Is there a lowest upper bound for superconductive transition temperatures?

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Abstract. The values of superconductive transition temperatures $T_c$ in conventional crystalline metallic superconductors are widely scattered, depend on the details of the Fermi surface (especially the density of states $N(E_F)$), and are typically below 1 K. By far the highest $T_c$'s ($\sim 100$ K) are found in the cuprates, and there $T_c$ is apparently insensitive to the geometry of the Fermi surface, while it depends strongly on dopant density and configuration. For the cuprates there is a smooth master curve $T_c^{\max}(\langle R \rangle)$ for the highest $T_c$'s as a function of the average number $\langle R \rangle$ of Pauling resonating bonds/atom in the parent (undoped) insulator. The existence of such an $\langle R \rangle$-dependent optimized $T_c$ is suggested by analogies with the microscopic theory of optimized molecular glass networks (such as window glass), but it remains to derive a rigorous quantum theory of the origin of $T_c^{\max}(\langle R \rangle)$.

Calculation of the superconductive transition temperatures $T_c$ in conventional crystalline metals is one of the most difficult problems in condensed matter physics. True, for metals composed of lighter elements the detailed microscopic Eliashberg theory, based on competing attractive electron-phonon and repulsive Coulomb interactions to form Cooper pairs between periodic Bloch states, has been very successful [1,2], but such detailed calculations become difficult for heavier elements because of core polarization effects. Establishing upper bounds on $T_c$ within the microscopic theory is also possible, and leads to results [3] for phonon (lattice instability)-limited $T_c$'s in good agreement with observed chemical trends in materials like MgB$_2$.

The most interesting materials for establishing upper bounds on $T_c$ are, of course, the cuprate high temperature superconductors (HTSC). Because of their complex chemistry these are exactly the materials that present the greatest difficulties for conventional microscopic theory: such calculations for cuprates yield $T_c$'s too small by factors $\sim 100$ [4]. Are the important interactions confined to the CuO$_2$ planes, as is often assumed? Specifically, are the electron-phonon interactions largest at the Cu ions (large $N(E_F)$ due to Cu d states), or at the highly polarizable oxygen ions, which have strong local interactions favored [3] by larger values of the Hopfield parameter $\eta$ and small atomic mass $M_O$? Are the remaining alkaline earth, rare earth, alkali and halide elements in other planes merely incidental spectators?

As we shall see, cuprate phenomenology is dominated by the old ideas of resonating chemical bonds developed most completely by Pauling in the 1930's [5], with special emphasis on heats of formation. In the 1950's many theoretical physicists considered these ideas to be obsolete expedients, and indeed
for crystals and small molecules they have been gradually replaced by modern self-consistent field theory [3], which works especially well for just those lighter metals for which Eliashberg theory accurately predicts $T_c$. In many respects Pauling’s chemical ideas were simplistic, but they had the considerable advantage of applying equally well to molecules and crystals at a time when the microscopic data base was still small. It has turned out that the cuprates are strongly disordered into 3 nm nanodomains by lattice instabilities and by dopants. Each nanodomain resembles an array of large, deformed (off-lattice) atoms more than it resembles an ideal crystal. This has had the unexpected effect of reincarnating Pauling’s ideas, which prove to be an effective and extremely accurate support for cuprate phenomenology.

Counting the number $R$ of Pauling’s resonating bonds in layered cuprates is perhaps the easiest exercise any theorist could propose. For lighter elements $i$ with valence $Z_i$, $R(i) = |Z_i|$, while for heavier elements both $Z_i$ and $R(i)$ are determined by the requirement that the oxide be neutral with $Z(O) = -2$. Thus the parent compound of $La_{2-x}Sr_xCuO_4$ (LSCO) is $La_2CuO_4$, and with $Z(La)= +3$, $Z(Cu) = +2$. With $Z(Cu) = +2$, the remaining values of $Z$ are easily determined. For instance, in $Bi_2Sr_2CaCu_2O_8$ (BSCCO), $Z(Sr) = Z(Ca) = +2$ and $Z(Bi) = +3$.

When HTSC was discovered in LBCO [6], the role of the Ba dopants and the phase diagram of $T_c(x)$ was unknown, and many factors were proposed to be important for HTSC. Anderson speculated [7] that superexchange causes HTSC, a view that he and others have maintained for many years [8]. Pauling himself tried to apply his own theory of metals to HTSC in the cuprates, but this led him to conclude that weak (not strong) electron-phonon interactions were required [9]. Cooper pairs formed by strong electron-phonon interactions imply lattice instabilities [10], and I suggested that these would lead to the formation of insulating regions with a pseudogap, now widely reported [11]. Gorkov and Sokol suggested that cuprate high normal-state resistivities could not be described by conventional Fermi liquid models [12].

Today we have a large data base with extensive phase diagrams. We know that $T_c(x)$ is nearly parabolic in the cuprates, and vanishes at the metal-insulator transition. This is in contrast to the “normal” behavior in the cubic perovskite alloys $Ba_{1-x}K_xBiO_3$ (BKBO), where $T_c(x)$ increases steeply with decreasing $x$, reaching a maximum $T_c$ of 34K at the metal-insulator transition, where dielectric screening of the electron-phonon interaction is minimal [13]. We have many other indicators that suggest that in the cuprates an intermediate phase has formed between the insulating and normal metallic phase [14]. This intermediate electronic phase is strongly disordered (because the dopants do not form a superlattice), and has distinctive topological properties, including pseudogaps [11] as well as superconductive gaps.

This complex background has made theories of HTSC highly controversial for the last 20 years. Given the large modern data base, let us do the simplest possible thing, and ask whether or not Pauling’s classical chemical concepts of resonating chemical bonds $R$ provide a factor that will help us to determine a lowest upper bound on $T_c$ in the cuprates. Clearly such a bound should depend on something other than the ubiquitous $CuO_2$ planes that are common to all the cuprate HTSC’s. If strong electron-phonon interactions and overall lattice softness are important factors [11], then one can take $<R>$, the average number of Pauling resonating chemical bonds/atom in the parent insulator (including all planes), as a variable; for example, $<R>(La_2CuO_4) = 16/7$. Plotting $T_c^{\text{max}}(<R>)$ yields the master curve shown in Fig. 1: a smooth, unambiguous cusp-like resonance emerges, with a sharp peak at $<R> = 2$. The chemical resonance is surprisingly symmetric. The master curve appears to be accurate to ~10K. Given that the temperature scale for soft lattices is fixed by the melting point ~10^3 K, this corresponds to an accuracy ~1%, which is even more impressive than the successes of Pauling’s model for heats of formation [5].
Figure 1. Chemical trends in $T_{c_{\text{max}}}$ with $<R> = <|Z|>$, which measures the global stiffness of the doped crystalline network, with $Z$(Cu) = 2, $Z$(Bi) = 3 (4) [BSCCO (Ba$_{1-x}$K$_x$BiO$_3$, BKBO), as in the parent insulators, where $\Sigma Z = 0$, and $Z$(O) = -2. Perovskites ($R = 2.40$) and pseudoperovskites are only marginally stable mechanically [14,21], and for HTSC cuprates $<R>$ lies in the region of floppy networks just below the isostatic (rigid but unstressed) range determined by studies of network glasses (wavy line). The peak in $T_{c_{\text{max}}}$ occurs at $<R> = 2$, as one would expect from mean field percolation theory. The point for BCCOF was added after the figure was drawn originally, and the original curve has not been modified. Acronyms: NCCOC (Na$_x$Ca$_{2-x-y}$CuO$_2$Cl$_2$), BCCOF (Ba$_2$Ca$_3$Cu$_4$O$_8$F$_2$), HBCO (HgBa$_2$CuO$_4$), YBCO (YBa$_2$Cu$_3$O$_{6+x}$), BSCCO (Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$), LSCO (La$_{2-x}$Sr$_x$CuO$_4$ and La$_{2-y}$Sr$_y$CuO$_{4+x}$).

Given the controversy that has surrounded the field of HTSC for 20 years, the success of the all-plane $<R>$ as the one factor that establishes not merely a qualitatively, but indeed a quantitatively very successful lowest upper bound on $T_c$ in the cuprates, is of course completely unexpected. At present there is no rigorous theory, similar to the Eliashberg theory of Bloch metals, which can account for such success. One can make some comments, however:

1. The CuO$_2$ planar lattice constants of the cuprates are almost constant, and it is clear that the primary role of the cuprate planes is architectonic – the planes are stiff, and they support a lattice that is soft overall, and would otherwise buckle, producing Jahn-Teller distortions and an insulating energy gap.

2. The overall scale $\Theta$ for $T_{c_{\text{max}}}$ must be set by Cu-O bonds, but not the rigid planar Cu-O bonds, rather the soft Cu-O axial bonds, which function as the weakest links in marginally stable mechanical networks. The weakest links should be sensitive to the average connectivity of the host network, measured by $<R>$.

The preceding comments can be tested by examining the planar Cu-O lattice unit cell areas with high resolution diffraction data [15]. The results for (Y,Ca)Ba$_2$Cu$_3$O$_x$ and HgBa$_2$CaCu$_2$O$_x$ are reproduced.
for the reader’s convenience in Fig. 2. In the intermediate phase these planar areas expand (CuO$_2$
planar bonds weaken), presumably as a result of strengthened and resonantly shortened Cu-O axial
bonds near “negative U” [16] interlayer dopants (usually interstitial O). The bulge shown in Fig. 2 is
analogous to the carbon-carbon bond length fluctuations found in aromatic hydrocarbons ([5], Sec. 7-5).

![Graph of basal area vs. composition](image)

**Figure 2.** Sketch of the Rohler bulges (lightly shaded) in basal area of CuO$_2$ planes [15].
The sketch here refers to (Y,Ca)Ba$_2$Cu$_3$O$_{6+x}$ and HgBa$_2$Ca$_2$Cu$_3$O$_{6+x}$, where the magnitude
of the bulge is about twice as large as in La$_{2-x}$Sr$_x$CuO$_4$, corresponding to smaller <$R$>,
stronger electron-phonon interactions and higher $T_c$ in the former. The bulge is a small (and
elusive!) effect (< 1%) because the interstitial oxygen dopants O$_x$ are not arranged on a
superlattice, but instead form an off-lattice network embedded in the soft host lattice [23].
Note that the intermediate phase bulge lies above the linearly extrapolated basal areas of the
insulating and normal metallic phases. Note also that because interactions are better
screened in the metallic phase, $x > x_2$, the slope is lower than in the insulating phase, $x < x_1$. In the most studied case, La$_{2-x}$Sr$_x$CuO$_4$, $x_0 = 0.16$, $x_1 = 0.06$, and $x_2 = 0.21$; HTSC
exists only between $x_1$ and $x_2$, and $T_c^{max}$ is reached at $x = x_0$.

Of course, the most striking feature of Fig.1 is that the sharp peak occurs at <$R$> = 2. In conventional
percolation theory (on a lattice) this would be the percolation threshold for a metal-insulator transition.
One could reason, in analogy with the phase diagram of BKBO, that this is where the peak should
occur. Then one has to explain how the resonance can be so symmetric, as in conventional percolation
theory $T_c$ should be zero (insulator) for <$R$> < 2. Again a symmetric resonance might be possible
dynamically, but one would have to provide details for such a dynamical model that includes not just a
few unstable lattice modes, but a nonadiabatic host lattice that is globally marginally stable, with
interactions near dopants that are symmetric with respect to <$R$> = 2.

Because marginal network elastic or mechanical stability is probably the cause of the resonance in Fig. 1,
it is natural to look for other examples of marginally stable networks that contain similar
intermediate phases. The most prominent physical examples are network glasses, for which an
intermediate topological phase is known [14]. In the composition range of this phase the non-
reversible part of the enthalpy of the glass transition is typically 10x smaller than for compositions
outside its range, and high-pressure experiments have shown that the network is internally stress-free.
The most familiar example of a network glass in an intermediate phase is ternary window glass, where
\(<R>\) is one of the two coordinates used to fix (with 1% accuracy, consistent with the quantitative
success of \(<R>\) in Fig. 1) the composition of the stress-free window glass network [15]. Many
examples of similar intermediate phases have been studied in chalcogenide alloys [14], for all of
which 2.27 < \(<R>\) < 2.52. This range is indicated by the wavy line in Fig. 1; it is centered on the
“magic” number 2.40 [14], which is also the value of \(<R>\) in ferroelectric perovskites. The value of
W = 2.52 – 2.27 = 0.25 provides a natural metric for soft glassy networks. Overall, \(<R>\) has proven
itself to be a far more accurate guide to the properties of network glasses than it has in crystals or even
small molecules, which means that strong disorder greatly enhances the value of \(<R>\) as a
configuration coordinate.

The resonance character of \(T_c^{\max}\) in Fig. 1 can be crudely represented by the resonance function
\(T_c^{\max}(\langle R \rangle) = \Theta f(\langle R \rangle)/f(2),\) with \(f(\langle R \rangle) = 1/[1 + b((\langle R \rangle - 2)/W)^2],\) with \(W = 0.25, \Theta = 150K,\) and \(b = 2\) (a number near 1). Here the scale factor \(\Theta\) in some sense reflects the “negative U” interactions [16]
at the dopants (usually interstitial O), yet it is a constant for all optimized cuprates, in spite of
differentiable differences in chemistry and structure. The most significant chemical trends are actually
contained in \(<R>\) (a pure number), which reflects the global softness of the host network. Clearly the
superconductive interactions are adaptive, and when superconductivity is optimized, the effective
value of the “hidden” variable \(U\) (never measured) is replaced by the constant \(\Theta.\) Note that the
progression of the cuprates from larger to smaller values of \(<R>\) is also that of the chronological order
in which good single-crystal samples became available (BKBO, LSCO, YBCO, BSCCO, HBCO, and
the \(<R> < 2\) Cl and F materials). This explains why the cuprates are so special: as \(<R>\) decreases and
the host network softens, growing good superconductors becomes more difficult for \(<R> < 2.40\) (the
perovskite value in BKBO), and the difficulty increases with decreasing \(<R>\). Also note that, while
the CuO\(_2\) planes reinforce the network, \(<R>\) averages over all planes with equal weighting.

In conclusion, the field of HTSC is probably the richest in reproducibly novel properties of any
inorganic system. These properties have provided a cornucopia of striking experimental results,
especially by angle-resolved photoemission (ARPES) [17-19] and high-resolution, large-area scanning
tunneling microscopy (STM) [20]. Many of these results are strongly influenced by details of both
dopant configurations [21] and superconductive and pseudogap nanodomains [20,22]. The overall
chemical trends in the lowest upper bound on \(T_c\) in the cuprates, shown by the master curve in Fig.1,
are so transparent, so simple, and so precise that one can justifiably say that they have been
overlooked until now because they have been “hidden in plain sight”. These trends unexpectedly
transcend all the special effects, and are unique to the cuprates. These trends suggest that optimized
and stress-free Pauling resonating bond networks are the primary factor determining \(T_c^{\max}\) in the
cuprates; indeed, it seems unlikely that an alternative coordinate \(S\) exists that would yield an equally
satisfactory master curve for \(T_c^{\max}(\langle S \rangle).\) Developing a microscopic quantum theory of such
dynamical and exponentially complex networks that goes beyond, but is still consistent with,
semiclassical resonating bond analogies with physical networks [23] is one of the greatest challenges
in theoretical physics.

Postscript. Several recent pump(fs)/probe(ps) experiments (on reflectance [24] and c-axis lattice
constant [25]) experiments have demonstrated spectacular dopant-dependent effects in cuprates even
at room temperature. The self-organized, dopant-centered percolative model [23] has already
explained the reflectance phase diagram of La\(_2\)Sr\(_x\)CuO\(_4\) (LSCO) [24]; here I discuss how the c-axis
lattice constant data [25] on one sample of La\(_2\)CuO\(_4+\delta\) fit into the percolative model. The first point to
realize is that forming such a network on the fs-ps time scale is a complex matter. It was suggested
[23] that the charge excitations produced optically could both self-organize and relax on the ps scale, and that by so doing the charge excitations could function as surrogate dopants (and form percolative paths). This conclusion, that the charge excitations function as surrogate dopants, has also been reached in the more recent dynamical diffraction experiments [25], which showed a giant photoexpansion effect for the c axis, large enough to melt the sample, with an offset (organizational threshold) in photon fluence for the otherwise linear effect. Such a giant effect would not be observed in most ionic crystals. However, it is perfectly natural that it should occur in the cuprates because these materials are marginally stable elastically. The offset is consistent with the charge excitations functioning as surrogate dopants and forming percolative paths when their density is large enough. However – and this is a key point – these percolative paths are glassy and generally couple only very weakly to the host lattice (see [23]'s discussion of precursive diamagnetic effects, Sec. 10). A channel for strong coupling opens up at optimal doping where Fermi liquid patches form due to unavoidable path overlap, and it is the onset of this channel that produces the offset.

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