Lecture 7. Cuprates II: S-State Properties
(somewhat doping-dependent: will quote results at optimal doping unless otherwise stated)
Will compare with BCS predictions where possible. ("√" = “agrees with BCS”)

1. Structural and elastic properties and electron density distribution:
essentially no change at $T_c$ or below √

2. Macroscopic EM properties:
i) strongly type-II  ii) strongly anisotropic ($\lambda_c \gg \lambda_{ab}, \xi_c \ll \xi_{ab}$)
extrapolated $H_{c2}(0) \sim 50$ T for $H || c$, 400 T for $H \perp c$
if interpreted by BCS, corresponds to $\xi_{ab}(0) \sim 15 - 30\text{Å}$, $\xi_c(0) \sim 2 - 3\text{Å}$.
(BCS: $\xi_{ab}(0) = 0.18\hbar v_F/k_B T_c \sim 30\text{Å}$ for $m^*/m = 4$)

3. Specific heat + condensation energy:
jump at $T_c$, $\Delta C_{n-s}/C_n \approx 1.6 - 2$ (BCS: 1.4)
for UD and OD, peak is considerably more rounded
for $T < T_c$ falls off sharply (√) but for $T \to 0$ power law $T^n$, probably consistent with $n = 1$.
Condensation energy: peaks sharply at $p = 0.19$ (↑ not “optimal” value 0.16), at a value $\sim 33\text{J/mol}$,
corresponding to $\Delta U_{ns}(0) \approx 2K/\text{CuO}_2$ unit.

4. NMR:
$T_1^{-1}$ drops precipitately below $T_c$, $\propto T^3$ for $T \to 0$
$\chi$ mostly BCS-like for $T \gtrsim 0.5T_c$.  

5. Penetration depth:
methods: magnetization-related (unreliable for strong anisotropy)
Fraunhofer diffraction in Josephson junction (not widely used)
μSR (muon spin resonance)
*microwave surface impedance
  i) ab-plane: behavior of \( \rho_s/\rho \propto \lambda^{-2} \)
near \( T_c \) probably \( \propto (T_c - T)^{2/3} \) (3D XY model)
\( T \to 0 \), (pure) \( 1 - \alpha T \)
(dirty) \( 1 - \alpha'T^2 \)
value of \( \lambda(0): \sim 1000\text{Å} \) (YBCO, optimal, b-axis)-4000Å (LSCO)
How well do data on \( \lambda_{ab}(0) \) fit “naive” (quasi-London) prediction
\[
\lambda^{-2}(0) = n_{3D} e^2 \mu_0 / m^* \ ?
\]
Can fit with \( m^* = 4m, n_{3D} = 10^{22}\text{cm}^{-3} \times p_{\text{eff}} \leftrightarrow \) effective number of carriers per CuO\(_2\) unit
provided that not \( p_{\text{eff}} = p \) but
\[
p_{\text{eff}} = 1 + p
\]
i.e. all holes in Cu 3\(d^9\) band, not just the excess ones over parent compound.
One puzzle: in YBCO, \( \lambda_a(0) \approx 1600\text{Å} \), \( \lambda_b(0) \approx 1000\text{Å} \)
⇒ chains appear to contribute (to \( \rho_s \)) 3/2 as much as both planes !!
ii) c-axis

$\lambda_c(0) \sim 11,000\,\text{Å (YBCO)} - 100 \,\mu \,(=0.1 \,\text{mm !}) \,(\text{BSCCO 2212})$

increases very rapidly with UD. Temperature-dependent at low T much weaker than $ab$-plane, may be fit by $\rho_{sc}/\rho \sim 1 - \alpha T^5$.

If we model interlayer contact as Josephson junction and apply standard Ambegaokar-Baratoff formula $I_c(0)R_N = \pi \Delta(0)/2e$, we expect

$$\lambda^{-2}_c(0)\rho_c d_{\text{int}}/\Delta(0) = \text{const.} \quad (d_{\text{int}} \equiv \text{mean spacing between multilayers})$$

agrees reasonably well with experiment.

6. ac conductivity ($\sigma_1(\omega)$)

complicated both in BCS superconductors and in cuprates, but 2 qualitative differences:

i) in cuprates, $\sigma_1(\omega)$ appreciable for $\omega < 2\Delta(0)$ (BCS : $\sigma_1(\omega) = 0$)

ii) for finite $\omega$, $\sigma_1(\omega)$ rises immediately below $T_c$ thereafter drops

$\Rightarrow$ suggests $\sigma_1$ limited by e-e scattering, and latter drops below $T_c$

7. Thermal conductivity

Kinetic-theory formula:

$$\kappa = \frac{1}{3}c_V\bar{v}\ell$$

$$\Rightarrow \quad \kappa_{\text{ph}}/\kappa_{\text{el}} \sim (T/\theta_D)^2(\ell_{\text{ph}}/\ell_{\text{el}}) \quad \text{(for } p \sim 1, \text{since } c_s/v_F \sim \omega_D/\varepsilon_F)$$

For BCS superconductors, $\kappa_{\text{ph}}/\kappa_{\text{el}} \ll 1$ at $T_c$, so $\kappa \sim \kappa_{\text{el}} \sim \rho_n \Rightarrow \kappa$ falls rapidly below $T_c$.

For cuprates $\kappa_{\text{ph}}/\kappa_{\text{el}} \gtrsim 1$, $\kappa$ rises below $T_c \Rightarrow$ phonons dominant, limited by scattering by electrons which drops below $T_c$. 
S-State Properties (cont.)

8. Tunneling

BCS: \( G \equiv \partial I / \partial V \) flat in N state. In S state,

\[
G_s(E)/G_n = \frac{\varepsilon}{\sqrt{\varepsilon^2 - \Delta^2}} \theta(\varepsilon - \Delta)
\]

In cuprates:
(a) in N state, \( G_n(E) \sim a + b(E) \)
(b) in S state: \( \Rightarrow \)

note
i) “dip” beyond peak
ii) \( G_s(0) \neq 0 \)
iii) peak-to-peak distance (“2\( \Delta \)”) typically \( \sim 7 - 8k_B T_c \) for \( ab \)-plane tunneling (BCS : \( 3.5 k_B T_c \)) but closer to BCS for \( c \)-axis tunneling (and overdoping).
9. ARPES

Note

(a) drop at $\varepsilon_F$ only $\sim 10\%$ in both N and S states
(b) dip beyond peak (c.f. tunneling)
(c) $\Delta \varepsilon(\pi, 0)$ (“pullback”) $\sim 4 - 5k_B T_c$.

Most interesting feature: dependence of $\Delta \varepsilon(n)$ and peak height on angle on Fermi surface.

Both height and pullback on maximum at $(\pi, 0)$ and almost certainly $\Rightarrow 0$ at $(\pi, \pi)$
i.e. at 45 to crystal axes

$\Rightarrow$ “gap” as seen in ARPES has nodes at $(\pi, \pi)$. 

\[
\begin{align*}
A(k, E) & \\
\Delta & \\
\theta & \\
\pi, 0 & \\
\pi, \pi & \\
k_x a & \\
k_y a & \\
45^\circ & \\
\end{align*}
\]
10. Neutron scattering (YBCO LSCO, Bi-2212)
Recall: in N state, $\sigma(q, \omega)$ fairly strongly peaked as $f(q)$ at $(0.5, 0.5)$ (magnetic superlattice values) but featureless as $f(\omega)$.

In the S state in YBCO and Bi-2212, nothing changes in “even” channel, but in “odd” channel ($q_z = \pi/d \leftarrow$ interlayer spacing) a striking peak is seen around $q = (0.5, 0.5)$ with $\omega \cong 41$ meV. Not seen in (single) channel of LSCO.

In this peak peculiar to bilayer cuprates?
In any case, what is its significance?

+ ________________ $\uparrow d$

- ________________ $\downarrow d$

+ ________________ $\uparrow d$

- ________________ $\downarrow d$
11. **Optics**

BCS-based prejudice: effect of superconductivity on optical behavior at frequency $\omega \gg \Delta$ should be

$$\lesssim (k_B T_c / \hbar \omega)^2 \sim 10^{-4} \text{ for } \hbar \omega \sim 1 \text{ eV} \Rightarrow \text{probably too small to see.}$$

Fact: at $\hbar \omega \sim 1 \text{ eV}$, changes in S state $\sim 1\%$!

Define $(R(\omega) \equiv \text{reflectivity})$

$$\eta(\omega) \equiv \frac{R_S(\omega)}{R_N(\omega)} - 1$$

Note: zero crossing of $\eta(\omega)$ almost exactly where $R_N(\omega)$ has minimum. Suggests

$$\eta(\omega) = -\delta (\partial R_N / \partial \omega) \quad (\star)$$

where $\delta$ is average downward shift of “initial” state (no change in final state). But

(a) would require $\delta \sim \Delta$, i.e. initial states strongly concentrated over energy range $\sim \Delta$ near $\varepsilon_F$ (no obvious reason for this)

(b) while $(\star)$ qualitatively fits data on reflectivity, does not seem to fit $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ (measured independently in ellipsometric experiment)

12. **EELS**

Published data for S states only for $\omega \lesssim 100 \text{ meV}$: no particularly interesting feature seen (probably not surprising)

No date yet on MIR (mid-infrared) region ($\omega \sim 0.5 - 1 \text{ eV}$)
WHAT DO WE KNOW FOR SURE ABOUT SUPERCONDUCTIVITY IN THE CUPRATES?

1. Flux quantization and Josephson experiments
   ⇒ ODLRO in 2-particle correlation function, i.e., superconductivity due to formation of Cooper pairs,
   i.e., basic “topology” of many-body wave function is
   \[
   \Psi_N \sim A[\phi(r_{1\sigma_1}; r_{2\sigma_2})\phi(r_{3\sigma_3}; r_{4\sigma_4}) \cdots \phi(r_{N-1\sigma_{N-1}}; r_{N\sigma_N})],
   \]
   where \( \phi \) is the same “molecular” wave function for all pairs (quasi-BEC!)
   For most purposes, it is more convenient to work in terms of related quantity
   \[
   F(r_1, r_2, \sigma_1, \sigma_2) = \langle \psi_{\sigma_1}^\dagger (r_1)\psi_{\sigma_2}^\dagger (r_2) \rangle \quad \text{ (“pair wave function” (anomalous average))}
   \]
   Note: “Macroscopic wave function” of Ginzburg and Landau, \( \Psi(R) \), is just \( F(r_1, r_2, \sigma_1, \sigma_2) \) for \( \sigma_1 = -\sigma_2 = +1 \), \( r_1 = r_2 = R \), i.e. wave function of COM of Cooper pairs.

2. “Universality” of high-\( T_c \) superconductors in cuprates with very different chemical compositions, etc.
   ⇒ Main actors in superconductivity are electrons in CuO\(_2\) planes.
3. NMR \((\chi_s, T_1, \ldots)\) (note: Spin Orbit interaction very small)
   \(\Rightarrow\) spin wave function of Cooper pairs is singlet not triplet, i.e.
   
   \[ F(r_1, r_2, \sigma_1, \sigma_2) = \frac{1}{\sqrt{2}} (\uparrow \downarrow - \downarrow \uparrow) F(r_1, r_2) \]

4. Absence of substantial FIR (far infra-red) absorption above gap edge
   \(\Rightarrow\) pair from time-reversed states (but cf. J. Tahir-Kheli)

5. Order-of-magnitude estimates from (a) \(T_c\) and (b) \(H_c\)
   \(\Rightarrow\) (in-plane) “radius” of Cooper pairs \(\sim\) a few lattice spacings. (thus, \(\xi_0/a \sim 3-10\): contrast \(\sim 10^4\) for Al.)
   \(\xi_0\): pair radius; \(a\): inter-cond. electron spacing
   \(\Rightarrow\) fluctuations much more important than in e.g. Al.

6. \(c\)-axis resistivity
   \(\Rightarrow\) hopping time between unit cells along \(c\)-axis \(\gg \hbar/k_B T\)
   \(\Rightarrow\) pairs in different multilayers effectively independent. (but cf. Anderson Interlayer Tunneling theory).

7. Absence of substantial isotope effect (in higher-\(T_c\) cuprates) + “folk-theorems” on \(T_c\)
   \(\Rightarrow\) phonons do not play major role in cuprate superconductivity (but cf. Newns and Tsuei).
WHAT DO WE KNOW FOR SURE... (cont.)

**SYMMETRY OF THE ORDER PARAMETER (GAP)**

In BCS theory, $\Delta(n)$ (fermionic gap) has (almost) same $n$-dependence as $\Psi(n)$ (order parameter $\equiv$ pair wave function). In a more general theory this is not guaranteed (but seem unlikely to be qualitatively different).

As we have seen, NMR experiments $\Rightarrow$ order parameter is spin singlet, i.e.

$$F(r_1, r_2, \sigma_1, \sigma_2) = \frac{1}{\sqrt{2}} (\uparrow_1 \downarrow_2 - \downarrow_2 \uparrow_1) F(r_1, r_2)$$

where $F(r_1, r_2)$ even-parity $\Rightarrow F_k$ even-parity. Assume relevant symmetry is that of CuO$_2$ plains, i.e. (approximately) tetragonal. Then symmetry group is $C_{4v}$ (symmetry group of square) with fundamental operations

(a) rotation through $\pi/2$ around $z$ ($\perp$) axis ($\hat{R}_{\pi/2}$)

(b) reflection in crystal axis, e.g. (100) ($\hat{I}_{\text{axis}}$)

(c) reflection in a 45° axis, e.g. (110) ($\hat{I}_{\pi/4}$)

Note (a)-(c) are not independent:

$$\hat{I}_{\text{axis}} \hat{I}_{\pi/4} \hat{R}_{\pi/2} \equiv 1$$

Evidently $\hat{I}_{\text{axis}}^2 = \hat{I}_{\pi/4}^2 = 1$, and even parity $\Rightarrow \hat{R}_{\pi/2}^2 = 1$.

$\Rightarrow$ only 4 possible irreps (irreducible representations), all 1-dimensional.
Informal name | group theoretic notation | $R_{\pi/2}$ | $I_{axis}$ | Representative state
--- | --- | --- | --- | ---
$s^+$ | $A_{1g}$ | +1 | +1 | const
$s^- (\text{`g'})$ | $A_{2g}$ | +1 | −1 | $xy(x^2 - y^2)$
$d_{x^2-y^2}$ | $B_{1g}$ | −1 | +1 | $x^2 - y^2$
$d_{xy}$ | $B_{2g}$ | −1 | −1 | $xy$

Are we sure order parameter belongs to a single irrep? In general, if $i$ labels different irreps,

$$F(T) = \sum_{ij} \alpha_{ij}(T) \psi_i^* \psi_j + \frac{1}{2} \sum_{ijkl} \beta_{ijkl}(T) \psi_i^* \psi_j^* \psi_k \psi_l$$

Quite generally (for any symmetry group!) $\alpha_{ij} \sim \alpha_{j} \delta_{ij}$, but in general terms such as $|\psi_i|^2 \psi_i^* \psi_j$ ($i \neq j$) allowed (e.g. SO(3), $i = p, j = f$). However, for even-parity representation of $C_{4v}$, such terms are forbidden by symmetry: only allowed forms are $A_1 \sim |\psi_i|^2 |\psi_j|^2$ and $A_2 \sim \psi_i^* \psi_i^* \psi_j \psi_j$. Thus most general form on $F$ is

$$F(T) = \sum_{i=1}^{4} \alpha_i(T)|\psi_i|^2 + \frac{1}{2} \sum_{i,j=1}^{4} \beta_{ij}(T)|\psi_i|^2 |\psi_j|^2 f(\phi_{ij})$$

where $\phi_{ij}$ is the relative phase of $\psi_i$ and $\psi_j$.

More than one $\psi_i \neq 0 \Rightarrow 2$ phase transitions. Not seen, so order parameter belongs to a single irrep.
According to above argument, must be just one of

\[ s \] favored by some types of theory, \[ d_{x^2-y^2} \] favored by spin-fluctuation theory, \[ d_{xy}, s^- \]

How to tell?

(a) \( d_{x^2-y^2}, d_{xy}, s^- \) must have (at least) 4 nodes on Fermi surface. \( s \) need not. \( \Rightarrow \) exponential decrease of quasiparticle-associated quantities \((\chi, T_1^{-1}, \Delta \lambda(T)...\) certainly \( \Rightarrow \) s-wave. Experimentally, all these quantities have power-law dependences consistent with 2D point node. Does this inevitably \( \Rightarrow \) not \( s \)? Unfortunately not, because even \( s \) state may have nodes allowed by symmetry (“extended s-wave”).

(b) More specifically, \( d_{x^2-y^2} \) (and \( s^- \)) must have nodes at \((\pi, \pi)\), \( s \) (and \( d_{xy} \)) would have them there only by pathology. \( \Rightarrow \) observation of node favors \( d_{x^2-y^2} \). ARPES data indeed indicates such a node. But...

i) “gap” seen in ARPES may not simply be superconducting gap (cf. pseudo gap regime.)

ii) “extended s-wave” state of form \( F(\theta) = A + B \cos 4\theta \) \((0 < B - A \ll A)\) may be difficult in practice to distinguish from \( d_{x^2-y^2} \).
So: need experiment which is directly sensitive to sign (or more generally phase) of order parameter \( \Rightarrow \) Josephson ("phase-sensitive") experiments.

Reminder: for simple s-wave case, to lowest order in \( \Psi \)'s

\[
E_J \propto -\text{const.}(\Psi_1^* \Psi_2 + \text{c.c.}) \sim -\text{const.} \cos \Delta \varphi
\]

(a) Josephson effect occurs for any geometry.

(b) in SQUID geometry, critical current max. at \( \Phi = n\Phi_0 \), and min. at \( \Phi = (n + 1/2)\Phi_0 \)

\[
\sum_i \Delta \varphi_i = 2\pi \Phi/\Phi_0
\]
Principles of Josephson experiment in cuprate (and other exotic) superconductor

(a) If bulk superconductor + junction described by Hamiltonian $\hat{H}$ invariant under symmetry group $G$, then Josephson coupling energy must be similarly invariant under $G$.

(b) For a circuit, the fundamental equation

$$\sum_i \Delta \varphi_i = 2\pi \Phi / \Phi_0$$

must hold provided the $\Phi$’s (hence the $\Delta \varphi_i$) consistently defined. Assume lowest-order Josephson effect (testable via Fraunhofer diffraction pattern etc), i.e.

$$E_J \sim -\text{const.}(\Psi_1^* \Psi_2 + \text{c.c.})$$

Application (a) alone:

Consider $\pi/2$ rotation around $z$-axis. $\Psi_{\text{Pb}} \rightarrow +\Psi_{\text{Pb}}$.

For YBCO, if s-wave ($s$ or $s^-$) $\Psi_{\text{YBCO}} \rightarrow +\Psi_{\text{YBCO}} \Rightarrow$ lowest-order Josephson effect allowed.

But if d-wave ($d_{x^2-y^2}$ or $d_{xy}$) then $\Psi_{\text{YBCO}} \rightarrow -\Psi_{\text{YBCO}} \Rightarrow$ lowest-order Josephson effect forbidden.

Application (b) alone:

Pb order parameter invariant under $\pi/2$ rotation $\Rightarrow$ “$\Psi_1$” identical at junctions 1 and 2. If YBCO is s-wave, same situation as in conventional dc SQUID. $\Rightarrow I_c(\Psi)$ is maximum at $\Psi = n \Psi_0$, min at $\Psi = (n + 1/2) \Psi_0$. If YBCO is d-wave, sign of “$\Psi_2$” changes between 1 and 2, so effectively adds $\pi$ to LHS of (*) $\Rightarrow I_c \text{ max at } \Psi = (n + 1/2) \Psi_0$.

[Application of (a) and (b) e.g. “tricrystal ring” experiment]

Conclusion from $\sim$ 20 phase-sensitive experiment:

order parameter of cuprates is $d_{x^2-y^2}$. 
How will we know when we have a “satisfactory” theory of high-$T_c$ superconductors in the cuprates?

Thesis:
We should (at least) be able to:

(A) give a blueprint for building a robust room-temperature superconductor,

OR (B) assert with confidence that we will never be able to build a (cuprate-related) room temperature superconductor

OR (C) say exactly why we cannot do either (A) or (B)

In the meantime, a few more specific questions:

1. Are the cuprates unique in showing high-$T_c$ superconductors?

2. If so, what is special about them?
   (e.g. band structure, 2-dimensionality, AF ....)

3. Should we think of high-$T_c$ superconductors as a consequence of the anomalous N-state properties, or vice versa?

4. Is there a second phase transition associated with the $T^*$-line? If so, what is the nature of the low temperature (“pseudogap”) phase?

5. If yes to (4), is this relevant to high-$T_c$ superconductors or a completely unconnected phenomenon?

6. Why does $T_c$ depends systematically on $n$ in homologous series?
Some representative classes of “models” of Cooper pairing in the cuprates (conservative ⇒ exotic)

1. Phonon-induced attraction (“BCS mechanism”)
   problems : N-state $\rho_{ab}(T) \propto T$ down to $T \sim 10$ K (Bi-2201 $T_c$)
   no isotope effect in higher-$T_c$ high-$T_c$ superconductors
   folk-theorems on $T_c$ (but ↑ : FeAs compounds)
2. Attraction induced by exchange of some other boson :
   — spin fluctuations
   — excitons
   — fluctuations of “stripes”
   — more exotic objects
3. Theories starting from single-band Hubbard model*:
   $$\hat{H} - t \sum_{ij\sigma} (c^{\dagger}_{i\sigma} c^\dagger_{j\sigma} + H.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$
   a. Attempt at direct solution, computational or analytic
   b. Theories based on postulate of “exotic ordering” in ground state (e.g. spin-charge separation)
   Problems : — to date, no direct evidence for exotic order
   — $T^*$-line appears to be unrelated to $T_c$
   (and “Nature has no duty ....”)