

Superconducting state II: Spectroscopic probes. Preliminary overview of the experimental situation

1. Tunneling*

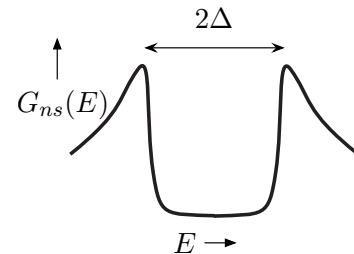
We recall

(a) that whereas in a classic superconductor in the normal state the differential tunneling conductance $G_{nn} \equiv \partial I / \partial V$ is essentially flat or at most weakly parabolic, in a typical cuprate it often (though not invariably) has the form $a + b|V|$.

(b) that for a classic (*s*-wave) superconductor in the superconducting state, the ratio of the differential conductance G_{ns} to its normal-state value G_{nn} is given by the ratio of the density of quasiparticle states and is thus of the form

$$G_{ns}(E)/G_{nn}(E) = E/\sqrt{E^2 - \Delta^2} \theta(E - \Delta) \quad (1)$$

Although in practice gap inhomogeneity over the Fermi surface, lifetime effects etc., tend to smooth out the singularity, the general pattern is as shown, with a peak to peak difference which is close to 2Δ as estimated independently.



In the cuprates one might expect the form of the tunneling spectrum to depend on the direction of the tunneling with respect to the crystal axes. In practice

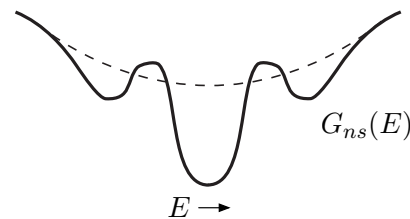
it is relatively straightforward to distinguish between *c*-axis and *ab*-plane tunneling, but less easy to tell which direction(s) one is tunneling into in the *ab*-plane (because of possible surface faceting etc.).

In the *c*-axis case, a typical $T \approx 0$ tunneling characteristic looks like that shown for YBCO [dashed line = G_{nn}].

Note:

(a) the ‘dip’ in the DOS beyond the peak (not present in classic superconductors)

(b) the fact that the DOS never goes strictly to zero.



As the temperature is increased the hole in the DOS gradually ‘fills in’, while the peak positions

remain approximately constant. If the gap Δ is taken to have the BCS value $1.75k_B T_c$, then the peak-to-peak splitting is generally somewhat greater than 2Δ , typically of order[†] 3Δ with the bottom of the dip occurring at around 3Δ from the origin. Those

*Refs: Renner et al., PRL **80**, 149 (1998); Matsuda et al., PRB **60**, 1377 (1999) [these change picture somewhat].

[†]Refs.: Renner et al., $5 - 6\Delta$ (83meV) at optimal doping; Matsuda et al., ~ 50 meV with little *T*-dependence of ‘gap’ itself.

features appear to be common to YBCO, BSCCO-2212 and LSCO.[‡]

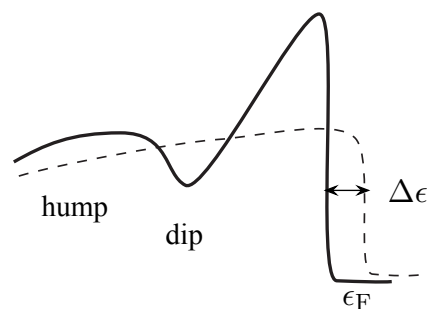
The situation is qualitatively similar for tunneling into the ab-plane, but with several significant differences. First, the ‘peak-to-peak’ distance appears to be considerably larger, $\sim 7 - 8k_B T_c$ (though it decreases towards a BCS-like value as the sample is overdoped). Secondly, the ‘hole’ in the DOS is considerably more pronounced. Thirdly, in recent measurements (primarily by LHG’s group) then appears a zero-bias anomaly (hump) in the DOS at zero voltage. The dependence of this anomaly on temperature, surface orientation and magnetic field is of great interest in the context of discussion of the symmetry of the OP, and I will return to it in lecture 10.

(Symmetry of the $I - V$ characteristic: Jim Eckstein’s recent results)

One conclusion one can draw with near-certainty from the tunneling data is that it is quite incompatible with any model in which the single-particle DOS vanishes below a minimum gap Δ_{\min} which is anywhere near of the order of $k_B T_c$. It is not even clear it can be fitted to a power-law DOS, at least unless the finite value at $E = 0$ is attributed to localized/Andreev bound states etc.

2. ARPES

Recall that the vast majority of ARPES experiments have been done on BSCCO with the surface in the ab-direction (but the surface itself is a BiO layer!) In principle, subject to the usual assumptions, the photo current measures the single-particle spectral function $A(\mathbf{k}, \omega)$ for \mathbf{k} in the ab-plane (cf. lecture 5).[§] In practice, the accuracy obtainable for \mathbf{k} (i.e. the ‘width’ of the resolution function in \mathbf{k} -space) is $\sim 0.01 - 0.05 \text{ \AA}^{-1}$, and the energy accuracy is now reduced to $\sim 2 \text{ meV}$ (see Damascelli et al.): note that these are smaller than the expected momentum and energy scales of the pairs, though in the momentum case still not by a large margin.



In the normal state, for given \mathbf{k} near the (inferred) Fermi momentum, the ARPES data as a function of energy have a steep drop at the (inferred) Fermi energy but are otherwise featureless. In the superconducting state, if we consider for definiteness the $(\pi, 0)$ direction, the curve develops a sharp peak whose leading edge is ‘pulled back’ from the Fermi energy by an amount $\Delta\epsilon$, and below the peak the curve dips below the N-state value (cf. the tunneling data). Beyond this point, there is a weak ‘hump’. At optimal doping both the height of the peak and its displacement $\Delta\epsilon$ from the Fermi energy increases smoothly as T falls below T_c , and at low temperature $\Delta\epsilon(\pi, 0) \approx 35 \text{ meV}$, corresponding to $\sim 4 - 5k_B T_c$. The shift is also seen in the underdoped materials though it is less pronounced and persists above T_c (cf. below).

The most interesting feature of the peak in the superconducting state is its dependence on the angle on the Fermi surface. Both the height and $\Delta\epsilon$ are a maximum in the $(\pi, 0)$ direction (i.e., along the crystal axes) and decrease towards zero as we move towards the (π, π) direction; it is now generally believed that both quantities are zero

[‡]However, in BSCCO-2212 the peak appears at $\sim 4k_B T_c$ (Iavarone et al., in SNS 97).

[§]see Campuzano et al., cond-mat/0209576; Damascelli et al., RMP **75**, 473 (2003) (good general review of ARPES).

when one sits precisely at (π, π) (though one cannot absolutely rule out the possibility that the zeros are split, on either side of this). [update: ‘flat’ regions?]

While the (few) ARPES data on YBCO appear qualitatively similar to those on BSCCO-2212, the data on LSCO so far show no peak-dip structure (see Fujimori et al., in SNS97): the raw data in the superconducting state look much like those of BSCCO in the normal state. It is not clear whether this reflects some disorder effect, either intrinsic or removable (cf. below). In contrast, experiments* on (La-doped) Bi-2201 show a clear peak (though no identifiable dip) at an energy which appears to behave as a function of angle similarly to that of Bi-2212 and to have a magnitude approximately 1/3 as large (which is also the ratio of the T_c 's). The peak is actually sharpest on the overdoped side.

3. Neutron scattering[†]

(mostly YBCO and LSCO, some BSCCO-2212)

As noted in lecture 5, the N-state neutron scattering data on all cuprates so far examined are fairly strongly peaked as a function of \mathbf{q} , with either single or multiple peaks close to $(0.5, 0.5)$ (the AF superlattice), but featureless as a function of energy. If we restrict ourselves to the energy range below $\sim 30\text{meV}$, then this statement remains qualitatively true for all systems in the S phase in the ‘even’ channel, although as function of \mathbf{q} the peaks sharpen somewhat. However, in YBCO a new feature appears in the ‘odd’ channel close to $(1/2, 1/2, 1)$ (i.e. $\mathbf{q}_x \approx \mathbf{q}_y \approx \pi/2a$, $\mathbf{q}_z = \pi/d$, where d is the intra-bilayer spacing ($\approx 3.1\text{\AA}$)): we get a striking peak at an energy which ranges from $\sim 41\text{meV}$ for optimally doped YBCO to $\sim 34\text{meV}$ for $x = 0.6$, with an energy width $\sim 5 - 10\text{meV}$ (narrow by neutron standards) and a momentum width $\sim 0.2\text{RLU}$.[§] The position of the peak appears to be independent of temperature, but its amplitude is strongly temperature-dependent and in optimally doped samples it cannot be seen above T_c . A peak with essentially the same properties has been seen in Bi-2212 (Keimer et al., ref. cit.), but searches in LSCO have failed to detect anything remotely similar (note that there is no trace, in YBCO, of this resonance in the ‘even’ $(\pi, \pi, 0)$ channel). As a function of doping, the energy of the peak seems to scale with T_c both for UD and OD regimes (but in all cases is independent of temperature); the weight scales with temperature roughly as $\Delta^2(T)$, where Δ is the ‘gap’ inferred from the photoemission spectrum (thus, in the UD regime, peak persists above T_c and up to some T^*).

Both the origin of this ‘41meV peak’, and its possible relation to the anomalies in the tunneling and ARPES spectra, are currently a topic of great interest: I return to these later. [update]

*Harris et al., PRL **79**, 143 (1997); cf. Lanzara (2002).

[†]Refs: Mook et al., Nature **395**, 580 (1998); Science **289**, 1344 (1999); Keimer et al., Nature **398**, 588 (1999); Birgeneau et al., J. Phys. Soc. Jpn. **75**, 111003 (2006)

[§]Mook et al., PRL **70**, 3490 (1993). Note that (at least roughly) the energy width is resolution-limited but the momentum width is not.

3. Raman[§]

We noted in lecture 5 that in the N state of optimally doped cuprates the Raman spectrum is essentially channel-independent and featureless for $\omega < 2\Delta$. In the S state things are much more interesting. In the first place, both for YBCO and for Bi-2212, a broad peak in the spectrum develops at a frequency of the order of 2Δ . However, the peak frequencies are different in the A_{1g} and B_{1g} channels, and the feature is not visible in B_{2g} : see Strohm et al., ref. cit. Fig. 4. Blumberg et al. (ref. cit.) argue that the B_{1g} peak, which centers at $\sim 600\text{cm}^{-1}$ or 75meV , actually corresponds to excitation of a bound pair of the magnon-like excitations seen at 41meV in the neutron scattering. Its polarization and other main properties (e.g. the apparent temperature-independence of its frequency) seem right for this identification. To the best of my knowledge this peak has not been seen (maybe not looked for) in LSCO.*

The second point of interest in the Raman behavior is the low-frequency dependence of the intensity. In Y123 (at least) this is somewhat similar for the A_{1g} and B_{1g} channels; in each case there is a term linear in ω , and in B_{1g} channel also a term of comparable magnitude proportional to ω^3 . In the OD regime the linear term in B_{1g} is reduced relative to the ω^3 one, and this behavior is also seen in overdoped Tl-2201 and (probably)[†] also in Bi-2212. The question of the difference between the asymptotic behavior of the Raman intensities in the 2 geometries (A_{1g} and B_{1g}) is of considerable significance in the context of the question of gap symmetry, and I return to it in lecture 10.

4. Optics

At least until quite recently, the investigation of the possible changes in the optical (visible-region) behavior of the cuprates when the system goes superconducting has not been a particularly fashionable subject. Probably the main reason for this lack of interest has been that any simple BCS-like theory would predict that any such relative changes are likely to be of the order of $(k_B T_c / \hbar\omega)^2$, which for ω in the optical region (say $\hbar\omega \sim 1\text{eV}$) would be $\sim 10^{-4}$, probably too small to see in most experiments. As we shall see, however, the experimentally observed changes are at least two orders of magnitude larger, and this must be an important input into any discussion of the mechanism of superconductivity in these materials.

The most systematic published study of the changes in the optical properties associated with the onset of superconductivity is the ‘thermal-difference reflectance’ work of Holcomb et al. (Phys. Rev. B **53**, 6734 (1996)); more recent ellipsometric work by van der Marel and by Rubhausen[¶] seems consistent with the results of Holcomb et

[§]Refs: Strohm + Cardona, PRB **55**, 12725 (1997); Blumberg et al., Science **278**, 1427 (1997); Rubhausen, in SNS 97. Note the data shown in Strohm are on 123, those of Blumberg et al. on 2212; Devereux et al., Revs. Mod. Phys. **79**, 175 (2007).

*It is seen in Bi-2212, Tl-2201, and YCa..., and in all cases its position shifts towards that of the A_{1g} peak with overdoping (Martin et al., Phys. Status. Solidi **214**, 9 (1999)).

[†]The original data (Staufer et al., PRL **68**, 1069 (1992)) were not analysed in this way, but the authors’ qualitative comments seem consistent with this.

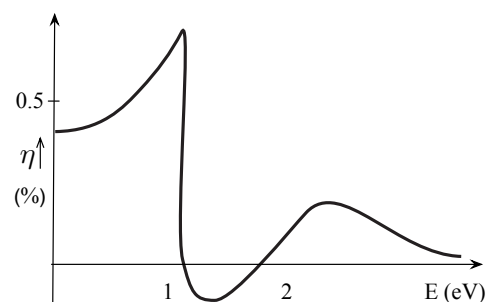
[¶]Molegroaf et al., Science **295**, 2239 (2002); Rubhausen et al., Phys. Rev. B **63**, 2295 (2001).

al. and, rather than measuring the reflectance only and inferring the complex dielectric constant by Kramers-Kronig transform, measures the latter directly. The raw data in the experiments of Holcomb et al. is the difference in reflectance (off a surface parallel to the ab-plane with the incident light unpolarized and at 45° to the normal) at two temperatures which typically differ by 5K; from this they can reconstruct the complete temperature-dependence of the reflectance down to ~ 0.75 of T_c . The experiments were done on YBCO, BiPb-2223, Tl-2212 and Tl-2223, and the results for these four materials are quite similar. Even in the N state, the reflectance is quite temperature-dependent right up to energies $\sim 3 - 4\text{eV}$: see Fig. 5. The amplitude ΔR_\perp of the difference in reflectance of temperature differing by (say) 5K is roughly proportional to T , and to calculate the ‘intrinsic’ changes associated with the onset of superconductivity Holcomb et al. extrapolate it below T_c and subtract it out; this point is not trivial, because crudely speaking the inferred ‘intrinsic’ changes looks much like the negative of the normal-state ΔR_\perp . At the end of the day one infers an ‘ideal’ ratio R_S/R_N , where R , is the reflectance actually measured in the superconducting state at a given temperature (say ~ 0.75 of T_c) and R_N is the inferred reflectance which the sample ‘would have had’ were it still in the N state at this temperature, as inferred by extrapolation of the $T > T_c$ data. The punch-line is the quantity $\eta \equiv R_S/R_N - 1$ which is in some sense a measure of the effects of superconductivity on the optical spectrum, and which e.g. for Tl-2223 at 90K ($0.75T_c$) can be read off from Fig. 18c, reproduced approximately here. What is striking is that η reaches a maximum of 0.8%, and even at 2.5eV is still $\sim 0.1\%$, very considerably in excess of the prediction of a simple BCS-type theory.

It is striking that the zero crossing of η occurs at almost exactly the energy where the normal-state reflectance $R_N(\omega)$ has a minimum. This suggests an obvious question: Can we account for the form of the quantity $\eta(\omega)$ simply by assuming that neither the ‘final’ (high-energy) states involved in the optical transition nor the matrix elements are affected by the superconducting transition, and that the only relevant change is in the energy of the initial state, which we may imagine is (possibly) close to the Fermi energy and hence particularly susceptible to the onset of superconductivity? Let’s imagine the most naive possible form of this hypothesis, namely that all the initial states are shifted downwards in energy uniformly by an amount δ . There we would have $R_S(\omega) = R_N(\omega - \delta)$, so that to linear order in δ we would expect

$$\eta(\omega) = -\delta \cdot \partial R_N / \partial \omega \quad (2)$$

This formula would appear to fit the raw data on the reflectance at least qualitatively, if we take δ (at $0.75T_c$ for Tl-2223) to have a value of order 10meV (which is in fact not so different from a ‘typical’ value of the energy gap). However, unless the initial states involved in the optical transition are very strongly concentrated near the Fermi energy, a value of $\delta \sim \Delta$ seems implausible; and would expect rather the smaller value



$\delta \sim \Delta^2/\epsilon$ where ϵ is the width of the range of initial states involved in the normal state. More seriously, the real and imaginary parts of the complex dielectric constant $\epsilon(\omega)$, as measured separately by ellipsometry, do not seem to satisfy a relation similar to (2). So the origin of these surprisingly large effects must at the moment be regarded as a major mystery of cuprate superconductivity.

5. EELS**

In view of the surprisingly large effects of the onset of superconductivity on the visible-region (1 – 3eV) optical properties, it would be very interesting to know whether the transmission EELS cross-section, which should be a direct measure of the charge fluctuations and thus the Coulomb energy, undergoes significant changes in this region of the spectrum. Unfortunately, there is at present no published data on the differential EELS cross-section (i.e., $\sigma_s(\mathbf{q}, \omega) - \sigma_n(\mathbf{q}, \omega)$) in this region. EELS experiments have been conducted (in the reflection geometry) in the superconducting state, but at considerably lower energies ($\sim 100\text{meV}$) and with disappointing results (see Mills et al., ref. cit.). In particular, there is no feature in the data which can be plausibly identified with the superconducting gap. Quite apart from the fact that the cross-section in this regime is in practice dominated by surface optical phonons, which may well mask any small changes, it is not clear to me that we should even expect to see anything interesting in this energy region, since theoretically the normal-state loss function is expected to be very small for $\omega < 100\text{meV}$. (However, it is possible that there are subtleties connected with the reflection geometry used which may invalidated this simple consideration).

6. Preliminary overview of the experimental situation

A. How universal are the properties of the cuprates?

In discussing this question one must of course bear in mind that for practical experimental reasons many types of experiment can only be carried out on a restricted class of the cuprates (e.g. ARPES can only be practically done on those which can be prepared with flat, clean surfaces). Considering first ‘qualitative’ universality, there are very few phenomena which demonstrably occur in some cuprates and demonstrably don’t occur in others: superconductivity itself is probably the most striking example, since as we have noted there is a fairly large class of cuprates which have not been induced to become superconducting even when subject to what are plausibly the ‘right’ conditions of doping, pressure etc. Apart from this, one could cite the crystallographic (orthorhombic-tetragonal) transition, which appears to be peculiar to LSCO and YBCO, the ‘superlattice’ structure which occurs in the Bi series and the occurrence of (weak) antiferromagnetism coexisting with superconductivity which appears to be peculiar to some of the RE $\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ materials (e.g. RE=Gd). It is clear that all of these latter effects are likely to involve essentially elements of the structure other than the CuO_2 planes, so it is not particularly surprising that they are not universal. A further

Refs.: Phelps et al., Phys. Rev. B **50, 6526 (1994); Mills et al., *ibid*, 6394.

group of properties which at least at first sight are non-universal is the c-axis transport properties: e.g. the N-phase dc c-axis resistivity $\rho_c(T)$ increases with T for some cuprates and decreases for others. On the other hand, it can usually be fitted to a power law ($\rho_c(T) \propto T^\alpha$), so it may be possible to argue that it is ‘qualitatively’ but not quantitatively universal. With these and possibly a few other exceptions (including one to be discussed below), the behavior of the cuprates indeed seems to be qualitatively universal.

The question of quantitative universality needs to be made a bit more precise. Let us first ask: Given a particular (superconducting) cuprate at the values of hole concentration p , impurity concentration (zero) etc. which maximize T_c , and at given $T > T_c$, are the properties ‘per CuO_2 plane’ uniquely determined, i.e. the same for all cuprates under these conditions? Within the error bars, the answer seems to be yes for at least two quantities, the Sommerfeld coefficient γ in the electronic specific heat, which seems to be $\approx 6.5 \text{mJ/mol}(\text{CuO}_2)\text{K}^2$ for all compounds on which it has been reliably measured, and the thermoelectric power S at room temperature (but not, interestingly, more generally). On the other hand, while the in-plane resistivity $\rho_{ab}(T)$ is fairly universally proportional to T and hence ‘qualitatively’ universal, the coefficient of proportionality is fairly clearly different for LSCO than for the higher- T_c materials (YBCO, Tl-2201, Bi-2212 ...) and it is not entirely clear that it is quantitatively universal even within the latter group. This difference may reflect in part the fact that transport properties, unlike thermal ones any such as the specific heat, are likely to be sensitive to the degree of localization (‘trapping’) of the in-plane carriers by near-plane disorder, such as naturally occurs in $\text{La}_{2-x}\text{Sr}_x\text{Cu}_2\text{O}_4$.

The (infrared and visible-region) ab-plane optical properties are evidently qualitatively universal (all known cuprates show the characteristic MIR peak); the question of quantitative universality is a bit more complicated, since as noted in lecture 5 the charge-reservoir material may contribute appreciably. However, it seems probable that the data below say 2eV are consistent with quantitative universality of the ‘per-plane’ response, the differences in the directly measured quantity (reflectance) arising primarily from the different density of planes in the different materials.

In the superconducting phase the natural question would seem to be: At a given value of p (e.g. the ‘optimal’ value ~ 0.16) and a given value of the reduced temperature $T/T_c(p)$ (e.g. zero), are the per-plane properties the same for different cuprates? Again, a tentative answer would seem to be that this is true for thermal properties such as the specific heat,* but that for transport-type properties such as the penetration depth $\lambda_{ab}(0)$ the universality is quantitative only among the higher- T_c materials (YBCO (a-axis), Tl-2223, probably Bi-2212 ...): cf. lecture 7. A more systematic experimental investigation of this question would seem to be of great value.

When we come to spectroscopic probes of the superconducting state, a very interesting situation arises: while the Raman and optical behaviour appears to be at least qualitatively universal, the neutron scattering shows a striking feature, namely the ‘41 meV peak’ which has been clearly observed in YBCO and BSCCO but equally reliably

*Except perhaps at the lowest temperatures (where it is very sensitive to impurity levels etc.)

observed not to occur in LSCO. Further, the ‘peak-dip’ structure in the ARPES characteristics appears in the former two compounds but not in the last (at least so far). This clear lack of even qualitative universality raises several obvious questions:

- (1) Is the origin of the 41 meV peak intrinsically associated with the bilayer structure of YBCO and BSCCO, or is its absence in LSCO a consequence of other factors (possibly the same ones as are responsible for the lack of quantitative universality of ρ_{ab} , $\lambda_{ab}(0)$ etc.)? Experiments on Tl-2201, if and when it can be made in sufficiently large samples, should definitively resolve this question.
- (2) Is there a causal connection between the 41 meV peak and the peak-dip structure of the ARPES spectrum (and possibly that of the tunneling spectrum)?
- (3) Does either phenomenon play a role in the mechanism of superconductivity?

B. Are there ‘hidden’ phase transitions?

It has become quite fashionable recently to suggest that apart from the standard breaking of $U(1)$ symmetry associated with the onset of superconductivity, the cuprates may undergo a more subtle breaking of some more sophisticated symmetry (often associated with local time-reversal invariance). This transition is often claimed to occur roughly at the ‘pseudogap’ temperature $T^*(p)$; to the objection that no discontinuities, etc., are visible there, it is replied that this is because the samples so far investigated are dirty and thus presumably inhomogeneous, so that the effect of the transition is smeared. It is difficult to comment on this scenario meaningfully in the absence of quantitative calculations of the likely effects of disorder on the specific type of symmetry-breaking assumed; all that one can usefully say is that

- (a) the qualitative continuity of the main experimental properties as a function of p for $T > T_c(p)$ is striking, and
- (b) Tallon and Loram argue rather convincingly that the crossover behaviour at $T^*(p)$ has a natural interpretation in terms of an energy scale $E_g(p)$ which does not correspond to any kind of phase transition but rather to a smooth crossover.

Needless to say, any reliable experimental detection of (say) a breaking of local time-reversal invariance in the pseudogap regime^{‡‡} would immediately change the picture qualitatively.

^{‡‡}Cf. Kaminskii et al., Nature **416**, 610 (2002). At the time of writing this work is controversial.