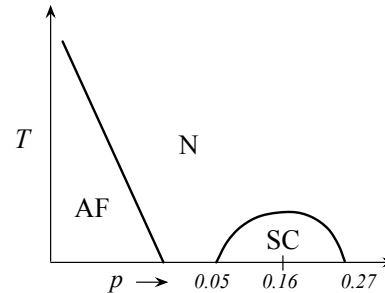


## The phase diagram: the ‘pseudogap’ regime. Systematics of $T_c$ .

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,  $T_c \approx 92\text{K}$ ) 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  $p$ , i.e. 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  $\text{YBa}_2\text{Cu}_4\text{O}_8$ , 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  $p \approx 0.25$ . 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  $x = 0.25$ ).<sup>†</sup>

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  $\text{La}_2\text{CuO}_4$ , the system appears to be a simple AF Mott insulator; recall we have 1 hole per  $\text{CuO}_2$  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  $2\pi/a$ ) 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

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

<sup>†</sup>Ino et al., J. Phys. Soc. Japan **68**, 1496 (1999).

nearest-neighbor Heisenberg Hamiltonian, i.e.

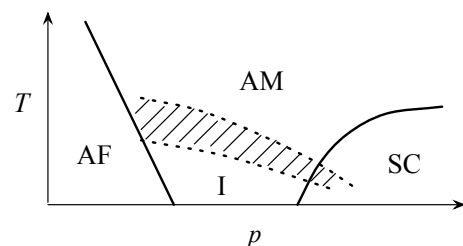
$$\hat{H} = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \quad (1)$$

with an AF coupling constant which is approximately 1000K.

In the bilayer material<sup>‡</sup> YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> the in-plane ordering seems to be the same as in La<sub>2</sub>CuO<sub>4</sub>; 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  $J_{\parallel}$  ( $\sim 1000\text{K}$ ) and the ‘interplane’ constant  $J_{\perp}$  ( $\sim 200\text{K}$ ). These values appear to be roughly consistent with the observed values of  $T_N(p=0)$  for La<sub>2</sub>CuO<sub>4</sub> (300K) and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> (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<sup>¶</sup> 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 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



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

<sup>¶</sup>Refs: Timusk and Statt, Reps. Prog. Phys. **62**, 61(1999). Tallon + Loram, cond-mat 0005063.

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.

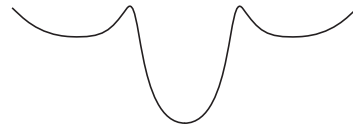
### ARPES (BSCCO series)

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  $\Delta(\mathbf{k})$  (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  $45^\circ$  ( $\pi/a, \pi/a$ ) 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  $\sim 300\text{K}$  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.

A gap feature is also seen in Bi-2201 (Harris et al., PRL, **79**, 143 (1997)) but it is less spectacular and the magnitude of  $\Delta$  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].



### NMR

As we have noted, in optimally doped YBCO, the  $^{63}\text{Cu}(2)$  NMR shift is constant above  $T_c$ . In underdoped YBCO, it starts falling as  $T$  is lowered well above  $T_c$  ( $T \sim 200\text{K}$ ) (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  $\sim 300\text{K}$ .

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

The nuclear spin relaxation time:  $(^{63}\text{T}_1T)^{-1}$  increases slowly with decreasing temperature, but starts to fall around  $T^*$  (it is not entirely clear that ‘ $T^*$ ’ is uniquely defined).

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

A rather puzzling feature is the effect of Zn substitution in the pseudogap regime: it appears to suppress the turnover in  $(^{63}\text{T}_1T)^{-1}$  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 ( $C_v$ ,  $\rho_{ab}$ ). 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  $\gamma = \text{const.}$  (i.e. independent of  $T$ ). This behavior is seen, independent of doping at sufficiently high  $T$ , with a  $\gamma$  which is almost  $x$ -independent in the overdoped regime but decreases with  $x$  in the underdoped regime. In optimally doped and overdoped samples,  $\gamma$  remains independent of  $T$  down to  $T_c$ . On the underdoped side, however,  $\gamma$  begins to fall off at a temperature  $\sim 250\text{K}$  ( $\sim T^*$ ). 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 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  $\sim 200\text{K}$ , dropping much more sharply below that temperature. In YBCO for  $x < 0.08$ , the curve starts to deviate from linear already at  $\sim 400\text{K}$ , then has a minimum at  $\sim 100\text{K}$  followed by an upturn. Underdoped Hg-1223 shows similar behavior.

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

†Ref: Mook et al., in SNS 97.

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 recently 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  $\sim 1200\text{K}$  ( $\sim J_{\parallel}$ ) at  $p = 0$  (i.e. for the AF insulator) down to  $\sim 180\text{K}$  at  $p = 0.15$  (see TL. Fig. 11) This energy scale is directly reflected in the frequency-dependence of physical quantities (recall  $1\text{K} \approx 0.66\text{cm}^{-1}$ , so a characteristic frequency of  $500\text{cm}^{-1}$  corresponds to  $750\text{K}$ ). 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.

## Systematics of $T_c$

The most important determinant of  $T_c$  in the cuprate superconductors is almost certainly the doping level  $x$  (or  $\delta$ ). 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  $\text{CuO}_2$  planes per  $\text{CuO}_2$  unit, i.e. the number of  $3d$  holes per  $\text{CuO}_2$  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.,  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ) it is almost certain that  $p$  is simply equal to  $x$ , in other cases (e.g.,  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ) 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 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)):

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

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  $T_c^{\text{max}}$  is quite surprising.

Given the (approximate) validity of the above formula, the question reduces to what determines  $T_c^{\text{max}}$ . One obvious relevant variable is sample purity, particularly as regards impurities in the  $\text{CuO}_2$  planes themselves. One much-studied substitution is that of other transition metals<sup>‡</sup> (Zn, Ni, Co ...) for the Cu(2)’s. Such substitutions always depress  $T_c$  dramatically<sup>§</sup> (a 2% 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,<sup>||</sup> 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  $\sim 1 - 2\text{K}$ ), but even ‘mixed’ compounds of the form (e.g.)  $\text{Y}_{1-x}\text{Er}_x$  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  $\text{CuO}_2$  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).

<sup>‡</sup>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.

<sup>§</sup>See e.g. Markert et al., in G I, fig. 28.

<sup>||</sup>If this were true, then (e.g.) substitution of Zn in underdoped YBCO should *increase*  $T_c$  contrary to experiment.

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.  $(\text{La, Nd})_{2-x}(\text{Ca, Sr, Ba})_x\text{CuO}_4$  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,  $\partial T_c / \partial \sigma^2 \approx 7000\text{K}/\text{\AA}^2$ ; 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 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 ( $\sim 15^\circ$ ) 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  $\sim 100\text{K}$  at ambient pressure to  $120\text{K}$  at  $20\text{GPa}$  (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

$$T_c(n) = T_c(1) + \text{const} (1 - 1/n) \quad (3)$$

However, it should be emphasized that there is no evidence at all that this formula works for  $n > 4$ . 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  $(\text{Ca})_{n-1}(\text{CuO}_2)_n\text{X}$ , 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  $\text{CuO}_2$  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

$$\frac{T_c(3) - T_c(2)}{T_c(2) - T_c(1)} = \frac{1}{3} \quad (4)$$

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\*McAllister et al., PRL **83**, 3289 (1999).

†DDabrowski et al., PRL **76**, 1348 (1996).

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

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

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<sup>¶</sup> is the bilayer homologues of LSCO: the pure Ca-intercalated material,  $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_6$ , 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 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  $\text{CuO}_2$  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 (de Lucio et al.)]

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<sup>§</sup>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.

<sup>¶</sup>H. Shaked et al., PRB **48**, 12941 (1993).