region (0.35K to 20K) the resistivity deviates from the simple quadratic behavior and was fit to a power-law-behavior  $\rho(T) = \rho_0 + C T^\beta$  (Fig. 16).



(Fig. 16)

The exponent  $\beta$  has a strong doping dependence and gets closer to 1 as Ce doping decreases from 0.19 to 0.17, but increasing as the doping is further decreased to  $x = 0.16$ . Dagan et al. extrapolate from their data a doping near  $x = 0.165$  with  $\beta = 1$ , hence linear  $T$  resistivity. This seems to be in good agreement with Fournier's result ( $x = 0.17$ ).

To further support their argument the “very low” temperature data is fitted to  $\rho(T) = \rho_0 + AT^2$ . Assuming the continuity of the resistivity,  $A$  should diverge as one approaches a QCP. Fig. 17 shows a large increase in  $A$  for  $x = 0.17$  consistent with the previously obtained result.

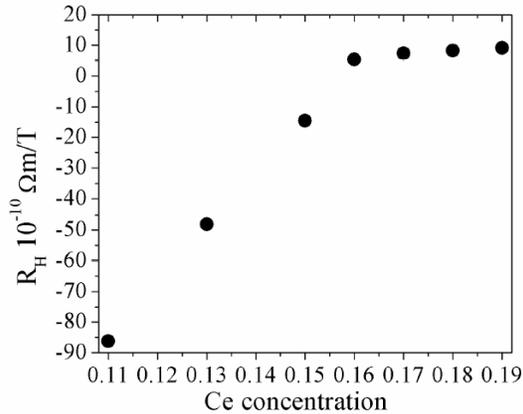


(Fig. 17)

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## Hall coefficient

The Hall coefficient was measured down to very low temperature in the normal state for different doping levels. At  $T = 0.35\text{K}$  a kink in the Hall coefficient appears at the same concentration ( $x=0.165$ ) where linear  $T$  resistivity is found (Fig. 18).



(Fig. 18)

Dagan et al. conclude that the resistivity and Hall measurements seem to support one another and argue for a QPT at a critical doping near  $x = 0.165$ .

- Criticism

In my opinion this conclusion is an over-interpretation of the existing data. It is not evident for me that the exponent  $\beta$  has to become one at all. There are not enough data points to justify the extrapolation to one. Therefore precise measurements for doping levels between  $x = 0.16$  and  $x = 0.17$  are needed to confirm the assumed trend.

The same argument is true for the hall coefficient. In addition, even when the kink really exists, I am not aware of a general argument why a kink in the hall coefficient is automatically linked to a QPT. Finally even the connection of linear  $T$  resistivity to a quantum critical scenario seems to be questionable in cuprates. Using three general assumptions:

- Existence of one critical length scale
- The charges are carried by the critical modes
- And charge conservation

P. Phillips and C. Chamon [44] have shown that linear  $T$  yields to an unphysical negative dynamical exponent. That is, in stead of diverging when  $T$  goes to zero, the correlations in time remain finite!!! But a finite  $\xi_t$  indicates that a gap persists. That is, a new length scale must be present to account for the linear  $T$ -behavior. Hence, interpreting  $T$ -linear resistivity as evidence for traditional quantum criticality is without base.

## Summary

In this paper the possible existence of two charge carriers in electron doped cuprates is discussed and an explanation for the "odd" occurrence  $T^2$  electrical resistivity of the normal state is given. In addition, evidence for a transition in the symmetry of the order parameter from d-wave to s-wave upon doping is presented. Finally the question, if a QCP scenario seems to be valid in n-type cuprates, is addressed. I have concluded, that this question is still open and requires more detailed experiments and confirmation by different experimental methods.

## Conclusion

The electron doped cuprates are very important materials, which can help us to understand the mechanism of high- $T_c$ . Seventeen years after their discovery more precise experiment on cleaner sample still reveal surprising properties. Many of these properties are still far from being completely understood. Especially the significance of subtle differences in n- and p-type cuprates, are not yet clear.

Trying to construct a theory that attempts to describe simultaneously all of the copper oxide superconductors makes the electron doped cuprates especially interesting for me. A detailed knowledge of their properties imposes significant constraints on new theories that I have to consider. For example, the observed asymmetry of n- and p- doped cuprates yields to the conclusion, that every theory trying to describe High- $T_c$  superconductivity, has to possess a mechanism to break particle-hole symmetry!!!

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