Fluctuating bond model of high temperature superconductivity in cuprates

D M Newns and C C Tsuei
IBM T.J. Watson Research Center, P.O.B. 218, Yorktown Heights, NY 10598, USA
E-mail: dennisn@us.ibm.com

Abstract. Despite extensive experimental and theoretical work, there is currently no consensus theory for the pairing mechanism in High Temperature Superconductors or for their other anomalous properties. We present a new theory based on a strong, local, nonlinear coupling between the electronic bond strength and oxygen motion in the Cu-O-Cu bond. This model is able to explain a wide range of properties involving superconductivity and symmetry breaking in these materials.

1. Introduction
The cuprate high temperature superconductors (HTS) consist of 25 families, with $T_c$ varying up to 140 K, all of which contain the 2D perovskite-structure CuO$_2$ plane, believed to be the active element. The HTS materials share many anomalous properties [1, 2] as compared with conventional metallic superconductors, as can be seen for example from the phase diagram.

Figure 1. Phase diagram for cuprate (see text).

A sketch of the phase diagram is shown in Fig. 1 in the temperature-doping plane. At low doping the material is an antiferromagnetic insulator (AFI), with a Néel temperature $T_N$, at higher doping it is a metal. The metallic phase is unusual in having a separatrix line $T^*$ [3, 4],
below which transport, NMR, ARPES and other measurements show the presence of a dip in the quasiparticle density of states (DOS) termed the pseudogap \[3, 4\]. There is evidence that \(T^*\) has a negative oxygen isotope shift (\(T^*\) larger for heavier \(O^{18}\) than for \(O^{16}\)) \[5, 6\]. A domed curve \(T_c\) forms the phase boundary of the superconducting (SC) region. The SC is of a novel type with a gap having \(d\)-wave, specifically \(d_{x^2-y^2}\), symmetry \[7\] (see Fig. 1), with nodal excitations which are clearly Fermi liquid-like \[8, 11\]. The isotope shift coefficient \(\alpha\) is negative \[a\] quasiparticle density of states (DOS) termed the pseudogap \[3, 4\]. There is evidence that below which transport, NMR, ARPES and other measurements show the presence of a dip in the superconducting phase \[12\], with a very low value relative to the BCS value \(\alpha = 0.5\) near the maximum \(T_c\), while rising away from the \(T_c\)-maximum to a value \(\sim 0.8\) on the underdoped side. STM studies have revealed the presence of nanoscale inhomogeneity \[13, 14\], continuing above \(T_c\), which may be related to the anomalously low values of superconducting stiffness \[15\].

At low doping the AFI is a Mott insulator due to the large intra-\(3d\) electron Coulomb repulsion \(U\) \[16\]. Although the critical role of \(U\) \[16\] in the metal-insulator transition is widely accepted, we believe that understanding the metallic phase, especially the superconductivity, requires consideration of interaction with the lattice.

There is substantial evidence for involvement of the lattice, mainly oxygen. In addition to the anomalous isotope shift, extensive Raman and neutron measurements show a sharp drop in phonon frequency below \(T_c\) \[17, 18\] while satellites on the SC gap seen in STM tunneling spectra show an isotope shift \[19\]. Much theoretical work in electron-phonon coupling theory \[20, 24\] has been stimulated by the foregoing results.

However, despite extensive experimental and theoretical work, no general consensus on a specific microscopic pairing mechanism, capable of consistently explaining the complex phenomenology of the superconducting and normal states, has emerged.

2. Fluctuating Bond Model (FBM)

The FBM \[25\] (referred to as I) is a nonlinearly-coupled electron-phonon model based on a strong local interaction between the vibrational motion of oxygen in a Cu-O-Cu bond in the CuO\(_2\) plane (Fig. 2) and the electronic state of the bond. Our work follows earlier theoretical studies of nonlinearly-coupled models of superconductivity in cuprates \[26, 27, 28, 29\] and more generally \[30\].

The CuO\(_2\) plane, the active element in the HTS, consists of a square lattice of Cu atoms with oxygen atoms formally at the bond centers (see Fig. 2). Electronically, the \(3d_{x^2-y^2}\) Cu orbital is fractionally filled, the other crystal-field split Cu \(3d\)-orbitals as well as \(O-2p\) being considered occupied. For simplicity, the CuO\(_2\) plane band structure is frequently modeled as a pure \(3d\) band, with Hamiltonian

\[
H^e = - \sum_{ij,\sigma} t_{i-j} c^+_i \sigma c_j \sigma,
\]

where \(c^+_i \sigma(c_i \sigma)\) is the creation (destruction) operator for an electron in the \(3d_{x^2-y^2}\) orbital on Cu site \(i\), and of spin \(\sigma\). The key hopping integral is the nearest neighbor (nn) \(t = t_{(1,0)}\). The single \(3d\) band resulting from (1) has bottom of the band at \(\Gamma = (0,0)\) in the Brillouin zone, top of the band at \((\pi, \pi)\) (taking unit lattice constant), and saddle-points (SP) at \(X = (\pi, 0)\) and \(Y = (0, \pi)\). The SP lie close to the Fermi level \(E_F\), and give rise to logarithmic van Hove singularities (vHs) in the DOS, which play a key role in the metallic phase of the cuprates.

The nn superexchange hopping integrals \(t\) are mediated by the mid-bond oxygen \(2p\)-orbitals. Hence they are sensitive to oxygen positions. The evidence points to oxygen motions radial to the bond (\(y\)- and \(z\)- in Fig. 2) being important. Because of symmetry, they can only be coupled to the bond in second order in the oxygen radial displacement. The coupling in the bond between Cu atoms \(i\) and \(j\) is to the bond order operator \(X_{ij} = \sum_\sigma \left[ c^+_i \sigma c_j \sigma + c^+_j \sigma c_i \sigma \right]\). The
Figure 2. Oxygen vibrations in the cuprate plane (see text).

The electron-phonon coupling Hamiltonian can then be written

\[ H_{eph} = \frac{v^2}{2n} \sum_{\text{bonds}(i,j)} X_{ij} r_{ij}^2, \]  

where \( r_{ij}^2 = y_{ij}^2 + z_{ij}^2 \) in Fig. 2 defines the radial displacement, \( v \) is the coupling constant (assumed \( > 0 \)), and \( n \) is the mode and electron spin degeneracy.

On average there is a term \( \frac{v^2}{2n} \langle X_{ij} \rangle r_{ij}^2 \) contributing to forming a parabolic potential well for the oxygen in the bond-transverse, or radial, direction, and thus stabilizing it. In the absence of this bonding stabilization term, the oxygen is considered to have a potential with the form of an upside down parabola, making it unstable with respect to motion transverse to the bond. To confine the oxygen, a quartic term \([31]\) is included in the bare phonon Hamiltonian

\[ H_{ph} = \sum_{\text{bonds}(i,j)} \left[ \frac{p_{ij}^2}{2M} - \frac{M \omega_0^2}{2} r_{ij}^2 + \frac{w}{8n} (r_{ij}^2)^2 \right], \]  

where the frequency \( \omega_0 \) quantifies the bare oxygen potential instability, \( p_{ij} \) is radial momentum, and \( w \) is the quartic interaction. Note that we here assume isotropy of the in-plane and out-of-plane modes and an Einstein model. The total FBM Hamiltonian is \( H_{FBM} = H^e + H_{ph} + H_{eph} \).

The FBM contains a pairing interaction between electrons. To see this most simply, the oxygen kinetic energy can be dropped, giving the potential energy in a given bond

\[ -tX + \frac{1}{2} \left( -M \omega_0^2 + \frac{v}{n} X \right) r^2 + \frac{w}{8n} (r^2)^2, \]  

which can be minimized with respect to \( r^2 \) to give a reduced renormalized hopping \( t \) (a polaronic mass enhancement effect \( \sim 20\% \)), and a pairing interaction

\[ -\left( t - \frac{v M \omega_0^2}{w} \right) X - \frac{K}{2n} X^2. \]  

Here \( K = v^2/w \) is the pairing interaction energy, which tries (opposed by the electronic kinetic energy) to localize a pair in the bond.

3. Mean Field: \( C_4 \) Symmetry-breaking, \( T^* \), and SC-induced Frequency Shifts

In a mean field approach to the FBM we can make the replacements \( \langle u_{ij}^2 \rangle \rightarrow 2 \langle u_{ij}^2 \rangle u_{ij}^2 \), \( u_{ij}^2 \rightarrow \langle X_{ij} \rangle u_{ij}^2 \), when the oxygen degrees of freedom in Eq. (3) become quadratic, defining
Figure 3. (color online) Contour plot of pseudogap in doping-temperature plane. Parameters $w = 0.5$ au, $v = 0.0841$ au, $t = 0.015$ au, $t'(1,1) = -0.003$ au, $t(2,0) = 0.00163$ au, $\omega_0 = 0.0011 + 2.17 \times 10^{-6} \Delta \mu$ au. $x$-axis is chemical potential $\Delta \mu$ (in meV) relative to energy of vHs.

quasi-harmonic oxygen vibrators. The decoupling $u_{ij}^2 X_{ij} \rightarrow X_{ij} \langle u_{ij}^2 \rangle$ is also possible, leading to renormalization of the $nn$ hopping, as in (5). The resulting simultaneous mean field equations can be solved for the expectation values, leading to reasonable effective oxygen quasi-harmonic frequencies $\omega_{[17, 18]}$ and effective $nn$ hoppings.

The mean field equations also have solutions in which the C$_4$ symmetry of the lattice is broken. In C$_4$ symmetry-breaking the $x$- and $y$- directions in the crystal become non-equivalent. In one direction, say $x$-, there is a large oxygen vibrational amplitude and a smaller renormalized hopping amplitude $t_x$, and in the other, $y$-, there is a smaller oxygen vibrational amplitude and a larger renormalized hopping amplitude $t_y$; the $y$- direction is more metallic, the $x$- direction less metallic in character.

Recently Kohsaka et al. [13] observed C$_4$ symmetry-breaking in two HTS systems via the electron/hole asymmetry in STM tunneling spectra. The phase of the $x/y$ symmetry breaking is nonuniform in space, with a wavelike behavior (quadrupolar or $d$-wave CDW), the coherent regions also forming nanoscale domains. We provisionally assume that this symmetry breaking underlies the pseudogap phenomenon and other observations of nanoscale inhomogeneity in HTS. The pseudogap is defined as $\Delta_{ps}^0 = 2(t_y - t_x)$. $\Delta_{ps}^0$ is plotted in Fig. 3.

The FBM mean field equations are of course parameter-dependent. In a reasonable parameter range we indeed find an upper boundary in temperature $T_{C4}$ for stability of the C$_4$-split phase (Fig. 3), whose behavior with doping typically resembles of $T^*$ in Fig. 1. The dispersion $\Delta_{ps}(k) = \Delta_{ps}^0 (\cos k_x - \cos k_y)/2$ in $k$-space leads to a splitting of the DOS peak associated with the vHs, forming a dip in the DOS; this $d$-wave character of the C$_4$ symmetry-breaking is compatible with the $d$-symmetry assigned to the spatially-averaged pseudogap in ARPES and other measurements [3, 4]. The magnitude of the pseudogap is $\Delta_{ps}^0 \sim 50$meV, the correct magnitude [3], with the correct trend with doping. The isotope shift of $T_{C4}$ is negative in sign, as observed for $T^*$, and is of order the experimental range [5, 6].

On the basis of this correspondence, we tentatively identify $T^*$ as the upper boundary $T_{C4}$ for stability of the C$_4$-split phase, and the pseudogap as originating in the C$_4$-splitting. The observed nanoscale inhomogeneity [13, 14, 19] is associated with spatial variations in phase and
magnitude of the \( C_4 \)-splitting order parameter, which is sensitive to charge and thus to pinning by the dopant distribution.

The softening of oxygen radial vibration frequencies below \( T_c \) [17, 18] can also be derived from the FBM mean field equations - a calculation which is quite different from earlier work based on conventional coupling [32, 33].

![Graph](image)

**Figure 4.** Calculated superconductivity-induced frequency shift vs. temperature, parameters similar to Fig. 3. Inset, data for two highest-\( T_c \) samples in Hewett *et al.* [17], line is guide to eye.

The term \( \langle \frac{\kappa}{2n} \rangle u_{ij}^2 \) contributes to the oscillator stiffness, and inserting the BCS coherence factors for a \( d \)-wave order parameter into the expression for \( \langle X_{ij} \rangle \), gives the relative frequency shift in the phonon frequency \( \omega \): \( \omega (T) - \omega (T_c) = \frac{\nu}{2M\omega_n N} \sum_{k,\sigma} (\cos k_x + \cos k_y) (f_{k,\sigma}(T) - f_{k,\sigma}(T_c)); T < T_c, \) \( (6) \) where \( f_{k,\sigma} \) is the Fermi function calculated in BCS approximation. Negative frequency shifts at the percentile level are predicted, as observed (see Fig. 4).

4. \( d \)-wave Superconductivity

The interaction between the quasiparticles, calculated beyond the classical argument (5), comes from considering fluctuations around mean field. The electron-electron interaction is obtained by summing all RPA-type diagrams with both fermion and phonon bubbles. The result for the interaction between an electron pair \( (k, -k) \), scattering them to \( (k + q, -k - q) \) with transfer of Matsubara frequency \( \omega_n \), is \( W(k, q, n) = |\xi_{k,k+q}|^2 V(q, n), \) \( (7) \) where \( \xi_{k,k'} = \frac{1}{2} \left[ \cos (k_x) + \cos (k_x') - \cos (k_y) - \cos (k_y') \right] \) and (omitting a static term for simplicity)

\[
V(q, n) = -\frac{4n^{-1} K \omega_n^2 \eta_q}{\omega_n^2 + 4\omega_n^2 \eta_q \left[ \frac{1}{2} - KR_{dd}(q, n) \right]},
\] \( (8) \)
Here $\omega_n = 2\pi nk_BT$, $\omega^2 = \hbar w\coth(\hbar\omega/k_BT)/4M^2\omega$ defines the anharmonic frequency component coming from the quartic interaction, and $\eta_q$ and the normal state $dd$ Response Function (electron-hole bubble) $R_{dd}$ are defined as $\eta_q = \frac{1}{2}\left[\cos^2(q_x/2) + \cos^2(q_y/2)\right]$ and

$$R_{dd}(q,n) = -\sum_k \frac{f_k - f_{k+q}}{i\omega_n + \epsilon_k - \epsilon_{k+q}}\xi_{k,k+q}\xi_{k,k+q}. \quad (9)$$

Strictly speaking the interaction (7) would be a $2\times 2$ matrix because of the 2 oxygen modes and 2 electronic bonds $x$- and $y$- in each unit cell. We simplified this using the potential divergence in the denominator of (8) (which can be shown, by comparison with the mean-field equations, to occur at the $C_4$ symmetry-breaking onset) dropping the non-divergent part. The retained part represents $d$-symmetry fluctuations, as seen in the form factor $\xi_{k,k'}$, occurring both in the pairing interaction and in the response function.

The transition temperature is obtained from the leading-$n$ gap equation at $T_c$

$$\Delta(k,n) = -T\sum_{k',n'}\xi_{k,k'}^2 V(k-k',n-n')G_2(k',n')\Delta(k',n'), \quad (10)$$

where $\Delta(k,n)$ is the gap and (taking $E_F$ as energy zero) $G_2(k,n) = (\nu_n + \epsilon_k^2)^{-1}(\nu_n = (2n + 1)\pi k_BT$, $\epsilon_k =$band energy). Solving the gap equation, we always find a $d_{z^2}$-wave gap $\Delta(k,n)$. In I we present some results for $T_c$ and oxygen isotope shift as a function of doping in the $C_4$-unsplit case (and different parameters). The results show the standard dome in $T_c$ as function of doping, and a very dramatic minimum in the isotope shift going down to almost zero around the $T_c$-maximum, while going up to values above the BCS $\alpha = 0.5$ on the underdoped side. In I we also presented experimental results for the isotope shift behavior found for several materials [12] along with the widely used "universal" empirical formula for $T_c$ [34]. It was seen that there is a remarkable degree of agreement between theory and experiment, as regards the doping dependence of both the transition temperature and isotope shift.

5. Discussion

The second-order electron-phonon coupling in the FBM is not necessarily weak, because it is strongly localized in a bond: the FBM describes the dependence of oxygen potential on chemical bond strength. What is unique about Cu relative to other transition metal perovskites, is that there is only $\sim$one hole per Cu atom, hence given that the $2p$ orbitals in $O^{2-}$ are filled, most of the orbitals available for bonding are filled and do not contribute to binding the oxygen. Each Cu-O link in Cu-O-Cu is a single charge transfer bond from oxygen to copper. Hence the ordinary fluctuations, of order one electron into and out of a bond, associated with itinerant electrons in the metallic state can cause significant fluctuations in the oxygen motions, thus modulating the chemical bond strength.

In mean field the presence is revealed of $C_4$ splitting, which has been recently observed [13]. The pseudogap is interpreted as due to the presence of $C_4$ splitting, and the temperature $T^*$ identified with the upper phase boundary $T_{C4}$ of the $C_4$ splitting region. The calculated symmetry and magnitude of the pseudogap and the sign of the $T^*$ isotope shift are consistent with observation. Mean field also leads to an understanding of the frequency shift of the oxygen vibrations below the SC transition temperature $T_c$, due to a weakening of the chemical bond by formation of the SC gap.

Superconductivity, in the absence of the $C_4$ splitting, comes from the interaction between fermion quasiparticles based on an RPA-like bubble sum of Feynman diagrams, which has strongly $d$-wave pairing tendencies. The Eliashberg equation shows that the observed dome of the SC transition temperature $T_c$, and the anomalous doping-dependent isotope shift can be understood in this framework.
The difficult problem not yet fully solved is that of the competing order parameters, C$_4$ splitting and superconductivity, which occur in the presence of spatial variation of the C$_4$ splitting on the nanoscale; a Landau-Ginzburg solution was given in I. A fully satisfactory solution to this problem should resolve the issue of superconducting stiffness [15], but may await understanding of the physics driving the nanoscale variation of the C$_4$ splitting order parameter.

References
[1] Brooks J and Schrieffer J 2007 Handbook of High-Temperature Superconductivity: Theory and Experiment (New York: Springer)
[2] Bonn D A 2006 Nature Physics 2 159-168
[3] T Timusk et al. 1999 Rep. Prog. Phys. 62 61-122
[4] Norman M R, Ding H, Randeria M, Campuzano J C, Yokoya T, Takeuchi T, Takahashi T, Mochiku T, Kadawaki K, GuptaSarma P and Hinks D G 1998 Nature 392 157-160
[5] Temprano D Rubio et al. 2002 Applied Physics A: Materials Science & Processing 74 Suppl.1 s1630-s1634
[6] Halliger P S, Podlesnyak A, Conder K, Ponomarkushina E and Furrer A 2006 Phys. Rev. B 74 184520
[7] Tsuei C C and Kirtley J R 2000 Phys. Rev. Lett. 84 1879-90; Chiao M, Hill R W, Lupian C, Taillefer L, Lambert P, Gagnon R and Fournier P 2000 Phys. Rev. B. 62 3554-58; Proust C, Boaknin E, Hill R W, Taillefer L and Mackenzie A P 2002 Phys. Rev. Lett. 89 147003; Bel R, Behnia K, Proust C, van der Linden P, Maude D and Vedeneev S I 2004 Phys. Rev. Lett. 92 177003
[8] Achkir D, Poirier M, Bonn D, Liang R and Hardy W N 1993 Phys. Rev. B. 48 13184-87
[9] Zhou X J et al. 2004 Phys. Rev. Lett. 92 187001-05
[10] Pringle D J, Williams G V M and Tallon J L 2000 Phys. Rev. B. 62 12527-33
[11] Kohsaka Y et al. 2006 Science 315 1380
[12] Gomes K K, Pasupathy A N, Pushp A, Ono S, Ando Y, Yazdani A 2007 Nature 447 569
[13] Homes C C et al. 2004 Nature 430 539
[14] Anderson P W, Lee P A, Randeria M, Rice T M, Trivedi N and Zhang F C 2004 J. Phys.: Condens. Mat. 16 R755-R769
[15] Hewitt K C, Chen X K, Chrzanowski J, Irwin J C, Altendorf E H, Liang R, Bonn D and Hardy W N 2004 Phys. Rev. B 69 064514; Kitaev Yu E, Limonov M F and Panfilov A G www.ioffe.ru/winners_en/winner98.html; Zhou Z, Cardona M, Colson D and Viallet V 1997 Phys. Rev. B. 55 12770-75
[16] Pintschovius L 2005 Phys. Stat. Sol. (b) 242 30-50; Harashina H, Kodama K, Shamoto S, Sato M, Kakurai K and Nishi M 1996 Physica C 263 257-259; Reznik D, Keimer B, Dogan F and Aksay I A 1995 Phys. Rev. Lett. 75 2396-9
[17] Jinho Lee et al. 2006 Nature 442 546
[18] Nikolic M L 2000 Phys. Repts. 338 1-264
[19] Cappelluti E and Pietronero L 1996 Phys. Rev. B. 53 932-944
[20] Salaik T, Poilblanc D and Scalapino D J 1997 Phys. Rev. B. 55 8445-51
[21] Fu H, Honerkamp C and Lee D-H 2006 Europhys. Lett. 75 146
[22] Schuttler H-B and Pao C-H 1995 Phys. Rev. Lett. 75 4504-07
[23] Newns D M and Tsuei C C 2007 Nature Physics 3 184
[24] Bussmann-Holder A and Keller H 2005 Eur. Phys. J. B 44 487-90; Bussmann-Holder A, Keller H, Bishop A R , Simon A, MicnasR and Miller K A 2005 Euro. Phys. Lett. 72 423 and references therein.
[25] Crespi Vincent H and Cohen Marvin L 1993 Phys. Rev. 48 398-406
[26] Muller K A to be published in Treatise on High Temperature Superconductivity (edited by J R Schrieffer)
[27] Song J and Annett J F 1995 Phys. Rev. B. 51 3840-49
[28] Mahan G D 1997 Phys. Rev. B. 56 8322-29
[29] Piazza F, Abraham E, Cianchi L, Del Giallo F, Spina G, Allegretti F and Ghigna P 2001 J. Superc. 14 675-681
[30] Zeyher Z and Zwicknagl G 1990 Z. Phys. B 78 175-190
[31] Presland M R, Tallon J L, Buckley R G, Liu R S and Flower N E 1991 Physica (Amsterdam) 176C 95-105