

THE CUPRATE PSEUDOGAP

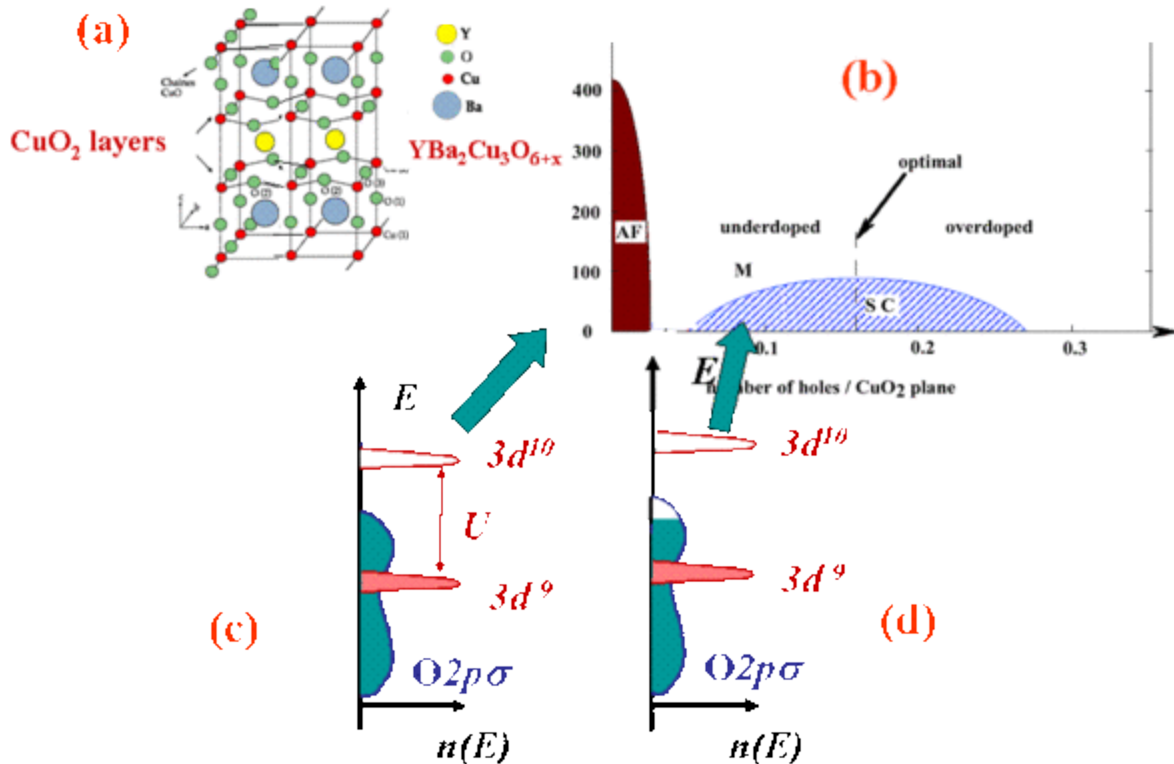


Figure 4: (a) Atomic structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. The O filling of the lower and upper CuO_x planes is responsible for hole doping. (b) Phase diagram versus hole doping of the CuO_2 planes in cuprates showing the fast decrease of AF Néel temperature, and the SC dome. (c) Band structure of the undoped parent compound. (d) possible two band electronic structure in the absence of interaction between Cu and O holes.

The cuprates contain as common elements CuO_2 planes (Fig. 4(a)) which are considered to contain all the important physics. Their structure is a stacking of such planes separated by other oxide layers, which maintain charge neutrality and the cohesion of the structure essentially through ionic interactions. They display the highest known superconducting temperature T_c obtained after chemical doping a parent state which is a Mott insulator (see SCES). Indeed in the undoped cuprates the Cu are in a $3d^9$ state in which the Cu hole bears a $S=1/2$ local moment (Fig. 4(c)). We shall discuss later on in section 8 how the magnetism of this Mott insulating state could be detected in NMR experiments. Those have been of course the physical properties which have driven the interest for these systems initially both for their fundamental aspects and their potential applications. Another aspect responsible for their appeal has certainly been the fact that the carrier concentration can be easily changed by chemical heterovalent substitutions or oxygen insertion in the layers separating the CuO_2 planes, which play the important role of charge reservoirs. Electron or hole doping can then be fairly continuously controlled from zero to about 0.3 charges per unit cell, which allows one to study

the evolution of the physical properties of these materials with doping and to map out their rich phase diagram(**Fig. 4(b)**). One important question raised concerning these doped compounds was that of the electronic structure of the band responsible for the metallic behavior. At a time where no ARPES experiments were available to map out the electronic structure, one expected that the doping holes would be located in an independent oxygen band, as exhibited in **Fig. 4(d)**. As recalled hereafter in **section 4.1**, the analysis of the ^{17}O , ^{89}Y and ^{63}Cu NMR shifts in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ cuprates has permitted to demonstrate unambiguously that the holes responsible for the measured macroscopic spin susceptibility are located on the Cu sites as expected for the undoped compound. The study of the evolution of the NMR shifts with hole doping (**section 4.2**) allowed then to reveal the occurrence of a pseudogap in the samples with lower than optimal doping. The latter was found quite generic of the clean cuprate families (**section 4.3**). The analysis of the NMR spin lattice relaxation suggested a \mathbf{k} space differentiation of the spin excitations which has been studied later in great detail by ARPES experiments (**section 4.4**).

Carriers and Hyperfine couplings

Let us assume that the Cu holes responsible for the local moments yielding the AF state of the parent compounds and of the doped holes expected to be located on the oxygen orbitals are uncorrelated. In that case the macroscopic magnetic susceptibility should sum up the contributions of these two bands, while the ^{63}Cu nuclear spins would probe the spin contribution on the copper sites. Similarly the ^{89}Y and ^{17}O nuclear spins would be more likely coupled to the oxygen holes. The determination of the hyperfine fields (**NMREPS**) which couple the nuclear spins with the susceptibility has been essential in the understanding of the electronic structure. The anisotropies of orbital contributions to the ^{63}Cu NMR shifts and of the ^{63}Cu spin hyperfine couplings permitted to establish that the Cu holes are located in the Cu $3d_{x^2-y^2}$ orbitals (Takigawa *et al* 1990). The evidence for a *negative* hyperfine coupling of ^{89}Y with the spin susceptibility allowed to demonstrate that ^{89}Y also probes the susceptibility localised on the Cu $3d_{x^2-y^2}$ orbitals through a transferred hyperfine coupling via $\text{O}2p_\sigma$ orbitals (Alloul *et al*, 1988), which was found identical for the insulating and doped compounds. This suggested that the spin susceptibility resides on a *single spin fluid* (Mila and Rice 1989), involving Cu $3d_{x^2-y^2}$ - $\text{O}2p_\sigma$ hybridized orbitals, so that the two type of holes are correlated and not independent as would be suggested by **Fig. 4 (d)**. This is fully confirmed below by the analysis of the T variations of the NMR shifts.

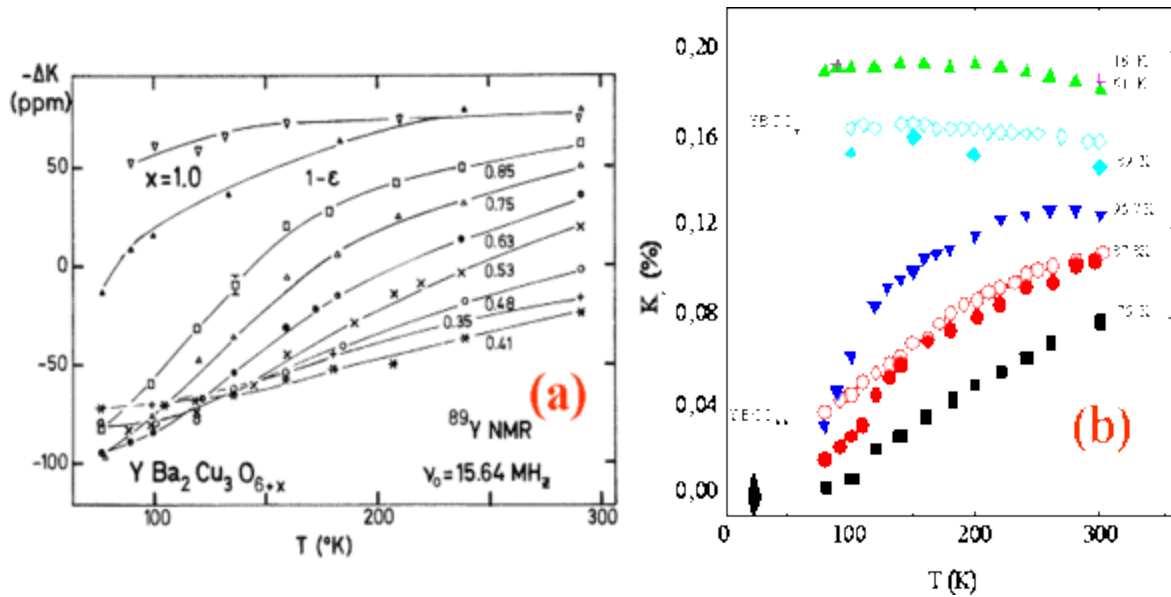


Figure 5: (a) Temperature variation of the ^{89}Y NMR shift $-\Delta K_s$ for $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ powder samples from optimal doping to a non-superconducting sample for $x=0.41$. The progressive increase of the pseudogap magnitude is apparent (from Alloul *et al*, 1989). (b) The comparison of the ^{17}O NMR shift data in YBCO and Hg1201 permits to demonstrate that the pseudogap temperature T^* are identical for these two compounds (from Bobroff *et al* 1997.)

Evidence for a pseudogap from NMR shift data

The optimally doped highest T_c compounds exhibited a rather regular T independent susceptibility together with a strange linear T variation of resistivity above T_c . The possibility to control the hole doping in the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ cuprate by decreasing the oxygen content which is inserted in the intermediate planes between the CuO_2 planes permitted controlled NMR experiments in the underdoped regime for which T_c drops with decreasing hole doping. Those experiments revealed a quite distinct behavior of the NMR shifts with a dramatic drop of the spin component K_s that is of the spin susceptibility with decreasing T . Such an observation done initially by ^{89}Y NMR measurements (see **Fig. 5 (a)**) remarkably revealed that for a composition with $T_c=60\text{K}$, the spin susceptibility drops of more than a factor three between room T and T_c (Alloul *et al* 1989). As the spin susceptibility remains still sizable at T_c , this appeared as the signature of the opening of an imperfect gap which was qualified as a **pseudogap** already in 1989. This is remarkable inasmuch as it was not experimentally possible to detect any further sharp decrease of the spin susceptibility below T_c . The other aspect which was revealed by these experiments is that the onset temperature T^* of the drop in K_s increases with decreasing doping. This had led to the indication that the pseudogap magnitude increases with decreasing doping that is with decreasing T_c . Most other experiments measuring uniform macroscopic responses, such as specific heat, planar resistivity ρ_{ab} , do detect an onset at similar temperatures as that of T^* , (Timusk and Statt 2000), which is undoubtedly the highest temperature

below which a detectable deviation with respect to the high T Pauli like behavior occurs. Signatures for the pseudogap have been seen as well on optical absorption, photoemission (ARPES), or tunnel effect experiments.

Universality of the pseudogap phase diagram

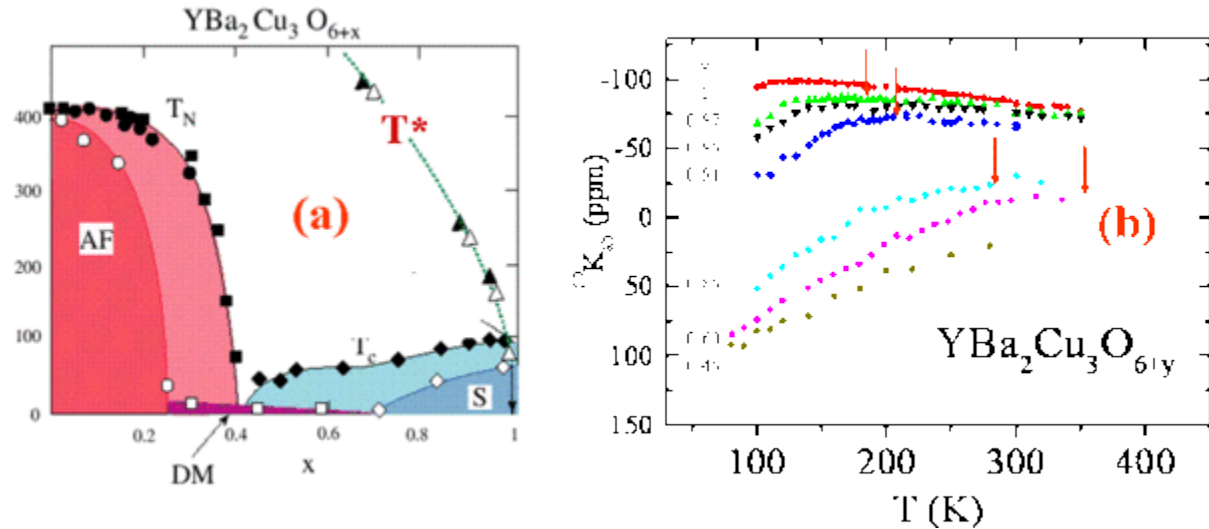


Figure 6: (a) Cuprate phase diagram obtained in the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ compound by changing the oxygen content x of the Cu intermediate planes. There the phase diagram obtained for Zn4% substitution on the Cu sites demonstrates that T_c is highly affected while T^* values are insensitive to disorder. (b) The determination of the T^* values from the departure of the ^{89}Y NMR shift from its high T constant value is illustrated here by arrows. Figure composed from experimental results reported by Alloul *et al* (2009)

Data taken for the spin components of the NMR shifts for ^{63}Cu or ^{17}O in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ have evidenced a perfect scaling of the T variations with that of ^{89}Y , which confirmed the idea of a single spin fluid contribution to the spin susceptibility. That was on line with the Zhang and Rice (1988) suggestion that oxygen holes just form singlets with Cu and only modify the Cu susceptibility, so that the Cu and O holes are highly correlated. This identical T variation found by NMR on the various nuclear spin sites has given a universality to the pseudogap T^* deduced by NMR. Comparison between ^{17}O NMR shifts in the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ two layer compound and the single layer compound $\text{Hg}_1\text{Ba}_2\text{CuO}_4$ evidenced that T^* is generic within the clean cuprate families (Bobroff *et al* 1997) (see Fig. 5 (b)). This has been confirmed by nearly all experimental determinations done by macroscopic measurements of T^* . This pseudogap T^* line introduced in the phase diagram of YBCO is displayed in Fig. 6 for pure samples but also when T_c and T_N have been decreased by 4% Zn substitution on the Cu sites, as will be discussed in section 7.

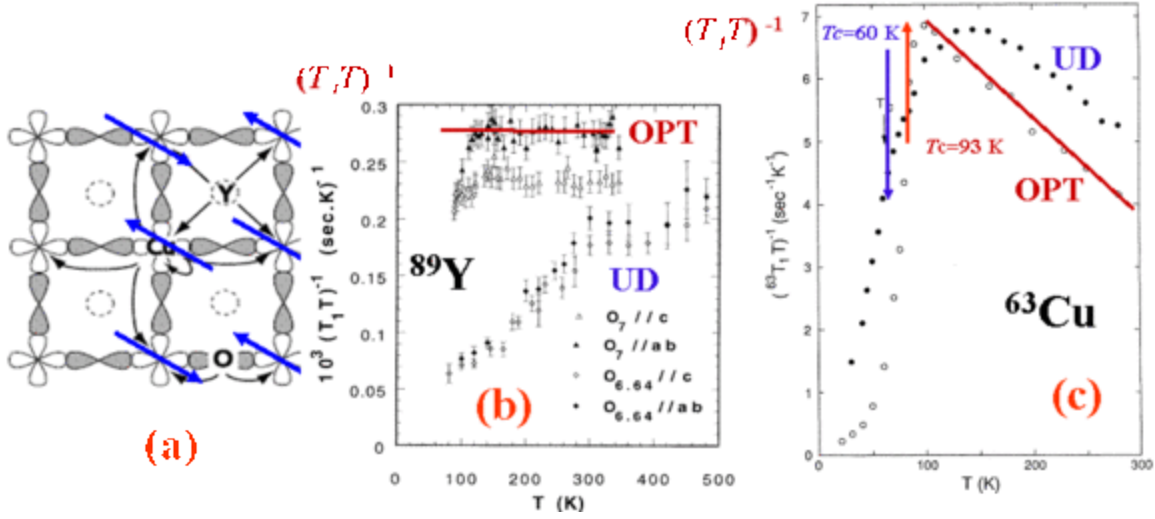


Figure 7: (a) Schematics of the Cu_{3d_{x²-y²} and O_{2p_σ} orbitals in the CuO₂ plane showing why the AF fluctuations are filtered at the ¹⁷O and ⁸⁹Y nuclei. This explains why the T variations of $(T_1 T)^{-1}$ taken for oriented powder samples of YBCO₇ ($T_c=90$ K) and YBCO_{6.6} ($T_c=60$ K) are quite different for ⁶³Cu and ⁸⁹Y. (b) ⁸⁹Y data taken from (Alloul *et al* 1993). (c) ⁶³Cu data taken from (Takigawa *et al* 1991). While the data for $T_c=90$ K are T independent for ⁸⁹Y, as does the Knight shift, they increase at low T for ⁶³Cu. Similarly for the underdoped samples both $(T_1 T)^{-1}$ and $89K$ increase regularly up to $T^* \sim 350$ K, while those for ⁶³Cu display a maximum at $T \sim 150$ K, assigned to a spin gap.}

Dynamic spin susceptibility and electronic correlations

We shall discuss below the actual information on the AF correlations given by the measurements of the spin lattice T_1 and transverse T_2 nuclear spin relaxation in the cuprates. As shown in NMREPS, the T_1 give determinations of $\chi''(q, \omega)$ while we shall show here that the transverse T_2 is related to $\chi'(q, 0)$.

The feature which had been clearly evidenced was that for ⁸⁹Y nuclear spins $(T_1 T)^{-1}$ and $89K$ have very similar T variations (with T and doping). This is illustrated in **Fig. 7 (b)** on data taken on field-aligned YBCO samples realized for two compositions, O₇ for which $(T_1 T)^{-1}$ is T independent as is $89K$, while for O_{6.6} both quantities exhibit large T increases. Similar results on the ¹⁷O NMR have been obtained, which established that the dynamic susceptibility viewed by these nuclei appeared quite correlated with the static susceptibility. It has been established that $T_1 T K_s$ is nearly T independent, which has been taken as an evidence for the presence of a Fermi-liquid like component in the magnetic response.

However, as was seen by many authors, the $(T_1 T)^{-1}$ of ⁶³Cu behaves quite differently (for references, see Walstedt, 2008). In the optimally doped compound $(T_1 T)^{-1}$ increases at low T while it goes through a maximum at a temperature much lower than T^* in the underdoped sample (see **Fig. 7 (c)**). This difference between ⁶³Cu and ¹⁷O (or ⁸⁹Y) NMR is understood as the two latter nuclear spins being coupled to two (or four) Cu moments do not detect AF fluctuations at the AF wave vector $\{Q\}_{AF}=(\pi, \pi)$, as sketched in **Fig. 7 (a)**. In other words, the ⁶³Cu data uniquely reveals the occurrence of a peaked response of $\chi''(q, \omega)$ at $\{Q\}_{AF}$. This

has been confirmed directly by inelastic neutron scattering experiments taken on underdoped samples. The maximum in $(T_1T)^{-1}$ for ^{63}Cu has been assigned to a spin gap which is quite distinct from the pseudogap T^* . It would increase much less rapidly than T^* for decreasing doping. Both the pseudogap T^* and the spin gap are detected only in underdoped samples, which suggests that they are connected.

Let us point out now that this strong magnetic response in cuprates induces a contribution to the nuclear spin transverse T_2 relaxation, which has been found quite important on the Cu sites. In weakly correlated solids T_2 , which is measured with spin echo experiments (see NMR wikipedia) is usually fully determined by the direct dipole-dipole interactions between nuclear spins. In cuprates and more generally in correlated systems, a nuclear spin at \mathbf{R}_i can be viewed as a moment which induces, through the \mathbf{q} dependent susceptibility $\chi(\mathbf{q},0)$, a polarization of the electronic spins which extends on the sites nearby \mathbf{R}_i . This polarization does in turn couple to the nuclear spins on these sites. This indirect (RKKY like) dipolar interaction between the nuclear spins induces a contribution to the spin echo decay. After summation of the interaction of a nuclear spin with all its neighbors, the spin echo is found to get a gaussian decay with a time constant T_{2g} given by

$$(1/T_{2g})^2 \propto A_{40} \sum_{\mathbf{q}} [\chi(\mathbf{q},0)]^2 - A_{40} [\sum_{\mathbf{q}} \chi(\mathbf{q},0)]^2. (7)$$

In the cuprates, $\chi(\mathbf{q},0)$ is expected to be peaked at Q_{AF} and the width of the peak defines a correlation length ζ for the AF response, which might be estimated from the T_{2g} data. Even in the underdoped pseudogapped regime ζ is found to increase steadily with decreasing T , as will be seen as well from impurity studies to be described in **section 6.2**.

Coming back to the pseudogap, more recently ARPES or STM experiments have given evidence that a gap in the charge excitations only occurs for the antinodal directions $(0,\pi)$ in $\{\mathbf{k}\}$ space. So the closed Fermi surface which occurs at high T in underdoped cuprates loses weight in the antinodal directions when T decreases, and the Fermi surface then reduces to Fermi arcs, which shrink with decreasing T (Kaminski *et al*, 2014). The experimental results on $(T_1T)^{-1}$ of ^{63}Cu are certainly precursor indications of this $\{\mathbf{k}\}$ space differentiation which has been found by $\{\mathbf{k}\}$ dependent spectroscopies.

Phenomenological attempts have been done to describe the shape functions of the spin susceptibilities $\chi''(\mathbf{q},\omega)$ and $\chi'(\mathbf{q},0)$, in order to fit the NMR data (Millis *et al* 1990). Satisfactory qualitative descriptions could be achieved, with ζ values of about two lattice constants at room T in both the optimal and underdoped samples, with much larger low T increases of ζ in the latter. However these approaches required to introduce by hand the Fermi liquid like metallic component and did not include explicitly the occurrence of the pseudogap. A complete theory of the physical phenomena at play would require a model which generates altogether the pseudogap, the AF correlation length and its T variation.

To conclude, the pseudogap is most probably intimately linked with the correlated nature of these systems, and its actual physical origin is intensely debated. One interpretation, proposed quite early on, is that it represents a

precursor pairing state, the superconducting phase being only established at T_c when the pairs achieve long range phase coherence (Emery and Kivelson 1995). Such an interpretation would imply that the SC gap increases with decreasing T_c . This is so far contradicted by direct or indirect determinations of the SC gap. Another class of interpretations could be the establishment of a hidden order disconnected from superconductivity such as a spin ordering, for instance a Resonant Valence Bond (RVB) state (Anderson,1987), a d-density wave (ddW), a charge segregation into stripe order or an ordering involving orbital currents. Such possibilities have been recently underlined by experimental discoveries of such type of orders, which appear system dependent, and often occur at temperatures below T^* . These experiments are so novel that they have initiated vivid debates on the pseudogap, but did not permit so far to resolve the issues they raised. The pseudogap remains still today the central point debated on the cuprates and at the present writing the understanding of the pseudogap state remains controversial. The author believes that magnetic short range correlations explain the pseudogap crossover at T^* and the Fermi surface differentiation, while the orders detected at lower T than T^* are rather consequences of the pseudogap formation than direct manifestations of the pseudogap itself.

The analysis of the hyperfine couplings established that the magnetic response of cuprate High T_c superconductors exhibit a single spin fluid behavior in which the Cu and O holes are hybridized. NMR shift experiments have allowed to evidence that a large progressive loss of spin susceptibility occurs for underdoped cuprates, that is for compounds on the left of the T_c dome. This strange behavior has been found generic for the various cuprate families. It onsets at a temperature $T^* \gg T_c$ and is attributed to a pseudogap in the density of states which corresponds to a transfer of spectral weight from low to high energies, assigned to strong electronic correlations. The difference of T dependence of T_1 for the nuclei in symmetric position in the Cu site lattice with respect to that of Cu nuclear spins confirms the existence of AF correlations between Cu electronic spins. Modifications in the Fermi surface topology have been confirmed by k dependent spectroscopy and various further reconstructions of the Fermi surface have been discovered to occur well below T^* .

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