LECTURE 6. Cuprates: generalities, N-state properties

Cuprates: only group of materials to date to show reproducible superconductivity above 100K. Not all cuprates superconduct, but more than 300 do, with $T_c \sim$ 110-120K for dozens.

Composition:

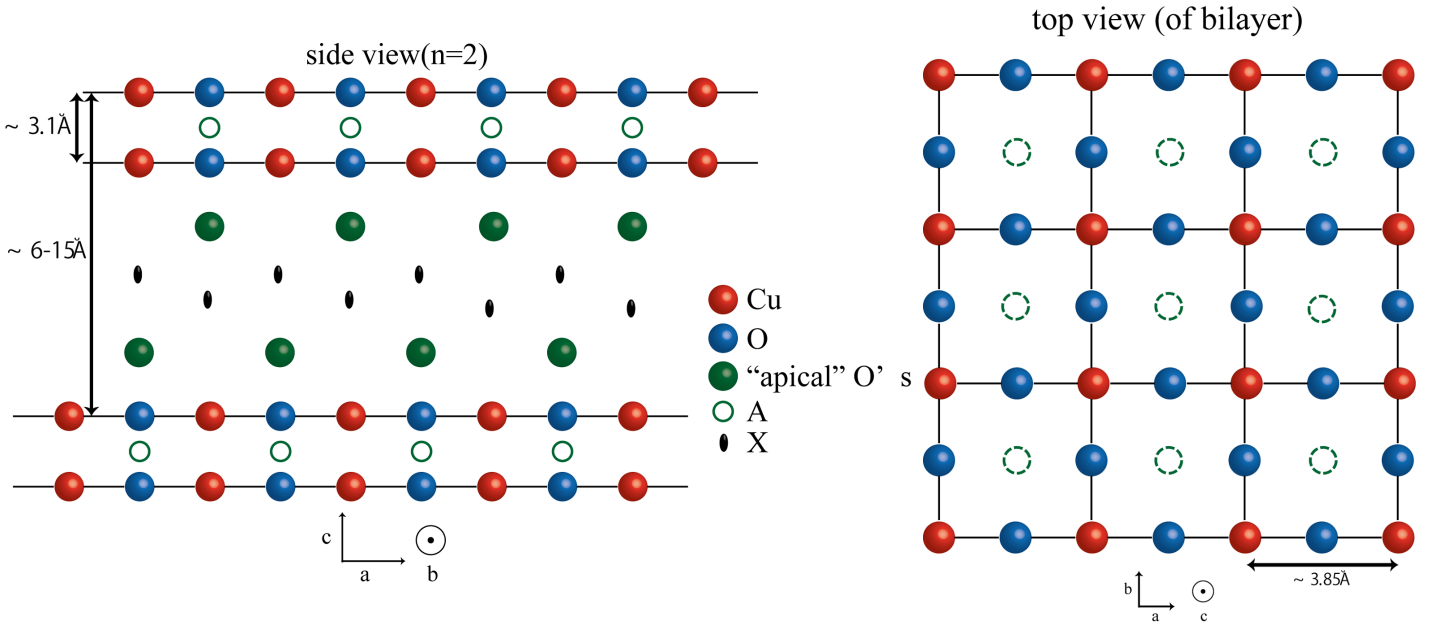
Natural (but unconventional!) notation:

$$(CuO_2)_n A_{n-1} X \qquad (\text{e.g.} YBa_2Cu_3O_{7-\delta};\ n=2,\ A=Y,\ X=BaCuO_{3-\delta})$$

A("intercalant") = alkaline earth (or rare earth, Y or La)

X("charge reservoir") = combination of elements, always including O

Structure:



Homologous series: sequence with $n = 1, 2, 3, \cdots$

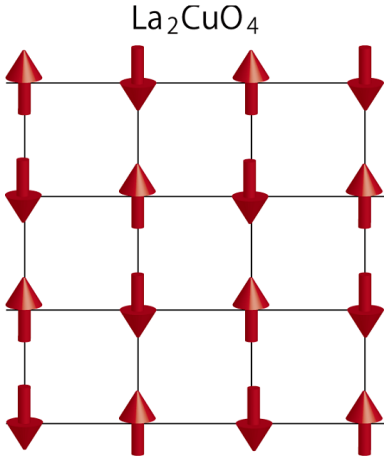
(e.g., $Tl_2Sr_2CuO_6$, $Tl_2Sr_2Ca\ Cu_2O_8$, $Tl_2Sr_2Ca_2Cu_3O_{10}$,$\cdots$)$\longrightarrow$.

Valence considerations:

can often start (for given X) with stoichiometric compound ("parent" compound) when valences balance, e.g.,

$$\begin{aligned} La_2CuO_4 &= (La^{3+})_2Cu^{2+}(O^{2-})_4, \\ YBa_2Cu_3O_6 &= Y^{3+}(Ba^{2+})_2(Cu^{2+})_2Cu^{+}(O^{2-})_6. \end{aligned}$$

Cu^{2+} (in plane) has $(3d^{10})(4s)^1 \rightarrow 3d^9$, i.e., 1hole in d-shell. per formula unit $\Rightarrow$ naively, should be metal. Actually, AF Mott insulator:



Doping:

Suppose one starts with a "parent" compound, say La_2CuO_4, and replaces in a fraction x of the unit cells, La with Sr, i.e.

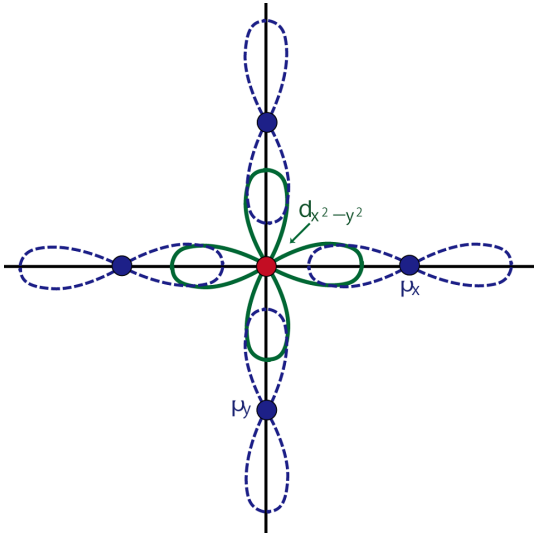
$$La_2CuO_4 \rightarrow La_{2-x}Sr_xCuO_4.$$

Since La has valence 3+ and Sr 2+, the effect is to add $-x$ electrons, i.e. x holes, per formula unit: in this case they have nowhere to go but the CuO_2 plane, so we can be fairly confident that the doping per CuO_2 unit above the "parent" compound, p, $= x$. Alternatively, consider adding δ O's per formula unit; then

$$La_2CuO_4 \rightarrow La_2CuO_{4+\delta}.$$

In this case, since the valence of O is $2-$, the effect is to add 2δ holes/ CuO_2 unit, i.e. $p = 2\delta$. In multiplane materials ($n > 1$) one must remember that any added holes have to be shared between the n planes per unit cell; hence, naively, for e.g. $YBe_2Cu_2O_{6+\delta}$ we expect $p = \frac{1}{2}(2\delta) = \delta$. However, in this case there are other complications because the added holes can go elsewhere than in the CuO_2 planes (e.g. in the "chains").

Orbital(s) occupied by the holes in the CuO_2 plane: both the 1 hole/ CuO_2 unit which was already there in the parent state and also any added holes are believed to occupy an orbital which is "mainly" $3d_{x^2\text{-}y^2}$, but somewhat hybridized with the p_x or p_y states on neighboring O's:



Electron doping

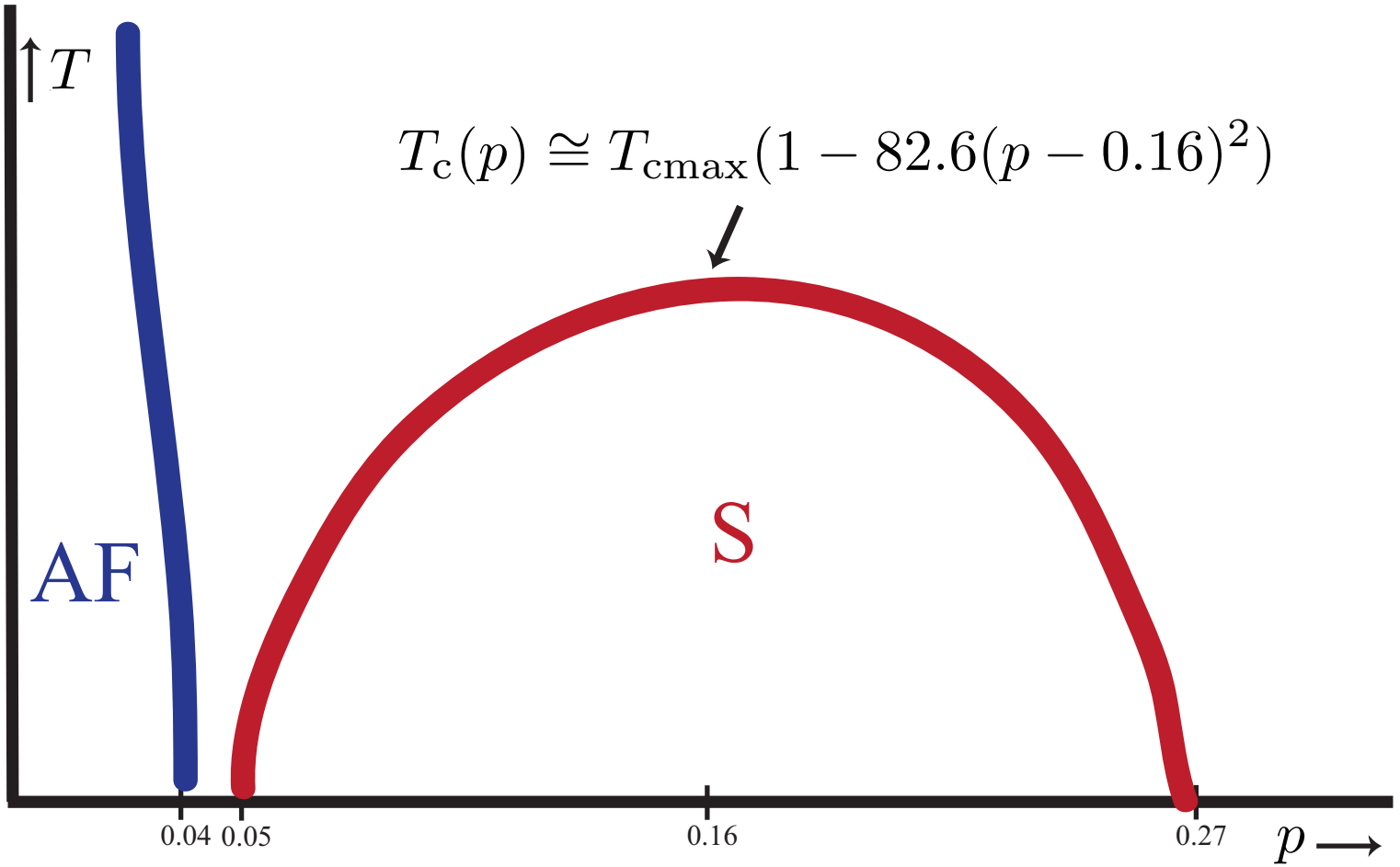
Vast majority of cuprate superconductors are hole-doped, but there are a very few that are electron-doped: best known is NCCO ($Nd_{1-x}Ce_xCuO_4$). Properties of electron-doped materials qualitatively similar to hole-doped ones.

Construction of phase diagram

"Act of faith" (but consistent with experiments): apart from T (temperature) main variable controlling "interesting" behavior is p (no. of holes/CuO_2 unit). Then (a) in cases where all added holes are known to go to CuO_2 planes (e.g. $La_{2-x}Sr_xCuO_4$) fix p from x (or δ): (b) in cases where destination of added holes ambiguous, fix p so that where accessible region overlaps case (a), p-dependence is consistent between the two.

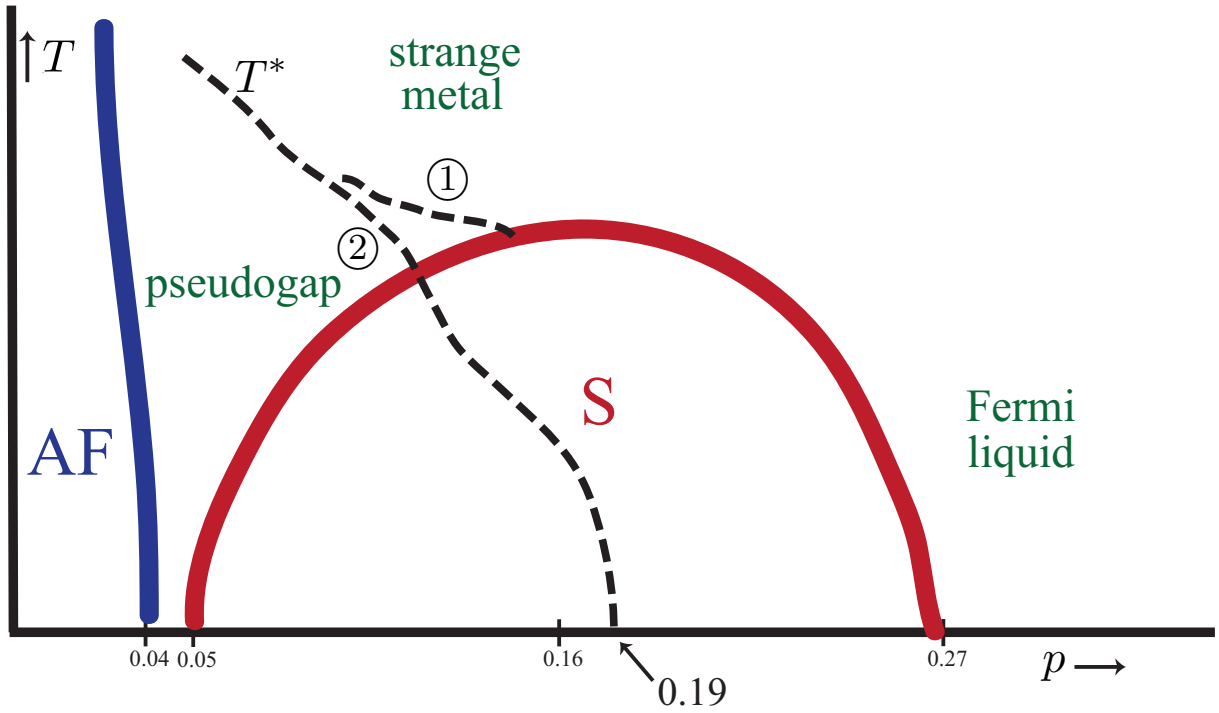
(Note whole range of p not explored in any single material.)

Phase diagram of the cuprates



↑: p-dependence universal[1], T-dependence (i.e. T_{cmax}) strongly material-dependent ($T_{cmax} \sim$ 10K for for Bi2201→ 160K for Hg2223 under 20GPa)

[1] but this is partly "by construction", cf. above.



T^*-line: locus of "crossover" behavior in various experimental quantities (C_v, χ, ρ_c,$\cdots$); two hypotheses for low-T behavior: (1) intersects S. phase, (2) joins smoothly on to line $T_c(p)$.

Determinants of T_c (other than p)

As noted, $T_{c\max}$ varies enormously between different cuprates. What determines it? Correlations with

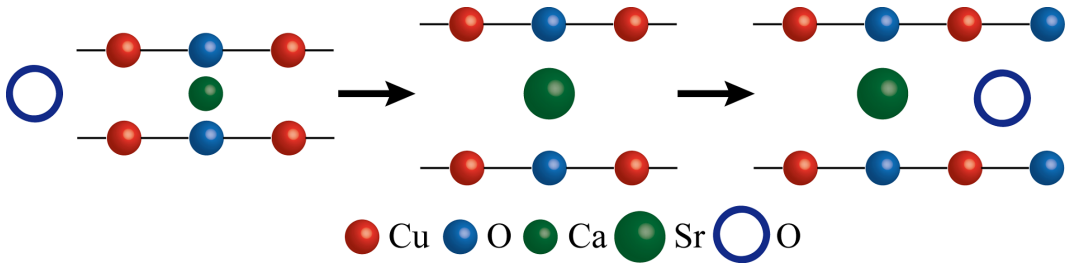
- degree of orthorhombic anisotropy
- degree of buckling of planes
- distance to apical O's
- chemical environment of planes

but none "overwhelming". However, in homologous series, very universal dependence of $T_{c\max}$ on n (no. of CuO_2 planes /unit cell).

Common name	X group	n=1	2	3	4	5
Hg-12,$n-1,n$	$HgBa_2O_{3+\delta}$	98	126	135	125	110
Tl-22,$n-1,n$	$Tl_2Ba_2O_4$	95	118	125	112	105
Tl-12,$n-1,n$	$TlBa_2O_{3-\delta}$	70(?)	103	123	112	107
Pb-22,$n-1,n$	$PbSr_2O_{3+\delta}$	~40	97(?)	122	107	
Bi-22,$n-1,n$	$Bi_2Sr_2O_4$	10-20	89	107		

note often $\Delta T_{c(2-3)} \simeq \frac{1}{3}\Delta T_{c(1-2)}$.

Digression: the "dogs which did not bark in the night-time": class of cuprates which never becomes superconducting. Little-noticed fact: without exception, all bi/tri-layer with alkaline-earth spacer (Sr, Ba) heavier than Ca. Effect of "intruder" O's?



Carrier density:

at "optimal" doping ($p \simeq 0.16$) density of (extra) holes in plane is $\sim 1.5 \times 10^{14}\text{cm}^{-2}$. Hence 3D density $\sim$ 1-2 $\times 10^{21}\text{cm}^{-3}$ (comparable to SRO, ferrropnictides,$\cdots$).

Some "interesting" cuprates:

$La_{2-x}Sr_xCuO_4$ (LSCO)	(almost) earliest HTS, large crystals
$YBa_2Cu_3O_{6+\delta}$ (YBCO)	first liquid nitrogen-temperature HTS, "E.Coli" of cuprates
$Bi_2Sr_2Ca_{n-1}Cu_nO_{(n+2+\delta)}$ (BSCCO)	"baklava", good for ARPES, EELS, etc; most anisotropic HTS known.
$HgBa_2Cu_nCa_{n-1}O_{2(n+1)}$ (HgBCO)	record holder for T_c($\sim$ 160K at 20GPa).
$Nd_{1-x}Ca_xCuO_4$ (NCCO)	electron-doped
$Ca_{1-x}Sr_xCuO_2$ (∞-layer)	no reservoir group X, infinite set of CuO_2 planes seperated by AE ions Ca/Sr.

Experimental properties; N state

↑: easy to vary T at fixed p, much more difficult to vary p at fixed T (though cf. electrical doping of thin films).

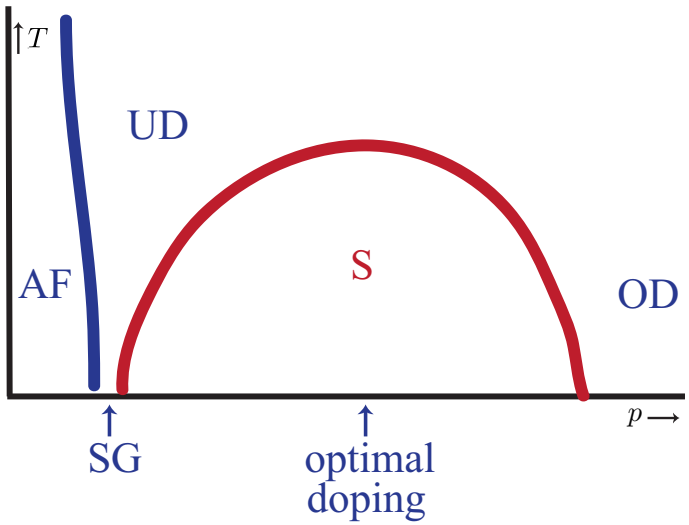
↑: many types of experiment specific to particular cuprates (e.g. ARPES; BSSCO, neutrons; LSCO).

A few regions of phase diagram relatively uncontroversial:

(a) AF phase is Mott AF: neutron scattering⇒ well described by nearest-neighbor Heisenberg Hamiltonian

$$\hat{H} = J \sum_{\langle ij \rangle} \hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j$$

with (in plane) $J \sim 1000$K, interplane J(bilayer) ~ 200K. Consistent with experimental T_N (300K at $p = 0$ for LSCO, 500K for YBCO).



(b) OD (overdoped) region to R of S dome is approx. standard Fermi liquid, getting "better" with increasing p.

(c) SG ("spin glass") region of p, $0.04 < p < 0.05$: few experiments but behavior of $\rho(T)$ (resistivity) seems to correspond to perfect insulator for $T \to 0$ (cf. disordered granular films).

The "controversial" regions:

1. Optimal doping

Thermodynamic properties:

$C_v^{\rm el} = \gamma T$ up to $\sim$ RT, $\gamma \simeq 6.5$mJ/mol(CuO_2)K^2, almost same for LSCO, YBCO, Tl-2201

if interpreted in Fermi liquid terms ⇒ $N(0) \simeq 1.4(\text{eV})^{-1}$ spin$^{-1}(CuO_2$ unit$)^{-1} \sim 4\times$2D free-electron value $(ma^2/2\pi\hbar^2)$.

⇒ consistent with FL model with $\frac{m^*}{m} \simeq 4$.

χ (mostly from Knight shift: YBCO) independent of T. In-plane Cu Knight shift $\gg$ that for Y or O.

$T_1^{-1} \propto T$ (Korringa relation)

So far, pretty much Fermi liquid-like...

Transport (↑: strongly anisotropic, quoted results *ab*-plane unless otherwise stated)

dc resistivity: at optimal doping, all cuprates have $\rho \propto T$ from $\sim$ 800K all the way down to T_c ($\sim$ 10K for Bi2201).

More generally, $\rho \propto T^\alpha$ where α varies continuously from ~ 2 in OD limit to < 0 in UD (SG) limit. For higher-T_c materials, the coefficient (per plane^{-1}) seems to be approximately universal. ($R_{\text{R.T.}} \sim 3\text{k}\Omega \sim 0.12 R_Q$).

Can the optimal-doping law $\rho \propto T$ be due to phonons? Almost certainly no, since typical Θ_D's are $\sim$ 300K.

ac resistivity can be fit to Drude form

$$\sigma(\omega) \sim \frac{ne^2\tau/m}{1 + i\omega\tau}$$

only if τ is allowed to be $f(\omega)$, with

$$\tau^{-1}(\omega) \sim \max(\omega, k_B T/\hbar).$$

Hall angle: for pure samples in high-field (8T) limit,

$$\cot \Theta_H \propto T^2$$

thermoelectric power: Room temperature value as $f(p)$ crosses 0 at almost exactly optimal doping.

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c-axis resistivity at optimal doping:

$\rho(T) \propto T^\alpha$, α ranges from ~ -1 to $+1$ for different cuprates.

Spectroscopic probes: Fermi surface

The most useful probes of the Fermi surface in a metal are angularly resolved photoemission spectroscopy (ARPES) and quantum-oscillation phenomena such as the de Haas-van Alphen effect (dHvA).

ARPES essentially measures the "spectral function" $A(\boldsymbol{k}, \varepsilon)$, that is, the probability, in the thermal equilibrium state, of an electron having momentum $\boldsymbol{k}$ and energy ε: for non-interacting electrons this would be $\propto \delta(\varepsilon - \varepsilon_k)$, when ε_k is the energy of Bloch wave $\boldsymbol{k}$.

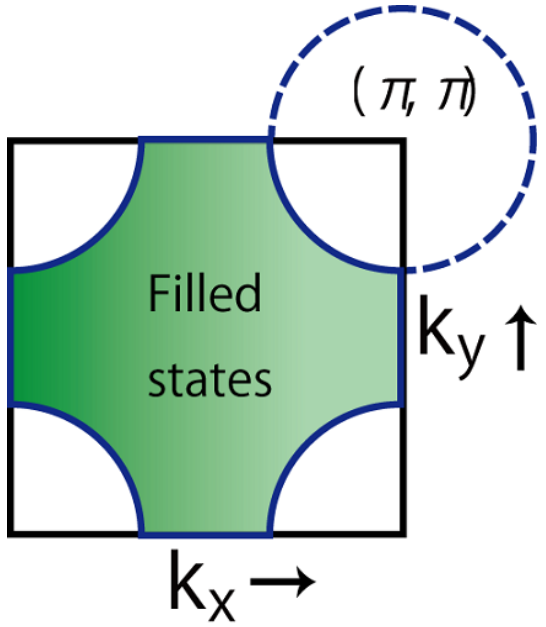
dHvA-type experiments measure the area(s) of those parts of the Fermi surface which correspond to "closed" orbits, but cannot say anything about their shape or position. Note that because of the strongly 2D (layered) nature of the cuprates, the magnetic field is always applied in the *c*-direction, and dHvA simply measures the area(s) of the 2D Fermi surface(s).

Results of ARPES experiments at optimal doping

(1) Spectral function $A(\boldsymbol{k}, \varepsilon)$ nothing like $\delta(\varepsilon - \varepsilon_k)$: incoherent background $\sim 90\%$ of total weight. Thus, if a Fermi liquid, a very "bad" one!

(2) However, energy-integrated function does show a jump ($\sim 10\%$) as a function of $|\boldsymbol{k}|$ for given $\hat{\boldsymbol{n}}$, which allows us to define a Fermi surface, as shown: this is hole-like and corresponds to a total no. of holes $n_h \simeq 1.19$ $(= 1 + p$, as naively expected).

dHvA experiments (on somewhat OD side) are consistent with this.



Some other spectroscopic probes (selective)

Neutron scattering: neutrons coupling mainly to electron spin, so cross section $\sigma(\boldsymbol{q}, \omega)$ is measure of spin fluctuations. For fixed $\boldsymbol{q}$ as $f(\omega)$, no marked structure. But for fixed ω as $f(\boldsymbol{q})$, marked peak as $f(\boldsymbol{q})$ at $(k_x a, k_y a) = (\frac{\pi}{2}, \frac{\pi}{2})$, which is exactly the Bragg vector of the magnetic superlattice in the AF phase.

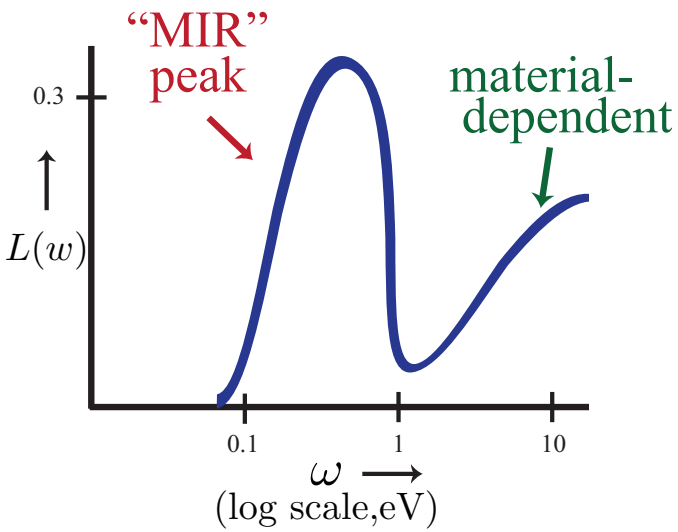
$\Rightarrow$ strong AF spin fluctuations persist in non-magnetic phase

Optics (*ab*-plane):

In most experiments raw data is optical reflectivity $R(\omega)$, but by using KK-relation can infer loss function $L(\omega) = -\mathrm{Im}\frac{1}{\varepsilon(\omega)}$.

$\uparrow$: $\varepsilon(\omega)$ is "3D" quantity, hence sensitive both to CuO_2 plane density and charge-reservoir contribution to Imε. Despite this, MIR (mid-infrared) peak is only fairly weakly material-dependent.

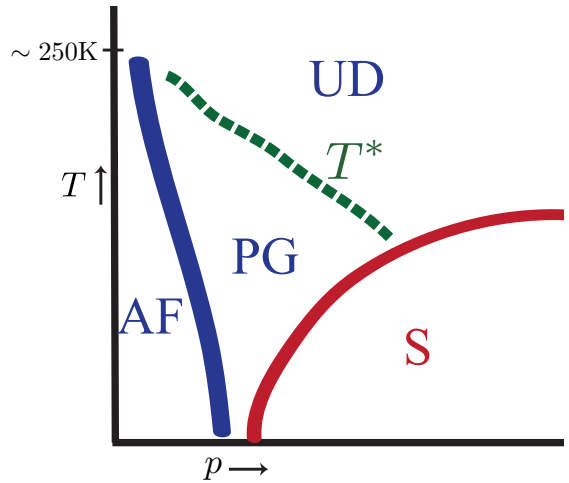
Consistent with transmission EELS experiments, which measure $L(\boldsymbol{q}, \omega)$ directly: MIR peak seen up to $q \sim 0.1\text{Å}^{-1}$ (for larger q somewhat attenuated).



The underdoped regime

The pseudo-gap

Since in the region labelled "underdoped" (UD) the system is not superconducting, it presumably does not possess ODLRO. Nevertheless, considerable evidence that below the T^*-line the fermionic excitation spectrum, or most of it, has an energy gap similar to that of the S phase. This evidence is from



(a) specific heat: $C_v \sim \gamma T$ for $T \gg T^*$, but for $T \leq T^*$ drops well below this line.

(b) static spin susceptibility (from Knight shift) : $\chi \sim$ const. for $T \gg T^*$, drops below it for $T \leq T^*$.
note: Wilson ratio (defined as $S/\chi T$ (rather than $c_V/\chi T$)) is close to independent of T for all T.

and

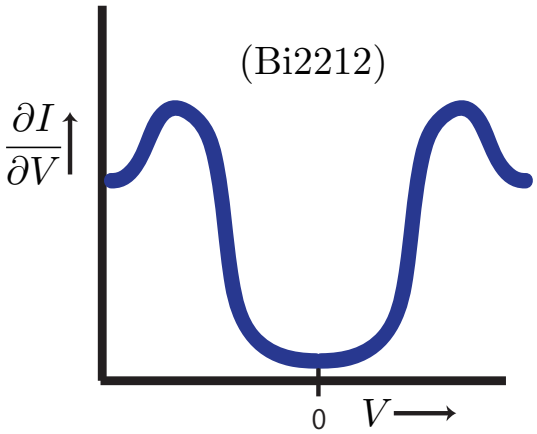
(c) nuclear spin relaxation rate: $T_1^{-1} \propto T$ (Korringa low) for $T \gg T^*$, falls below this for $T \leq T^*$.

(d) transport: both $\rho_{ab}(T)$ and $\rho_c(T)$ drop, for $T \leq T^*$, at frequencies $\omega \leq 500\text{cm}^{-1}$ (corresponds to $\sim$ 750K).
All of these suggest a reduced DOS below $E \sim$ a few 100 K, but not directly on actual energy gap.

More direct evidence for gap:

(e) Tunnelling: gap-like feature seen in tunnelling characteristics, above T_c and up to $\sim$ Room Temperatures

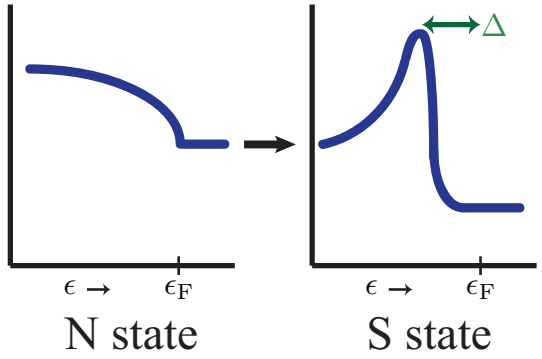
(f) ARPES (see below)



Some evidence (recent + somewhat controversial) for spontaneous breaking of rotational $\left(\frac{\pi}{2}\right)$ invariances in PG regime. Also some claims of spontaneous violation of T-symmetry (also controversial).

ARPES in the pseudogap regime: the puzzle of the Fermi surface

In the superconducting state at optimal doping, the diffuse N-state ARPES spectrum develops a sharp peak which is pulled well back from the Fermi energy: the ($\hat{\boldsymbol{n}}$-dependent) difference is usually taken as a measure of the gap $\Delta(\hat{\boldsymbol{k}})$; it is of $d_{x^2\text{-}y^2}$ form, i.e. 0 at (π, π) and largest along crystal axes. At optimal doping and on OD side, the $\Delta(\hat{\boldsymbol{n}})$ so defined appears to vanish for $T > T_c$. In the UD regime a gap of similar $d_{x^2\text{-}y^2}$ form is seen in the S state and persists above T_c; $\Delta(\hat{\boldsymbol{n}} : T)$ appears to be more or less T-independent, but the amplitude of the peak decreases, and it disappears at $\sim$ the room temperature.



The puzzle: The ARPES data appear to show (modulo the gap) that even in the PG regime the Fermi surface is well-defined and is quite similar to that seen at optimal and OD values of p, i.e. "large" ($\sim 1 + p$). However dHvA data seem to indicate equally definitively that the only Fermi surface/s is very small, so that even with 4 symmetry, related surfaces the total hole concentration in the Fermi sees would be only $\sim p$, not $\sim (1 + p)$.

One possible resolution: dHvA has to be conducted in high fields ($\sim$ 20T), and it is conceivable at those might qualitatively change nature of the ground state. Irrespective of this, combination of this dHvA data with that in OD regime.
$\Rightarrow$ at least at large fields, there must be a discontinuity or crossover in the qualitative nature of the GS as a function of p. As of now (dHvA only $\sim$ 3 years old!) unknown exactly where this occurs.