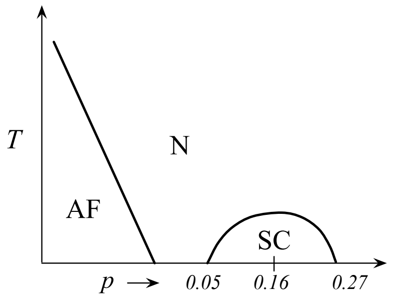
The phase diagram: the 'pseudogap' regime. Systematics of $\mathbf{T_c}$.

There is fairly general agreement that the identifiable phase transitions partition the phase diagram of a 'typical' cuprate as shown. (but note that there is no case known in which the whole range of p is stable ! – the phase diagram shown is a composite.)



The height of the superconducting regime (i.e. $T_{\max}$) varies a lot from material to material, but its width in p is relatively constant and the maximum always seems to occur close to $p = 0.16$ (cf. below). A point to note is that one can often start with a material with a reasonable value of T_c (e.g. optimally doped YBCO, $T_c \approx 92$K) and by doping with in-plane Zn or Ni impurities, drive T_c down and eventually to zero, thus eliminating the 'S' phase in the diagram. Additionally, some cuprates even when undoped with Zn appear to have no S region. (cf. below, part II).

In discussing more subtle aspects of the phase diagram, one should remember that it is easy to vary the temperature at constant p, ie. to move up and down, but difficult to vary p at constant T, i.e., move sideways: very few experiments have done the latter.[*] (In some cases, such as $YBa_2Cu_4O_8$, which is generally believed to be 'naturally underdoped' with $p \approx 0.12$, the stoichiometry cannot be varied so we are stuck with a single value of p from the start).

Let's start with a couple of regions of the phase diagram where there is little controversy. To the right of the max of T_c one has the so-called 'overdoped' regime: as we move to the right, the properties appear to become closer and closer to those of a standard textbook Fermi liquid, e.g. for Tl-2201 a log-log plot of $\rho_{ab}(T)$ against T shows a slope which varies from close to 1 for $p = 0.16$ to close to 2 for $p \approx 0.25$. The Hall coefficient also appears consistent with a Fermi surface containing (1+p) electrons, as does the ARPES data. (see below). Moreover, the transition to the superconducting state at this side of the diagram appears sharp and BCS-like, without any obvious precursors. (Complication: LSCO Fermi surface appears to change from hole-like to electron-like somewhere near $x = 0.25$).[†]

A second regime of the phase diagram which is generally believed to be well understood is the AF phase which occurs at small p ($p \leq 0.04$). We consider its form for $p = 0$. In a single-plane material like La_2CuO_4, the system appears to be a simple AF Mott insulator; recall we have 1 hole per CuO_2 unit in the $3d$ shell, and this hole is believed to be localized, approximately, on the Cu's, and to order antiferromagnetically. Thus, the crystallographic ab-plane reciprocal lattice (a simple square lattice with side $2\pi/a$)

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[*] Loram et al., J. Phys. Chem. Sol. **59**, 2091 (1998); Wuyts et al, Phys. Rev. B **53**, 9418 (1996)

[†] Ino et al., J. Phys. Soc. Japan **68**, 1496 (1999). A similar phenomenon occurs for BSCCO2212 and Bi2201: see Kaminski et al., PRB 73, 174511 (2006). However, this can be understood within a "textbook" band-structure scheme.

is accompanied by a magnetic superlattice, with extra points at $(\pi/a, \pi/a)$, or in the conventional notation $(0.5, 0.5)$; in the AF phase we indeed get elastic spin-flip neutron scattering at the wave vectors. In inelastic neutron scattering we can observe spin waves, and from a study of their dispersion relation we infer that system is well-described by a nearest-neighbor Heisenberg Hamiltonian, i.e.

$$\hat{H} = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \tag{1}$$

with an AF coupling constant which is approximately 1000K.

In the bilayer material[‡] $YBa_2Cu_3O_6$ the in-plane ordering seems to be the same as in La_2CuO_4; moreover the two planes order 'antiferromagnetically' relative to one another, i.e. the Cu spins sitting 'opposite' one another are oppositely oriented. One then gets 'acoustic' and 'optical' spin waves, and from their spectrum one can deduce the in-plane AF coupling constant $J_{\|}$ ($\sim$ 1000K) and the 'interplane' constant $J_{\perp}$ ($\sim$ 200K). These values appear to be roughly consistent with the observed values of $T_{\mathrm{N}}(p = 0)$ for La_2CuO_4 (300K) and $YBa_2Cu_3O_6$ (500K).

Now let's turn to the controversial part of the phase diagram, namely the slice lying to the right of the AF phase but to the left of the point of max T_c ($p \approx 0.16$). This region is variously called the 'underdoped', 'pseudogap' or 'strange-metal' region. There are two major features of this region which are currently not well understood. First, to the immediate right of the AF phase boundary (which is a genuine 2nd order phase transition, marked by the appearance of AF LRO) there is a slice of the phase diagram where the system appears to lack any identifiable LRO but nevertheless to be effectively insulating (or at least so have a $\rho \gg$ that of the optimally doped material just above T_c); for want of a better name this is sometimes called the 'spin-glass' regime (though this may have misleading connotations). Although direct evidence is hard to come by, it is often believed that the small portion of the p-axis at zero T between the vanishing of antiferromagnetism at $p \approx 0.04$ and the onset of superconductivity at $p \approx 0.05$ corresponds to a perfect insulator. Since at sufficiently high T this 'slice' is reasonably metallic with a $\rho(T)$ which increases with T, there has to be a crossover as a function of temperature. This question has been investigated in detail for LSCO; one finds that for any given p, the resistivity $\rho_{ab}(T)$ has a minimum as a function of T, at a temperature which varies linearly from about 200K for $p \approx 0.05$ to T_c at $p \approx 0.15$. By doping with Zn, the superconductivity can be suppressed and the behavior of $T_{\min}(p)$ followed down to $p \approx 0.19$ where it tends to zero. The transition from the anomalous metallic behavior to an effectively insulating one thus does not appear to correspond to a phase transition, but rather to a smooth crossover of the type by now familiar, e.g., in thin granular films.

A second major feature[¶] of the underdoped regime, which may or may not be related to the above, is the appearance of a so-called 'pseudogap' below a characteristic

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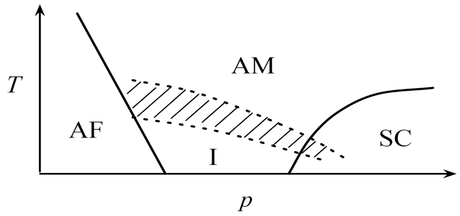
[‡] Because of the requirement in neutron scattering experiments for large samples, the AF phase has been studied in detail only for LSCO and YBCO.

[¶] Refs: Timusk and Statt, Reps. Prog. Phys. **62**, 61(1999). Tallon + Loram , Physica **349**, 53 (2001).



temperature $T^*(p)$ which rises to RT or above: Although the system does not display superconducting long range order, it behaves as very much as if there were a gap in the single-particle energy spectrum. The pseudogap was observed early on in the NMR behavior, but is now known to manifest itself in just about all measurable properties in the underdoped regime; it has become a major subject of experimental investigation and theoretical speculation in the last few years. Its most direct manifestations are in ARPES and tunneling, so I start with these.

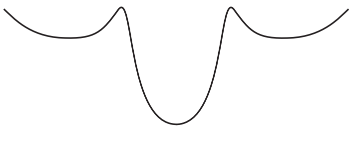
ARPES (BSCCO series)

In the superconducting state of Bi-2212 at optimal doping, the rather diffuse N-state ARPES spectrum develops a sharp peak which is well separated from the Fermi energy; the separation is normally taken as a measure of the superconducting energy gap $\Delta(\hat{\mathbf{k}}))$ (see lecture 8). The gap appears to have approximately the so-called $d_{x^2-y^2}$ symmetry, i.e., it is largest along the crystal axes and vanishes in the 45° $(\pi/a, \pi/a)$ directions (more details in lecture 7). This gap feature persists in the superconducting state in the underdoped regime ($p < 0.16$), but in this case it appears to persist also above T_c; the energy appears to be more or less independent of temperature[**] (at about 25meV $\sim$ 300K for $p \sim$ it increases slightly as p decreases), but the amplitude of the feature gradually decreases and it vanishes somewhere around RT. It always appears to have the $d_{x^2-y^2}$ symmetry. No such feature is seen above T_c on the overdoped side. (More details below)

A gap feature is also seen in Bi-2201 (Harris et at., PRL, **79**, 143 (1997)) but it is less spectacular and the magnitude of Δ is down relative to that of Bi-2212 by a factor 3 (roughly the same as the ratio of the T_c’s) .

Tunneling

In underdoped Bi-2212, the superconducting phase shows a DOS which is strongly attenuated below a ‘gap’ which appears to be almost independent of T. This gap persists above T_c but the low energy region gradually gets filled in; the feature is still just visible at RT. See also Renner et al., PRL **80**, 149 (1998); Matsuda et al., Phys. Rev. B **60**, 1377 (1999) [gap persists into *overdoped* regime].



[**] Cf. TL. op. cit., p. 9: the ‘visual’ impression that the gap closes is misleading.

NMR

As we have noted, in optimally doped YBCO, the ^{63}Cu(2) NMR shift is constant above T_c. In underdoped YBCO, it starts falling as T is lowered well above T_c ($T \sim 200$K) (and in fact T_c is hardly noticeable in the T-dependence). The same behavior is found in 1248, where the temperature at which the decrease starts ($\equiv T^*$) is ~ 300K.

The ^{89}Y shift in 1248 also shows a change in behavior at ~ 300K where it starts to decrease more rapidly, actually changing sign at ~ 160K. A similar T^* is found for Hg-1223 (~ 250K); in general, T^* as measured by Knight shift seems to be roughly the same for single and multilayer materials.

The nuclear spin relaxation time: $(^{63}T_1T)^{-1}$ increases slowly with decreasing temperature, but starts to fall around T^* (it is not entirely clear that 'T^*' is uniquely defined).

A rather puzzling feature is the effect of Zn substitution in the pseudogap regime: it appears to suppress the turnover in $(^{63}T_1T)^{-1}$ for concentration as low as 1%, but the magnitude and temperature-dependence of the Knight-shift is completely unaffected, and so are other measured properties (C_v, ρ_{ab}). This is very significant, because the superconducting transition is extremely sensitive to Zn substitution. (2% of Zn suppress T_c by 30% in fully-oxygenated YBCO).

Specific heat*

The specific heat $C_v(x,T)$ is conventionally written as $\gamma(x,T)T$, so that the 'textbook' behavior corresponds to $\gamma =$const. (i.e. independent of T). This behavior is seen, independent of doping at sufficiently high T, with a γ which is almost x-independent in the overdoped regime but decreases with x in the underdoped regime. In optimally doped and overdoped samples, γ remains independent of T down to T_c. On the underdoped side, however, γ begins to fall off at a temperature ~ 250K ($\sim T^*$). Also, the jump at T_c (in lecture 7) is much decreased, so that the entropy at high T is in fact rather similar for samples of different x. A very important observation is that independently of x, the ratio of S/T to the magnetic susceptibility $\chi(T)$ inferred from the Knight shift is very close to independent of T (i.e. the Wilson ratio, when expressed as $S/\chi T$, is constant).

Raman

As mentioned in lecture 5, at optimal doping the Raman spectrum is essentially featureless and polarization-independent. As we go towards underdoping (in YBCO) a very broad peak emerges, in the B_{1g} channel only, centered on a frequency which appears to be independent of x and $\sim 500\text{cm}^{-1}$ (40meV).

(Magnetic) neutron scattering†

In neutron scattering from LSCO, and scattering in the 'odd' channel from YBCO, the peak seen at low T in the optimally-doped case near (0.5, 0.5) sharpens up with

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*Ref: Loram et al., Physica C **235-240**, 134 (1994).

†Ref: Mook et al., in SNS 97.

underdoping and eventually demonstrably splits as a function of q, indicating 'incommensurability'. For YBCO $6.6-6.7$ it survives up to $\sim$ RT, well above T_c (see Mook et al., Figs. 2,3). The question of the persistence of the so called 41meV peak seen in the superconducting phase (lecture 8) into the pseudogap regime is at present controversial.

Transport properties

In 1248, the ab-phase dc resistivity $\rho_{ab}(T)$ has a clear break in slope at $\sim$ 200K, dropping much more sharply below that temperature. In YBCO for $x < 0.08$, the curve starts to deviate from linear already at $\sim$ 400K, then has a minimum at $\sim$ 100K followed by an upturn. Underdoped Hg-1223 shows similar behavior.

If one attempts to interpret the ab-plane ac conductivity in terms of a frequency-dependent scattering rate $\tau^{-1}(\omega)$ and effective mass $m^*(\omega)$, then one finds that for $\omega < 500\text{cm}^{-1}$, in 1248, the scattering rate decreases with temperature and the effective mass rises by a factor $2-3$ (so that for fixed $\omega \gg T$ the conductivity increases as T drops). This is qualitatively similar to what happens in the superconducting phase, and it is tempting to interpret it in terms of a decrease in scattering owing to the thinning out of low energy electronic states by the pseudogap phenomenon.

The c-axis conductivity $\sigma_c(\omega)$ behaves oppositely (remember that it was essentially featureless in the optimally doped material): For $\omega < 500\text{cm}^{-1}$ it decreases at low frequencies, for $T < T^*$.

Finally, a very interesting study of the ac conductivity at THz frequencies has been carried out by Orenstein and collaborators, on underdoped BSCCO; they find that the anomalous static EM response characteristic of the superconductivity state (Meissner effect) persists in the dynamic response to temperatures well above T_c. (I hope to discuss this further in lecture 11).

Discussion

Tallon + Loram argue convincingly that all the above data can be understood in terms of a phenomenological picture with the following properties:

(1) The 'pseudogap' phenomenon is not associated with a phase transition but is a crossover phenomenon.

(2) Associated with the phenomenon is a unique energy scale $E_g(p)$, which varies from $\sim$ 1200K ($\sim J_{||}$) at $p = 0$ (i.e. for the AF insulator) down to $\sim$ 180K at $p = 0.15$ (see TL. Fig. 11) This energy scale is directly reflected in the frequency-dependence of physical quantities (recall 1K$\approx$0.66cm^{-1}, so a characteristic frequency of 500cm^{-1} corresponds to 750K). By contrast, the characteristic temperature T^* at which crossover occur is of the order of $0.4E_g(p)$ rather than $E_g(p)$ itself (because of the general form of the Fermi and Bose functions).

(3) The crossover temperature $T^*(p)$ does not join smoothly on to the curve $T_c(p)$ near $p \approx 0.16$, as is often asserted, but rather cuts straight through the curve of $T_c(p)$. $E_g(p)$ and hence $T^*(p)$ go to zero abruptly at $p = 0.19$.

(4) It follows from (3) that the pseudogap phenomenon has nothing directly to do with superconductivity.

[This conclusion is certainly likely to be controversial!]

Other recent experiments on the pseudogap regime:

(1) Nernst effect

(2) evidence for 'nematic' behavior

(3) dHvA-type experiments.

Fermiology of the pseudogap regime

In the last five years or so, a question which has become increasingly urgent and perplexing is that of the shape and nature of the Fermi surface in the underdoped (or pseudogap) regime. The two experimental techniques which are generally believed to be most informative in this respect are ARPES (which essentially measures the quasiparticle energy spectrum and the discontinuity in the occupation number $n(\mathbf{k}) \equiv \langle a^+_{\mathbf{k}} a_{\mathbf{k}} \rangle$ as we cross the Fermi surface) and quantum-oscillation experiments (hereafter referred to generically as dHvA, although in reality most of the experiments actually conducted are technically Shubnikov-de Haas), which measure the area of the Fermi surface(s), and in principle, the effective mass on it. Unfortunately, in the case of the cuprates the inferences most naturally drawn from those two classes of experiment appear prima facie to be mutually inconsistent.

Let's start with the ARPES data*. If we consider the normal state in the pseudogap regime just above T_c, the ARPES spectrum looks essentially indistinguishable from its form in the superconducting state (see l. 8); i.e. there are relatively sharp quasiparticle-like peaks in the spectral density $A(\mathbf{k}, \epsilon)$ which are "pulled back" from the Fermi energy ϵ_F by a gap Δ which appears to be roughly proportional to $|\cos 2\theta|$ where θ is the angle with a crystal axis, i.e. roughly of the so-called $d_{x^2-y^2}$ form; note that Δ is zero at (but only at!) the 45° directions. If now we raise the temperature, a set of so-called "Fermi arcs" appears around these nodal points: that is, the "pseudogap" Δ appears to become zero over a finite range of angles around the original nodes, the extent of this range increasing with temperature, until by around a temperature T^* (which increases strongly with underdoping) it is zero over the whole surface. Thus, a "Fermi surface" in the sense seen in a normal textbook metal appears to exist for certain directions of $\mathbf{k}$ (the "arcs") but not for others. However, the behavior in the regions in which a "Fermi surface" does not exist ("gapped" regions) appears to be similar to that in the superconducting state, indicating prima facie that while there is some rearrangement of the states (due perhaps to pairing, or something else) over a region of $\sim \Delta$ close to the original Fermi energy, the bulk of the Fermi sea is unaffected. What needs to be particularly emphasized in the present context is that the ARPES data (or at least those

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*Kanigel et al., Nature Phys. **2**, 497 (2006) currently obtained) appear to be entirely consistent with a smooth evolution of the Fermi surface (or more accurately the Fermi sea) as a function of p between the overdoped and underdoped (pseudogap) regimes; in particular, they are entirely consistent with a Fermi sea containing (1+p) holes per CuO_2 unit.

Now let's turn to the dHvA-type (quantum oscillation) experiments. To assess their significance we need a little theory; fortunately, this is considerable simpler in the quasi-2D case likely to be relevant to the cuprates. A somewhat simplified version of the standard Onsager-Lifshitz-Kosevich (textbook) theory goes as follows: Consider first a simple Bloch model of a 2D metal (i.e. with nontrivial band band structure $\epsilon(\mathbf{k})$ but no interactions). In a magnetic field $\mathbf{B}$ perpendicular to the 2D plane, the quasiclassical equation of motion of a single-electron is

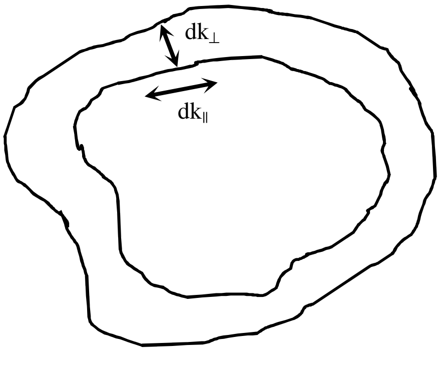
$$\hbar\,\frac{d\mathbf{k}}{dt} = \mathbf{F} = e\mathbf{v}_k \times \mathbf{B} \tag{2}$$

where $\mathbf{v}_k \equiv \hbar^{-1}\partial\epsilon(\mathbf{k})/\partial\mathbf{k}$ is the electron velocity. Thus the electron moves along a curve of constant energy. Assuming for the moment that the orbit in question is closed and that we can neglect scattering, the period is given by the formula

$$T \equiv \oint dt = \oint \frac{dk_{\|}}{dk_{\|}/dt} = \frac{\hbar^2}{e}\oint \frac{dk_{\|}}{(d\epsilon/dk_{\perp})\cdot B} = \frac{\hbar^2}{eB}\oint dk_{\|}\frac{dk_{\perp}}{d\epsilon} \equiv \frac{\hbar^2}{eB}\left(\frac{dS}{d\epsilon}\right) \tag{3}$$

where $S(\epsilon)$ is the area in $\mathbf{k}$-space enclosed by a contour of energy ϵ; note that T is in general a function of ϵ*.

Now in quantum mechanics, at the level of the correspondence principle, the motion corresponding to a classical closed orbit is quantized, with the allowed energies separated by $h/T(\epsilon)$ where T is the classical period; in particular, in a magnetic field the original continuous energy spectrum $\epsilon(\mathbf{k})$ "condenses" on to a set of discrete levels separated by $h/T(\epsilon) \equiv \hbar\omega_c(\epsilon)$.



The point, now, which is generic to all experiments of the dHvA type is that one would expect the physical behavior of the system to repeat itself every time one of the quantized levels passes through the chemical potential μ (which generally speaking will be controlled by the leads to the system, and thus can be treated as fixed). This requires the condition, for some integer n,

$$\sum_{j=1}^{n} \hbar\omega_c(j)\left(\frac{\partial S}{\partial\epsilon}\right)(j) \;=\; S \tag{4}$$

where S is the area of the Fermi surface corresponding to μ. However, inserting eqn. (3).

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*An exception is the Sommerfeld (free-electron) limit, where we easily check that $T = 2\pi/\omega_c$ with ω_c the free-electron cyclotron frequency eB/m.

we find that this is equivalent to the simple condition[†]

$$n\frac{eB}{h} = S \tag{5}$$

or equivalently

$$B_n^{-1} = ne/hS \tag{6}$$

i.e. the behavior of (e.g.) the resistivity should be periodic in B^{-1} with period (e/hS). Thus, the periodicity in B^{-1} is a direct measure of the area of the Fermi surface.

This argument certainly seems foolproof for the simple Bloch model, and arguments have been given in the literature that it should still work for a simple Landau Fermi-liquid generalization of that model. However, it is not entirely obvious that it still works even for a Fermi liquid in the presence of umklapp processes, let alone for a non-Fermi liquid state (where since the Fermi surface is in general not defined, one would assume prima facie that there should be no well-defined periodicity).

Turning to the dHvA experiments of the last five years[*], we find that in the overdoped regime of Tl-2201 (p≅ 0.25) they show a single well-defined periodicity of 18 kT, corresponding to a"large" Fermi surface (occupation 1+p); this agrees well with other experiments in this regime. However, for underdoped YBCO (p = 0.1) there is, again, a single periodicity, but now it is 0.54-kT, 30 times smaller! If we interpret this result in the standard way, this means that any Fermi surface(s) which occur in the pseudogap regime must be $\sim$ 30 times smaller than that in the overdoped regime. With 4 such "pockets" we could accommodate approximately p (not 1+p!) holes.

At the time of this writing the apparent inconsistency of the ARPES and *dHvA* results is an unresolved puzzle. A further and somewhat related puzzle concerns the question of whether one or more symmetries (time reversal, tetragonal...) is broken in the pseudogap phase; I return to this question later in the course.

Systematics of T_c

The most important determinant of T_c in the cuprate superconductors is almost certainly the doping level x (or δ). When T_c is expressed directly in terms of the departure from stoichiometry, the picture looks rather confusing. However, as we saw in lecture 4, it is more natural to express it in terms of p, the number of free carriers in the CuO_2 planes per CuO_2 unit, i.e. the number of $3d$ holes per CuO_2 unit over and above the 1 present in the 'parent' compound (which, of course, need not actually exist in chemically stable form for the particular compound in question). In some cases (e.g., $La_{2-x}Sr_xCuO_4$) it is almost certain that p is simply equal to x, in other cases (e.g., $YBa_2Cu_3O_{6+x}$) some guesswork is needed, but it seems there is always a consistent choice of p which, at least over a certain range, is proportional to x with a chemically sensible constant of

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[†] Note that this condition is in some sense "dual" to that for the integral quantum Hall effect: the (k-space) Fermi sea should contain an integral number of inverse flux quanta! The exact result actually has $n \to n + \gamma$ where γ is an (a priori unknown) offset, but this does not affect the argument.

[*] For a concise review, see L. Taillefer, J. Phys.: Cond Matt. **21**, 164212 (2009)

proportionality. When this is done, it is widely believed that the formula for the shape of the $T_c(p)$ curve is universal and well approximated by the parabolic formula (Presland et al., Physica C **165**, 391 (1991)):

$$T_c(p) = T_c^{\max}(1 - 86(p - 0.16)^2) \tag{7}$$

thus T_c has a maximum at $p = 0.16$ and tends to zero at $p \approx 0.05$ on the underdoped side and at $p \approx 0.27$ on the overdoped side. The fact that this equation seems to fit the data reasonably well irrespective of the actual scale $T_c^{\max}$ is quite surprising.

Given the (approximate) validity of the above formula, the question reduces to what determines $T_c^{\max}$. One obvious relevant variable is sample purity, particularly as regards impurities in the CuO_2 planes themselves. One much-studied substitution is that of other transition metals[‡] (Zn, Ni, Co ...) for the Cu(2)'s. Such substitutions always depress T_c dramatically[§] (a 2% Zn substitution in YBCO7 already depresses T_c by $\sim$ 30%). Although substitution (of Zn or Ni) changes p, it seems very unlikely that this is the main effect,[‖] and it is usually understood in terms of 'pair-breaking' due to the disorder introduced in the potential seen by the mobile holes.

Substitution of off-plane atoms has much less effect, at least so long as it does not change p ('isovalent' substitution). A particularly striking example is the substitution of RE elements for Y in YBCO7: not only does 100% substitution change T_c negligibly (sometimes raising it by $\sim 1 - 2$K), but even 'mixed' compounds of the form (e.g.) $Y_{1-x}Er_x$ also have essentially the same T_c. Thus, it seems that even though the radii of the various RE's vary by $\sim$ 15%, this does not introduce any important disorder into the CuO_2 planes themselves. On the other hand, substitution of Ca by Sr or Ba sometimes has dramatic effects (see below).

Oddly enough, the situation seems a bit different when one introduces disorder in the atoms adjacent to the plane (i.e., in the 'spacing' rather than the 'intercalant' position). Attfield and co-workers[*] carried out an interesting study on LSCO-type compounds in which they substituted La with Nd, Ca, Sr, or Ba in such a way (i.e. $(La, Nd)_{2-x}(Ca, Sr, Ba)_x CuO_4$ when $x = 0.15$) that the hole concentration p (as calculated from standard valence rules) remains fixed while the degree of 'structural' disorder, quantified by the mean square dispersion $\sigma^2 = \langle r_A^2 \rangle - \langle r_A \rangle^2$, of the cation (La-site) atoms, can be varied. They found a quite severe depression of T_c by the structural disorder, $\partial T_c / \partial \sigma^2 \approx 7000\text{K}/\text{Å}^2$; they suggest that this may be due to trapping of a fraction of the in-plane holes by the structural disorder. If this is right, the effect could presumably be compensated by slightly overdoping the sample (McAllister et al. always worked at optimal doping, so could not determine this).

It is possible that there is a connection between these results and the effect of plane

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[‡] Ni was formerly thought to be an exception in this rule, but more recent studies conclude that its effects are similar to those of Zn.

[§] See e.g. Markert et al., in G I, fig. 28.

[‖] If this were true, then (e.g.) substitution of Zn in underdoped YBCO should *increase* T_c, contrary to experiment.

[*] Mcallister et al., PRL **83**, 3289 (1999).

buckling on T_c; there is a fair amount of evidence[†] that at constant p, T_c decreases with buckling angle,[‡] though the effect is not large (about 2K/degree in a LSCO-type material, see Fig. 3 of Dabrowski et al). One may speculate that the T_c of YBCO might be comparable to that of 2-layer or even 3-layer HgBCO were it possible to avoid the severe ($\sim 15°$) buckling that actually characterizes it.

One more variable which has a substantial effect on T_c is pressure, either hydrostatic or uniaxial. A particular striking example is Hg-1201, where T_c can be varied from a value of $\sim$ 100K at ambient pressure to 120K at 20GPa (after which it gradually declines again). It is often believed that the increase is a result of the shortening of the Cu-apical O bond length, which is the structural feature most sensitive to pressure.

Undoubtedly the most intriguing variable in the context of the systematics of T_c is the layer multiplicity n in homologous series. In the Bi, Tl and Hg series the $n = 2$ members always have a T_c higher than the $n = 1$ one, and the $n = 3$ members a higher temperature still. In fact, a number of papers in the literature have attempted to fit $T_c(n)$ to a formula which is predicted by at least three different scenarios, namely

$$T_c(n) = T_c(1) + \text{const } (1 - 1/n) \tag{8}$$

However, it should be emphasized that there is no evidence at all that this formula works for $n \geqslant 4$. The situation is complicated, because it often turns out that systems with the nominal composition corresponding to a given n are not in fact single-phase; but where one can be sure that the structure really is $(\mathrm{Ca})_{n-1}(\mathrm{CuO_2})_n\mathrm{X}$, all the evidence is that the T_c of the $n = 4$ and higher compounds is actually less than that of the $n = 3$ member, in other words, that three $\mathrm{CuO_2}$ planes are 'optimal'. (Cf. in particular the 2-Tl series, in Shaked et al.). It is still possible to ask whether the single relation which can be inferred from the above equation applied up to $n = 3$, namely

$$\frac{T_c(3) - T_c(2)}{T_c(2) - T_c(1)} = \frac{1}{3} \tag{9}$$

holds? I believe it does, at least for the 2-Tl and Hg series (AJL, PRL **85**, 3984 (2000)).[§]

An even more intriguing observation is that the statement that T_c is higher for the $n = 2$ and 3 members of a homologous series than the $n = 1$ member is true only when the intercalant A is Ca. Indeed, until very recently there was no known case of any bi- (or tri-) layer cuprate intercalated entirely with Sr or Ba which is superconducting at any temperature! A particularly striking exhibit in this connection[¶] is the bilayer homologues of LSCO: the pure Ca-intercalated material, $\mathrm{La_{2-x}Sr_xCaCu_2O_6}$, is a superconductor with a T_c of 58 K, decently higher than that of the single-layer material in accordance with the general rule. However, as the Ca is progressively substituted with Sr, T_c falls, and tends to zero at an (in-plane) Sr concentration of around 80%. This behavior is at

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[†] DDabrowskiet al., PRL **76**, 1348 (1996).

[‡] Where p is itself varied the situation is more complicated (Chmaissem et al., Nature **347**,45 (1999)).

[§] It may hold also for the 1-Tl and Bi series where $T_c(1)$ is much lower, but if so I believe this is probably a coincidence with no great significance.

[¶] H. Shaked et al., PRB **48**, 12941 (1993).

first sight quite puzzling, as Sr is isovalent to Ca and not that different in atomic size (1.26Å vs 1.12Å). However, Shaked et al. found that this small difference is sufficient to push the planes far enough apart to permit 'intruder' oxygens to occupy the so-called O(3) sites between the CuO_2 planes, and they were able to correlate the decrease of T_c with the occupancy of this site (see their Fig. 11(a)); it appears that an occupancy $\sim 10\%$ is enough to destroy superconductivity altogether. The reason for this is at present unclear.

[Recent work on Sr-intercalated BSCCO (di Luccio et al.)]