High temperature cuprate superconductivity: science puzzles and computational challenges

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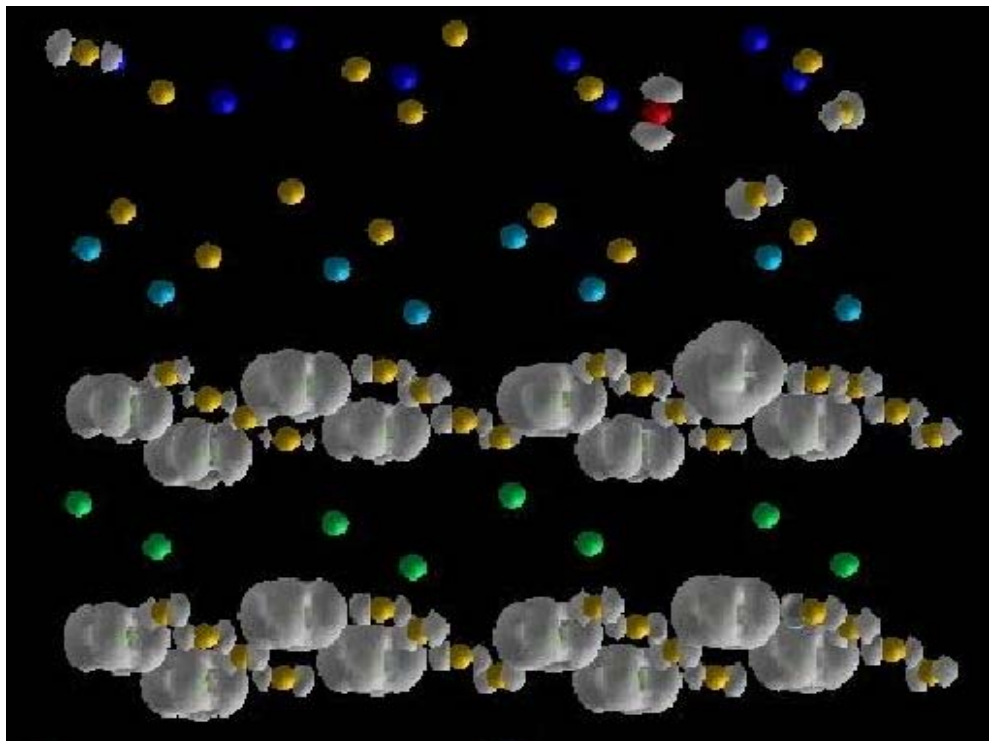
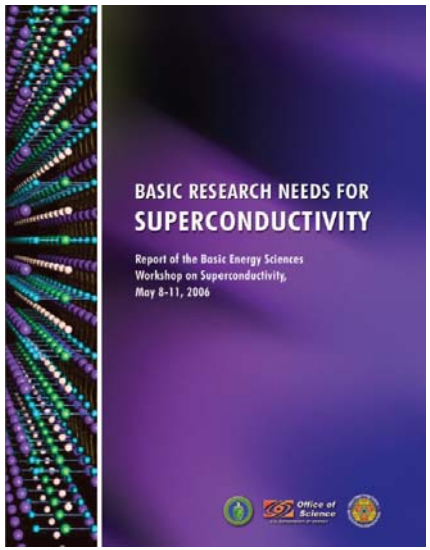


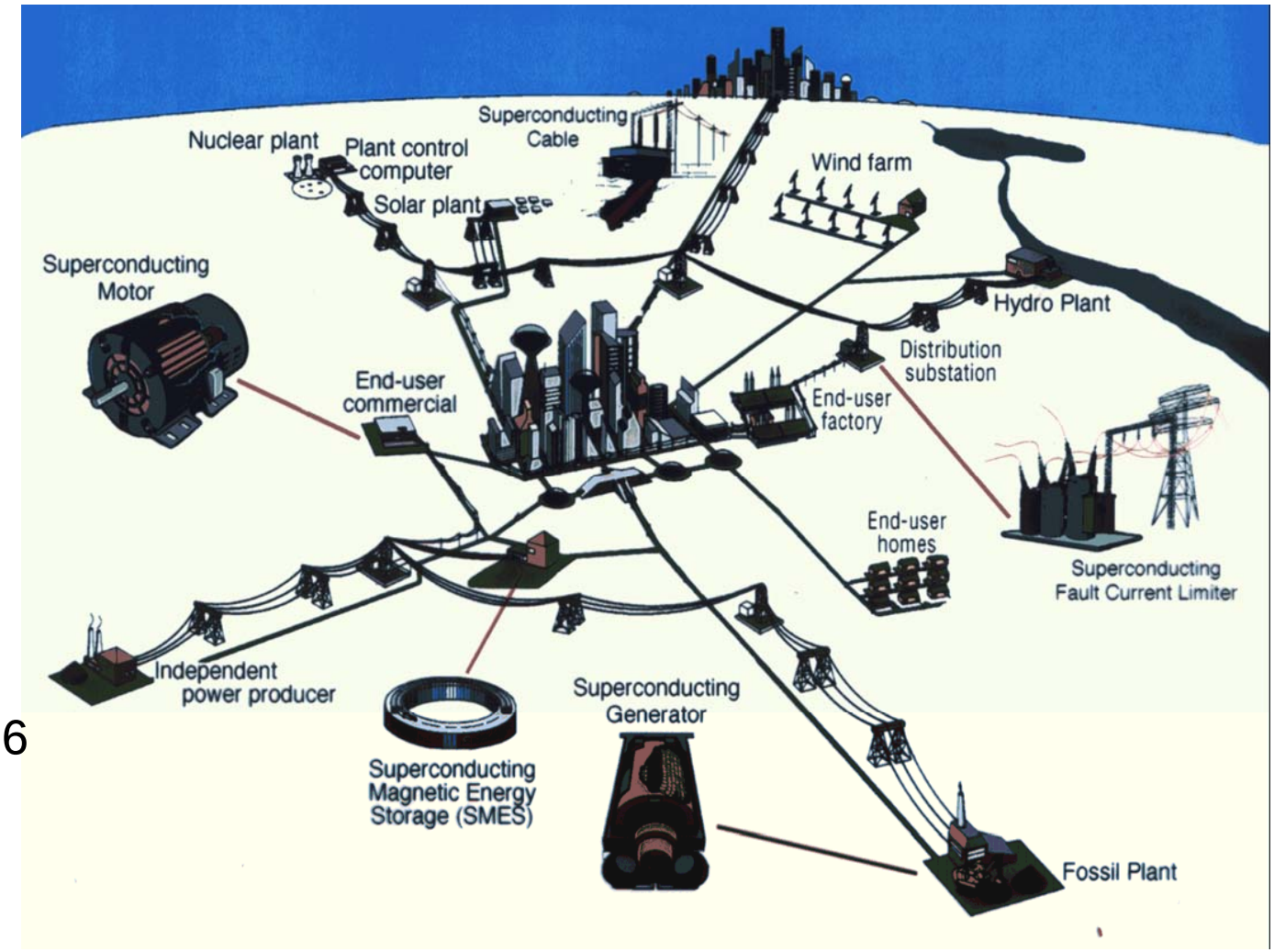
Maui, Jan 2008

The promise of high temperature superconductivity

Future Superconducting Power Generation, Transmission and Distribution Network



Report of DOE workshop May 2006



Promise, cont'd

US:

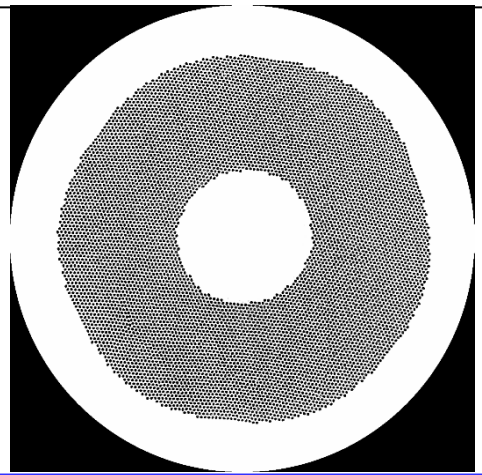
Energy transported in powerlines per year: ~ $3*10^{12}$ kWh

Use of high-T_c cables and transformers:

- reduction of transmission and distribution losses: ~ $6*10^{10}$ kWh / year
- corresponding to savings of: ~ $1.5*10^{11}$ kWh primary energy
- emissions avoided: 100 000 t NO_x
  200 000 t SO_x
  30 000 000 t CO_2

R. D. Blaughter, Research and Innovation, Siemens, Vol. 1/ 98, March 1998

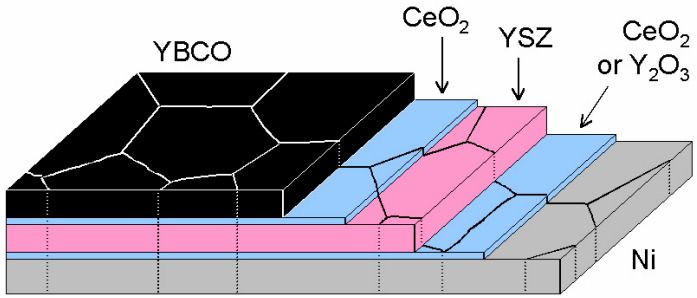
Progress in applied SC



Workhorse Nb-Ti *low-T_c* conductor

Generation I high-Tc conductor – in production

GB-engineered Generation II high-Tc coated conductor



Present projects include:

100 MVA Generator

several >100 MVA cables

35 MW Ship propulsion motor

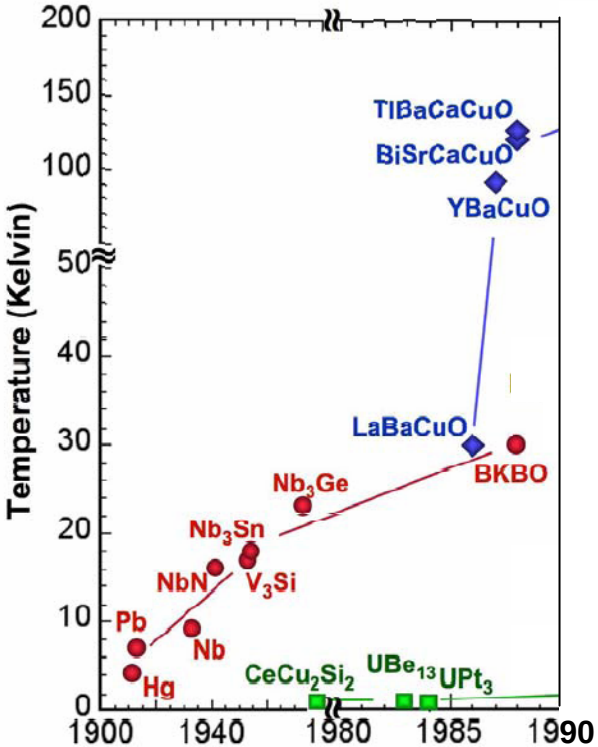
10 MVA transformer

History: initial optimism

Possible High T_c Superconductivity in the Ba – La – Cu – O System

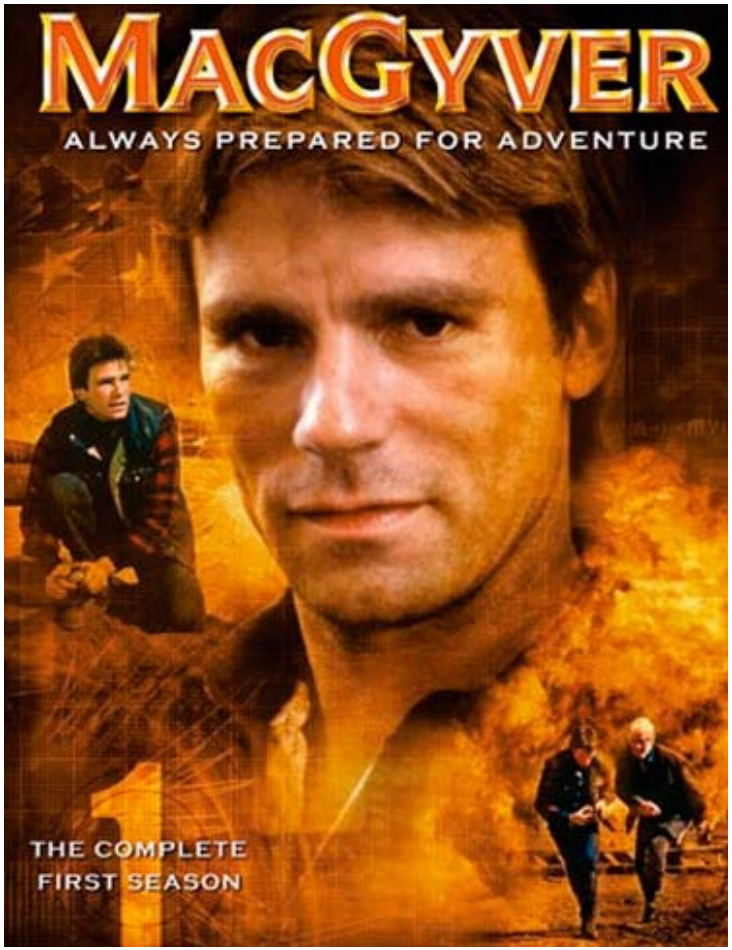
J.G. Bednorz and K.A. Müller
IBM Zürich Research Laboratory, Rüschlikon, Switzerland

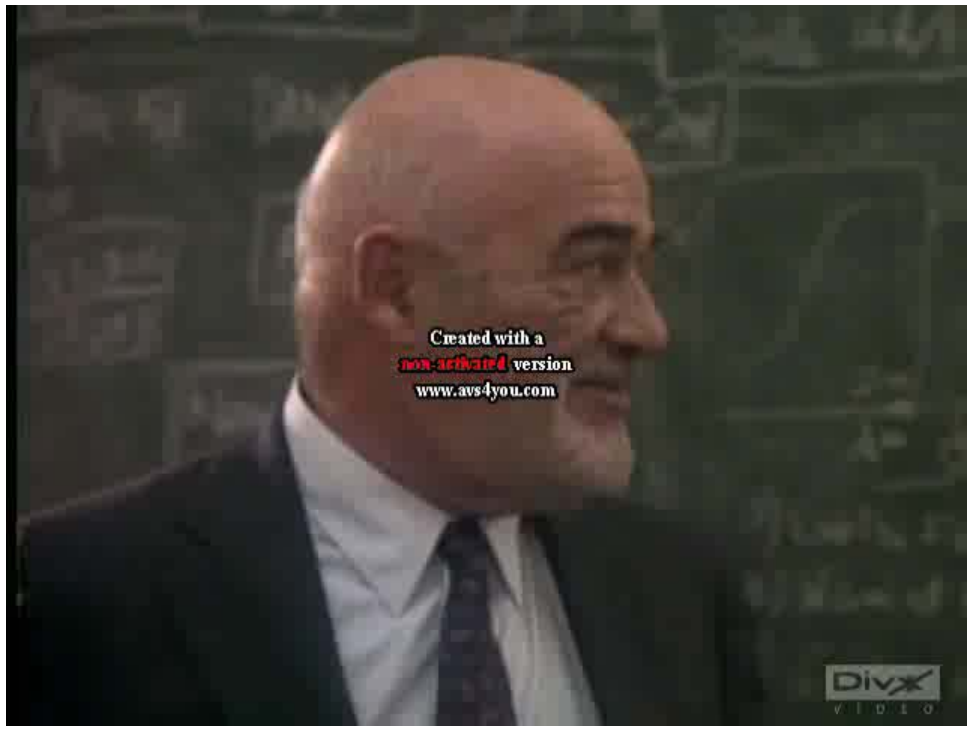
Received April 17, 1986



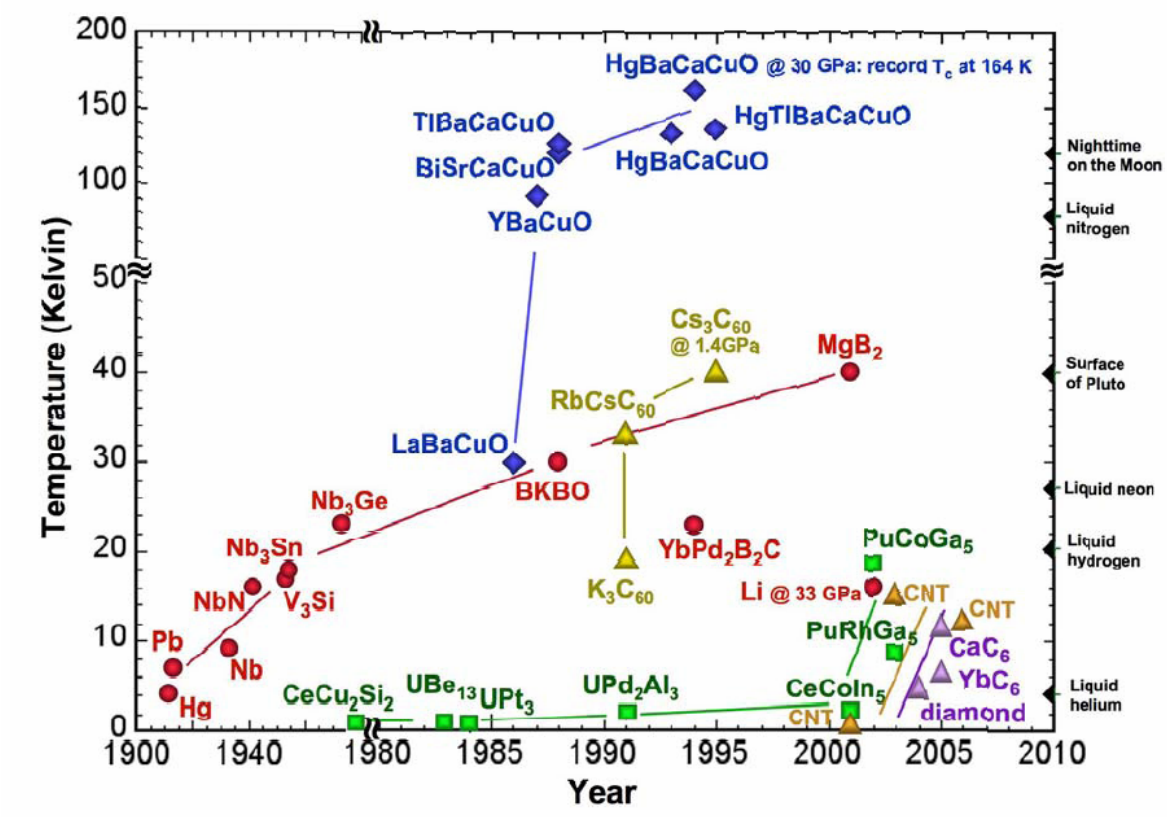
1987 nobel prize to Bednorz & Müller 1987

Initial optimism: MacGyver c. 1988





“Failure” to achieve technological promise: Tc saturates at ~150K



Also: materials are brittle
grain boundaries limit critical current
d-wave nature gives rise to nonlinear μwave response
large thermal fluctuations at higher T

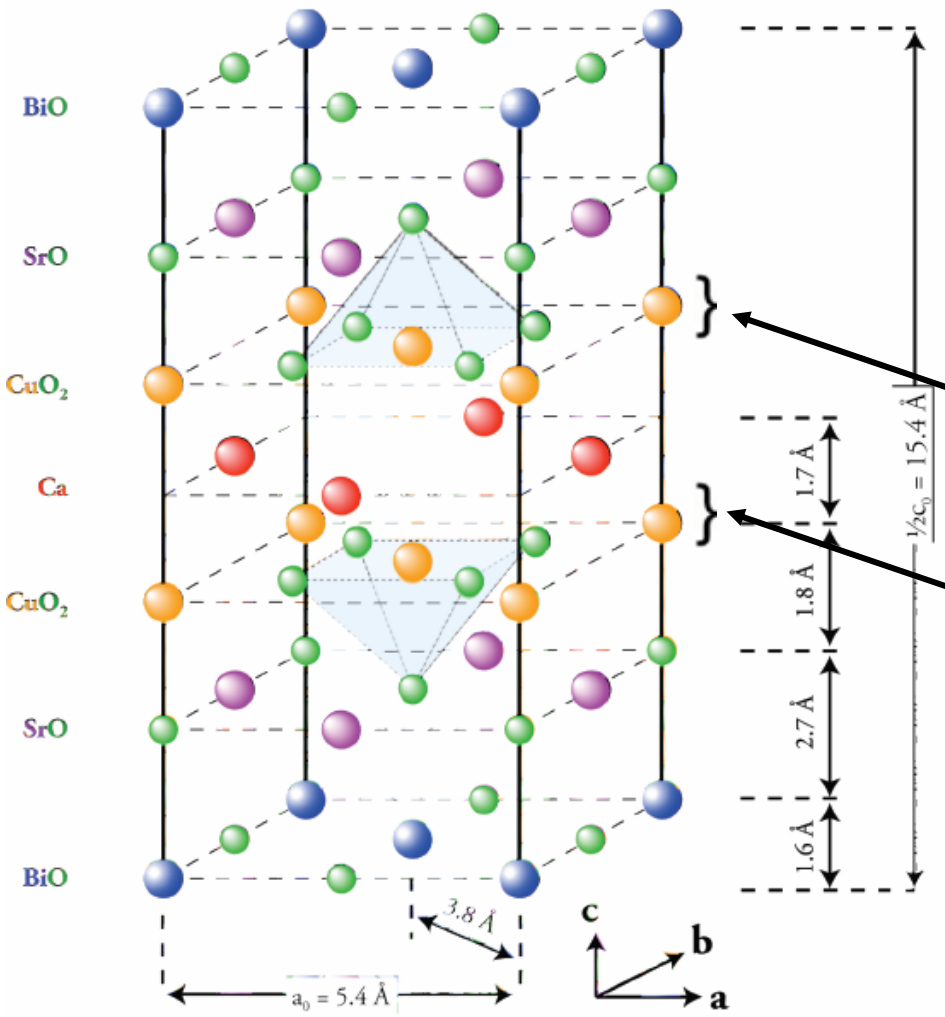
“Failure” on theoretical front: no consensual theory of HTS

after 20 years:

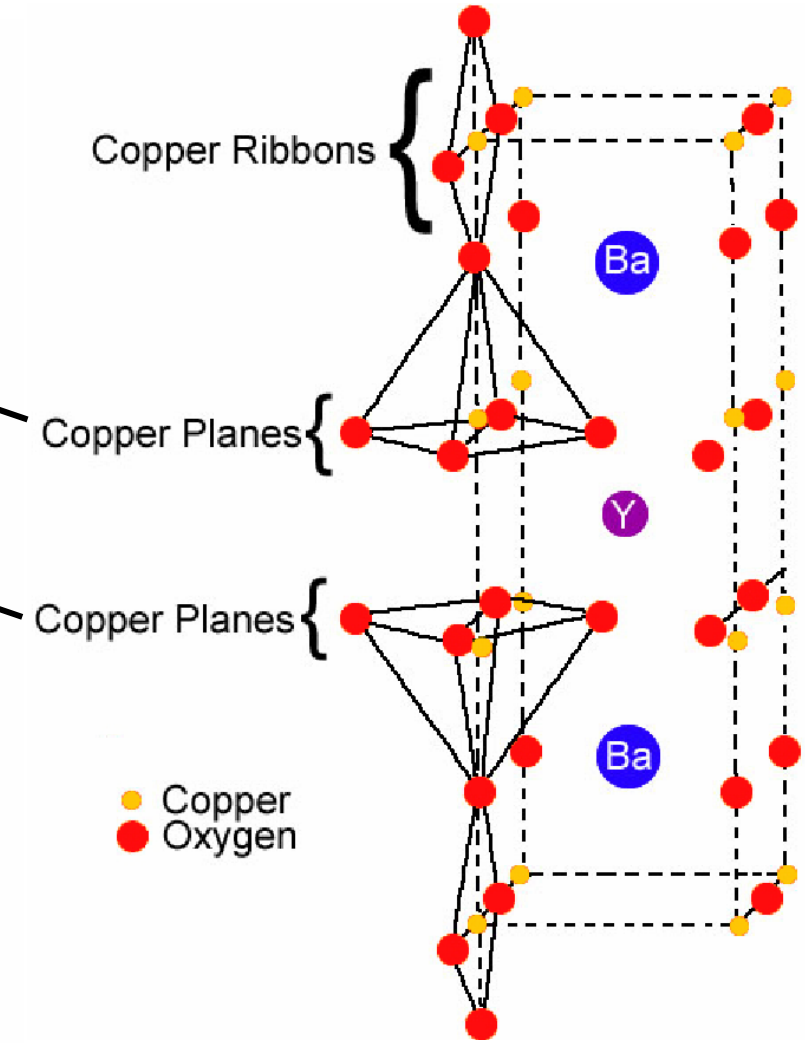
- No predictive power for T_c in known materials
- No predictive power for design of new SC materials
- No explanation for pseudogap phase (see later)
- No theory of unusual transport properties
- No controlled solution for proposed effective Hamiltonians
- Only partial consensus on which materials aspects are essential

Cuprate physics

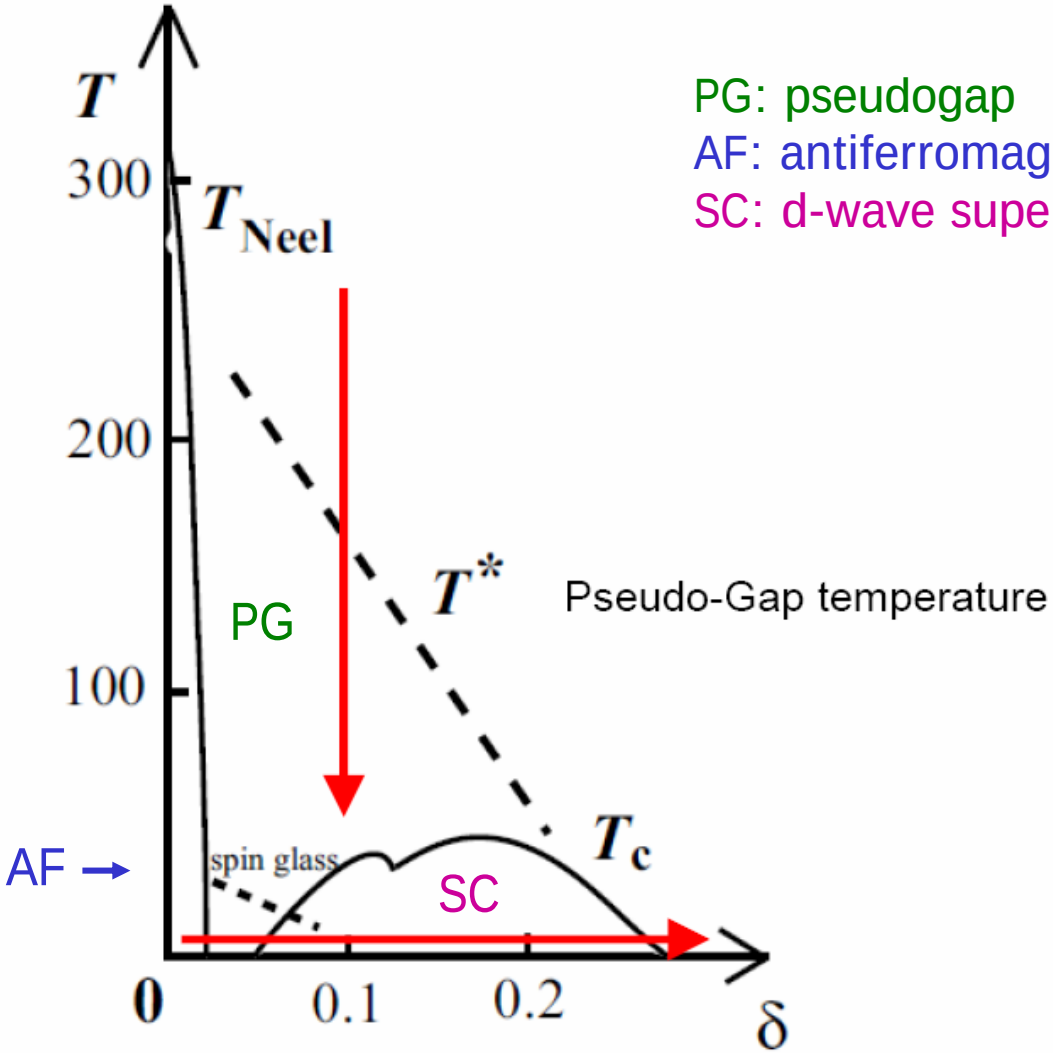
$Ba_2Sr_2CaCu_2O_8$



$YBa_2Cu_3O_7$

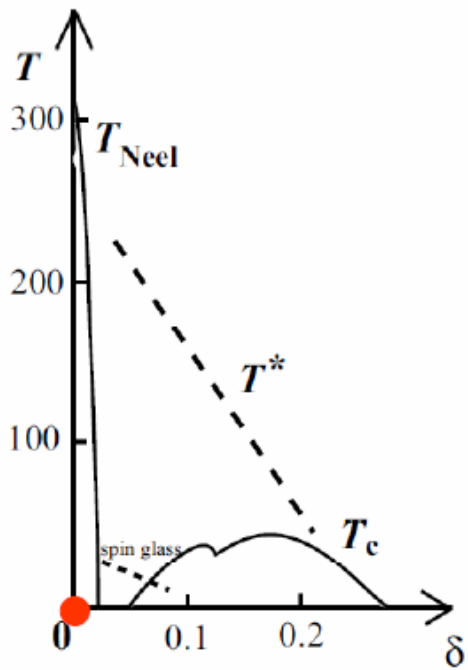


Phase Diagram



PG: pseudogap
AF: antiferromagnet
SC: d-wave superconductor

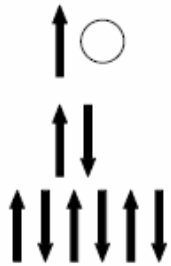
1. $\delta = 0$



La_2CuO_4

La^{3+}
Cu^{2+} --- $(3d^9)$ one hole S = 1/2
O^{2-}

d_{x2-y2} orbital



Half-filled band: n = 1

Insulator ---- Band calculation failed !
1 electron per Cu = 1/2 spin per Cu

Heisenberg model on 2-Dimensional Square lattice

$$\mathcal{H}_J = J \sum_{\langle i,j \rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j,$$

0.5 μ_B per Cu

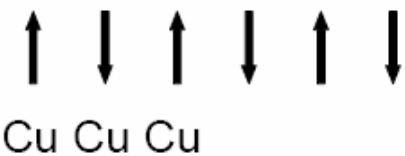
$J = 0.13\text{–}0.14$ eV	for LSCO
$J = 0.130$ eV	for $Sr_2CuO_2Cl_2$
$J = 0.125$ eV	for BSCCO
$J = 0.10\text{–}0.110$ eV	for YBCO,

Hubbard model

$$H = -t \sum_{\langle ij \rangle \sigma} c_{i\sigma}^{+} c_{j\sigma} + U \sum_{j} n_{j\uparrow} n_{j\downarrow} \qquad (U \geq 0)$$

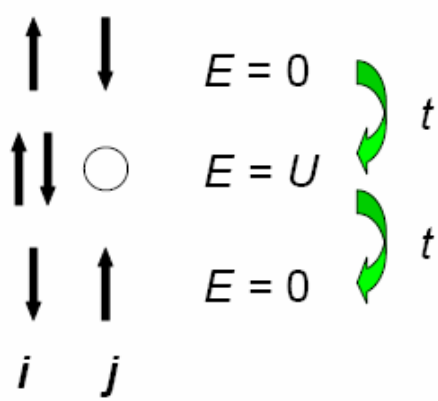
***U* = 10 eV = 10,000 K**

No double occupancy for T< 300 K



can not move = Mott insulator
We need effective theories at low T.

But virtual states are allowed in Quantum Mechanics



Super-exchange mechanism
(Anderson)

Virtual state (second-order perturbation)

$$\frac{2t^2}{U} S_i^- S_j^+ \Longrightarrow \frac{4t^2}{U} \boldsymbol{S}_i \cdot \boldsymbol{S}_j$$

$$J = \frac{4t^2}{U} = 0.1\mathrm{eV}$$

Double occupancy occurs only in virtual states

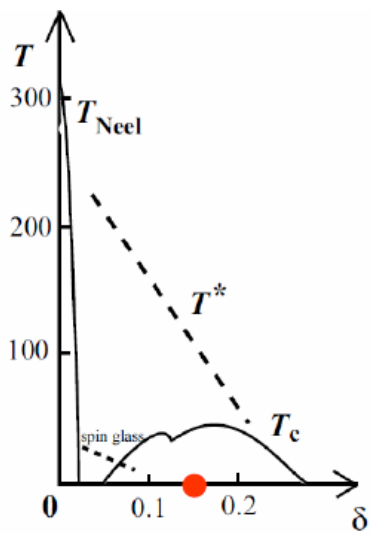
⟷ U < Uc many double occupancies (Mott transition at Uc)

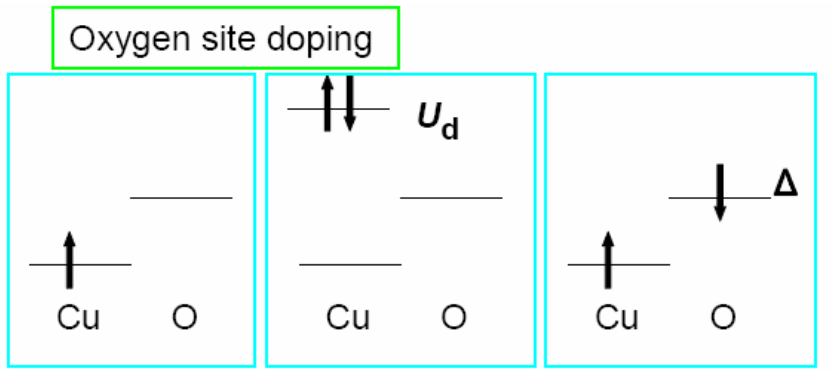
2. Hole doping δ > 0

large U limit of Hubbard at d>0: t-J model

$$H_{t-J} = \sum_{\langle i,j \rangle} \tilde{c}_i^{\dagger} \tilde{c}_j + h.c. + J \sum_{\langle i,j \rangle} S_i \cdot S_j$$

But:

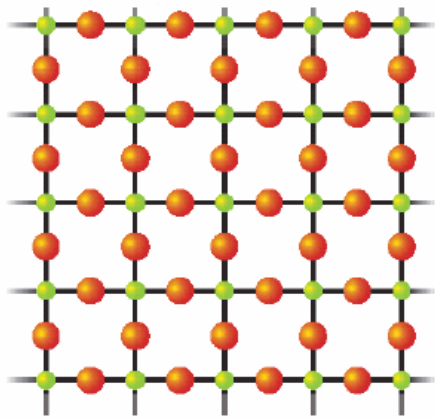




(hole representation)

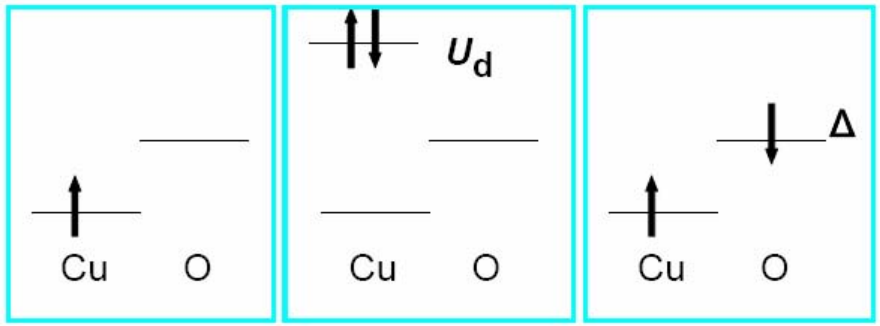
Oxygen sites should be considered.

d-p model (Emery)



Planar cuprate

3-band Hubbard or d-p model

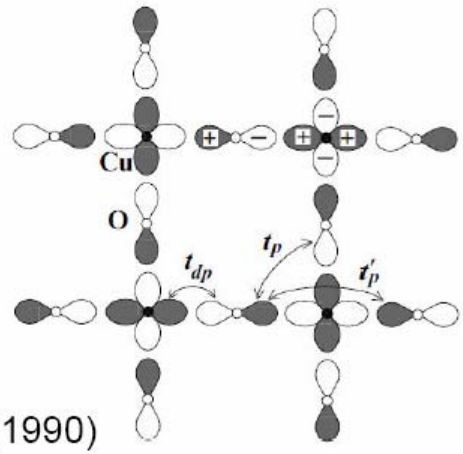


d-p model

$$\mathcal{H}_{\rm dp} = -t_{dp}\sum\left(d^\dagger_{i\sigma}p_{j\sigma}+\text{h.c.}\right) - t_p\sum\left(p^\dagger_{j\sigma}p_{j'\sigma}+\text{h.c.}\right)$$
$$+t'_p\sum_{\langle j,j''\rangle\sigma}\left(p^\dagger_{j\sigma}p_{j''\sigma}+\text{h.c.}\right)+\Delta\sum_{j\sigma}n_{p,j\sigma}$$
$$+U_d\sum_i n_{d,i\uparrow}n_{d,i\downarrow}+U_p\sum_j n_{p,j\uparrow}n_{p,j\downarrow}+V\sum_{\langle i\ \rangle} n_{d,i}n_{p,j},$$

(hole operators)

$t_{dp} = 1.3$ eV (1.5 eV)
$t_p = 0.65$ eV (0.6 eV)
$\Delta = 3.6$ eV (3.5 eV)
$U_d = 10.5$ eV (9.4 eV)
$U_p = 4$ eV (4.7 eV)
$V = 1.5$ eV (0.8 eV).



Hybertsen et al PRB 39, 9028 (1989), McMahan (1990)

-- reduces to *t-J* model in realistic limit!

Remarks:

NB: These are all models of CuO_2 plane only!
1-layer cuprate materials have wildly different Tc's (Bi-2201 Tc=10K, Tl-2201 Tc=90K). Some out-of-plane physics is essential to understand!

20 years: great progress in understanding Hubbard model, 3-band model, t-J model—numerical methods:

1) QMC
2) DMFT, CDMFT
3) DMRG

But: do we even know if the model has a superconducting ground state? Not for sure. Pair susceptibilities imply strong superconducting tendency.

If we knew this, would we have solved HTS? What does it mean to solve the problem?

Solving hard problems in condensed matter physics

Schrödinger eqn. for 10^{23} e^-,N with Coulomb forces

(normal metal) ↙ ↘ (cuprate)

$$H = H_{el}^0 + H_{el-ph} + H_{Coul}$$

$$\downarrow$$

$$H = H_{el}^0 + H_{el-ph}^{screened} + H_{Coul}^{screened}$$

$$\downarrow$$

$$H = H_0 + V\psi^\dagger\psi^\dagger\psi\psi \text{ (Fermi liquid)}$$

$$\downarrow$$

$$H = H_0 - \Delta^*\psi\psi - h.c. \text{ (BCS)}$$

$$H = H_{el}^0 + H_{el-ph} + H_{Coul}$$

$$\downarrow$$

$$H = H_{2DHubbard}(?) + \text{interlayer}(?) + \text{screening}(?) + \text{phonons } (?)$$

$$\downarrow$$

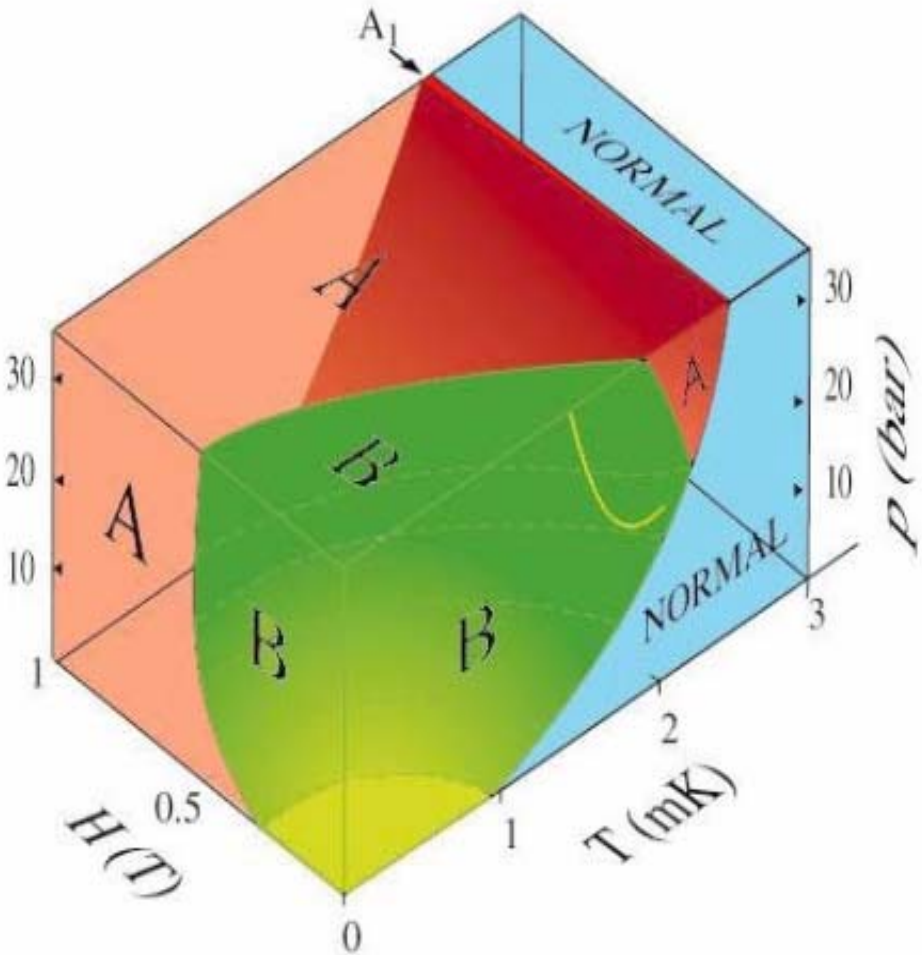
?

$$\downarrow$$

$$H = H_{BCS-d} + \text{pseudogap} + ?$$

Reminder: superfluid ^{3}He

- Well-defined Fermi liquid with $T_F \simeq 1K$
- Landau parameters $F_\ell^{s,a}$ known from experiment
- p-wave, spin triplet superfluid below $T_c(p) \simeq 1-3mK$.
- Subdominant pair component (f-wave) known from quantitative fits to BCS WC+ theory.



Theory of superfluid ^{3}He

But:

- no controlled microscopic calculation of $F_\ell^{s,a}$

- no consensus on microscopic pair interaction: spin vs. density fluctuations

  Anderson Brinkman 1973

  Rainer Serene 1976

Q: Why do we think we understand ^{3}He?

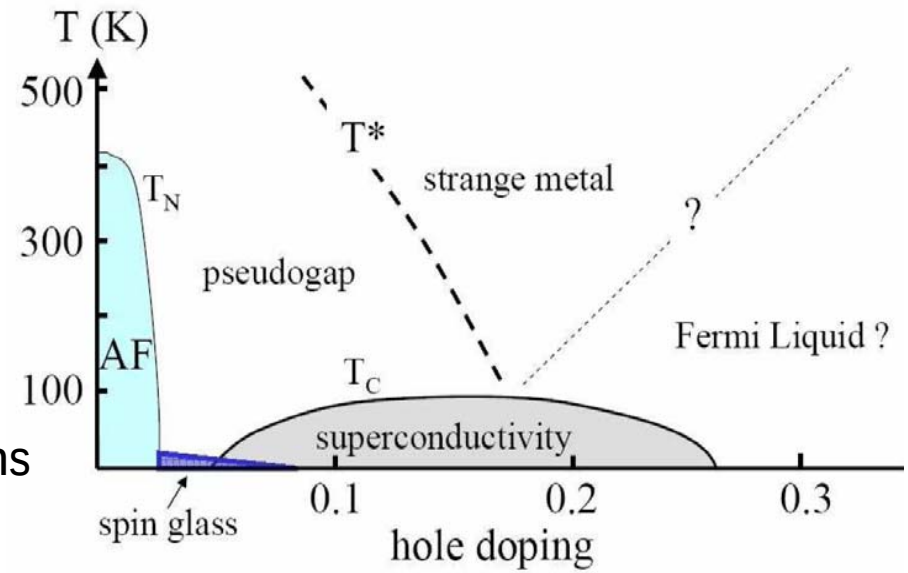
- Phenomenology of disordered phase (Landau thy)

- Phenomenological theory *within* each low temperature phase

- Qualitative understanding of each phase transition.

Q: By *this standard*, have we solved HTS?

- SC phase symmetry understood phenomenology available (BCS)
- AF phase symmetry understood, quantitative calculations possible
- (claim) spin glass phase understood as disorder-induced magnetic correlations (stripes at special fillings)



- nature of pseudogap, strange metal unknown, many proposals

A: not quite, but close!

But: to make materials-specific predictions, to aid discovery or engineering of new, higher T_c compounds, we need a higher standard!

Avenues to further progress

- Understanding origin of pairing in Hubbard, *t-J* type effective models

- Adding correlations to DFT

- "Bridges" between ab initio and model calculations

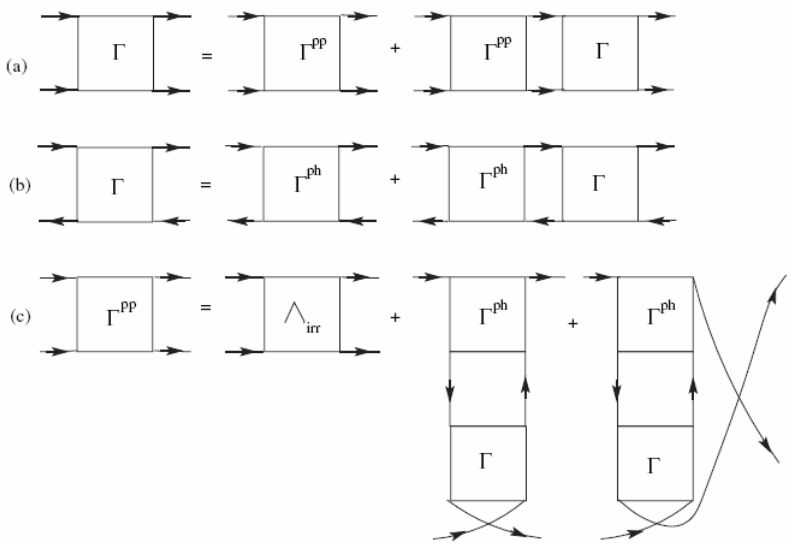
- New paradigms to study and engineer pairing interaction: spatial inhomogeneities

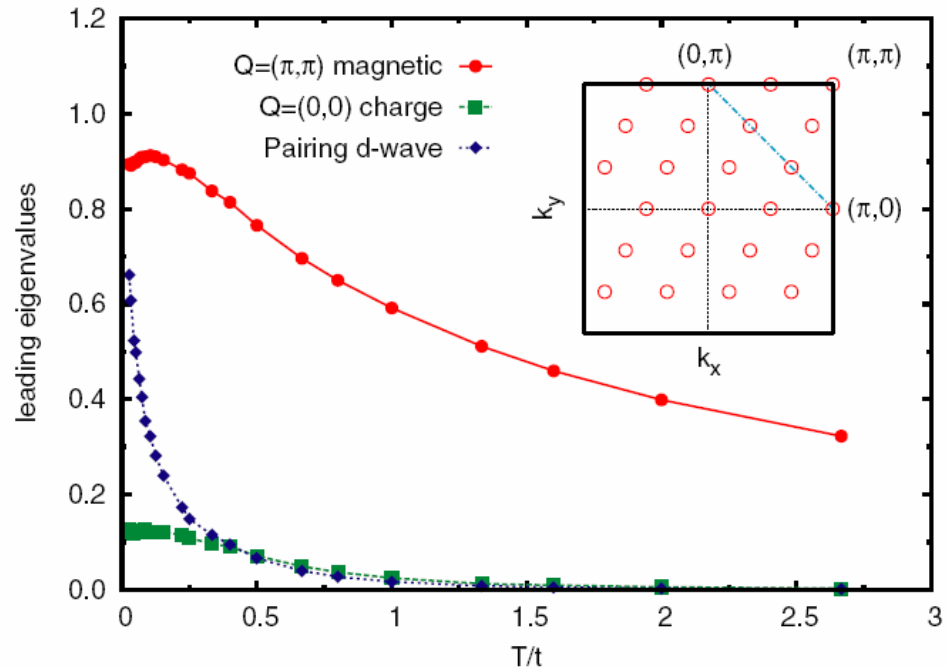
All will require petascale computing power!

Pairing in Hubbard-type models

Maier, Jarrell, & Scalapino 2006 et seq.

Dynamic cluster QMC calculations





Strong tendency to pair in $d_{x^2-y^2}$ channel!

Inclusion of correlations in Density Functional Theory

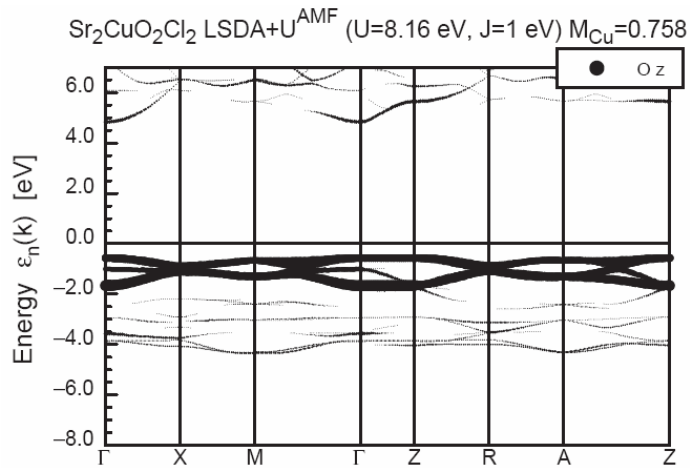
- LDA = local density approximation
- GGA = generalized gradient approximation
  - Include the density gradient for the higher order correction
  - preserving the sum rule for the exchage-correlation hole
- GW = Green's function + screened interaction potential
  - Self-energy correction by

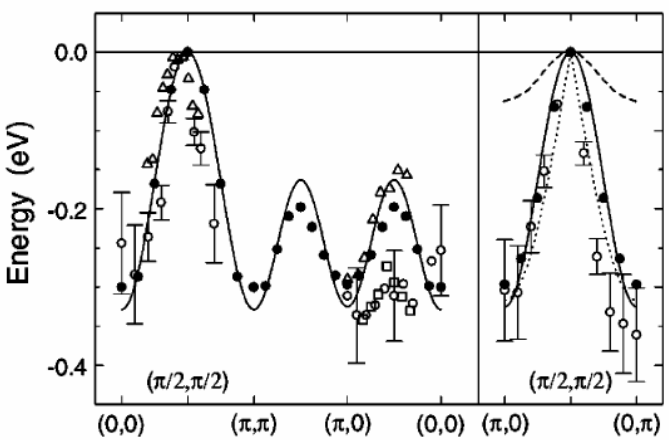
"DFT+"

$$\Sigma(\mathbf{r},\mathbf{r}';\omega) \approx G(\mathbf{r},\mathbf{r}';\omega)\epsilon^{-1}(\mathbf{r},\mathbf{r}';\omega)V_{eff}(\mathbf{r},\mathbf{r}')$$

- LDA+U
  - Unrestricted Hartree-Fock treatments for the localized orbital states

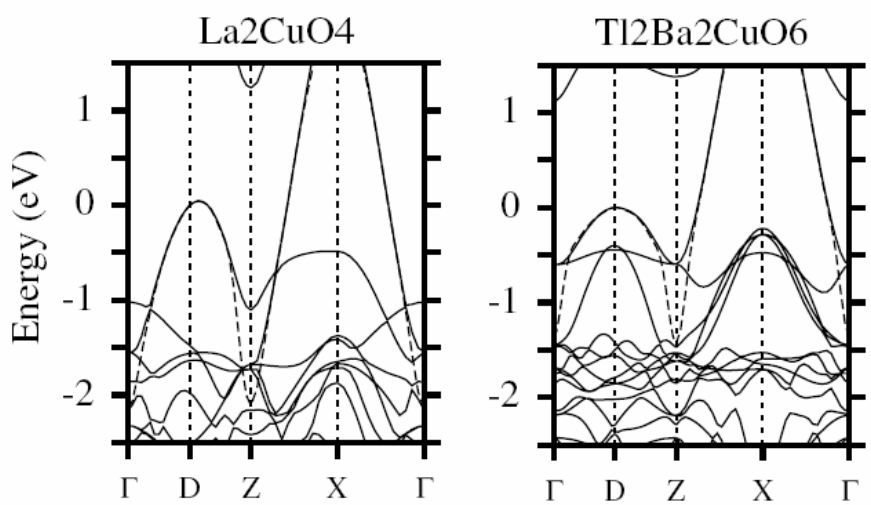
Eschrig et al 2003 LDA+U $Sr_2CuO_2Cl_2$



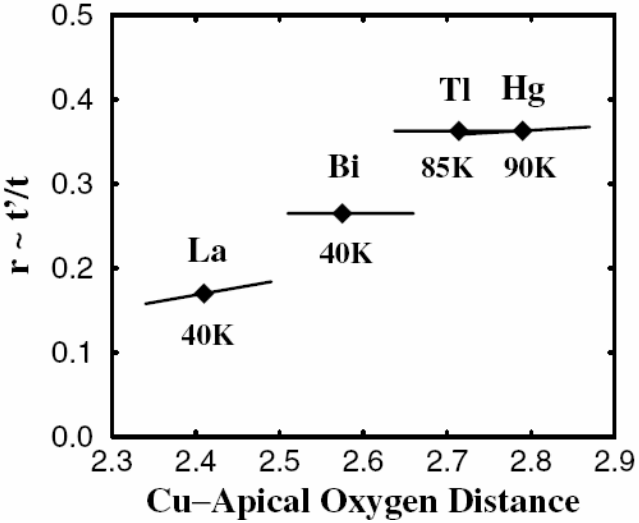


“Bridges” between ‘DFT+’ and effective models

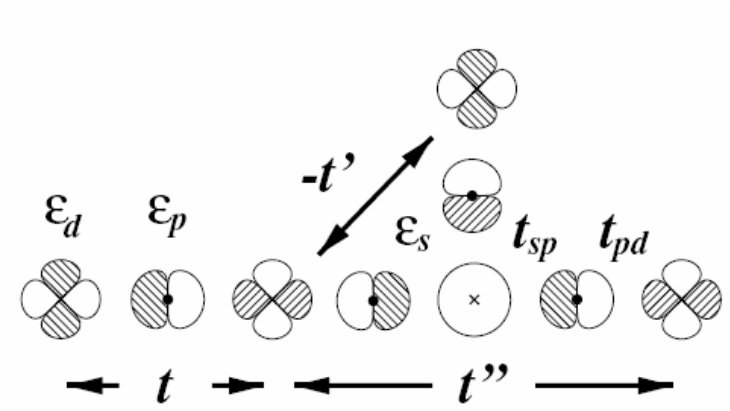
Pavarini et al 2001 – 1) calculate spaghetti:



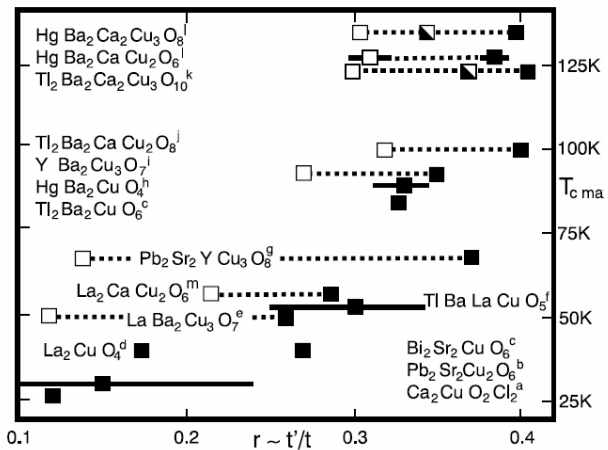
3) show how model parameters depend on atomic positions...



2) then “downfold” onto effective model with small set of orbitals



4) ... which are linked to macroscopic observables (T_c!)



Combining “downfolding’ and strong correlations

Kent et al 2008: try to use downfolded band structure for different materials to obtain systematics of T_c within 3-band Hubbard model

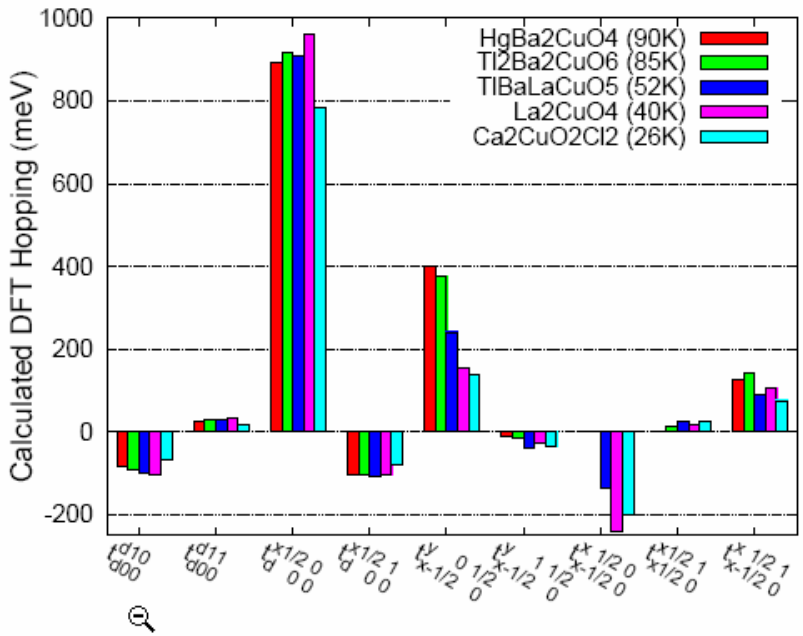
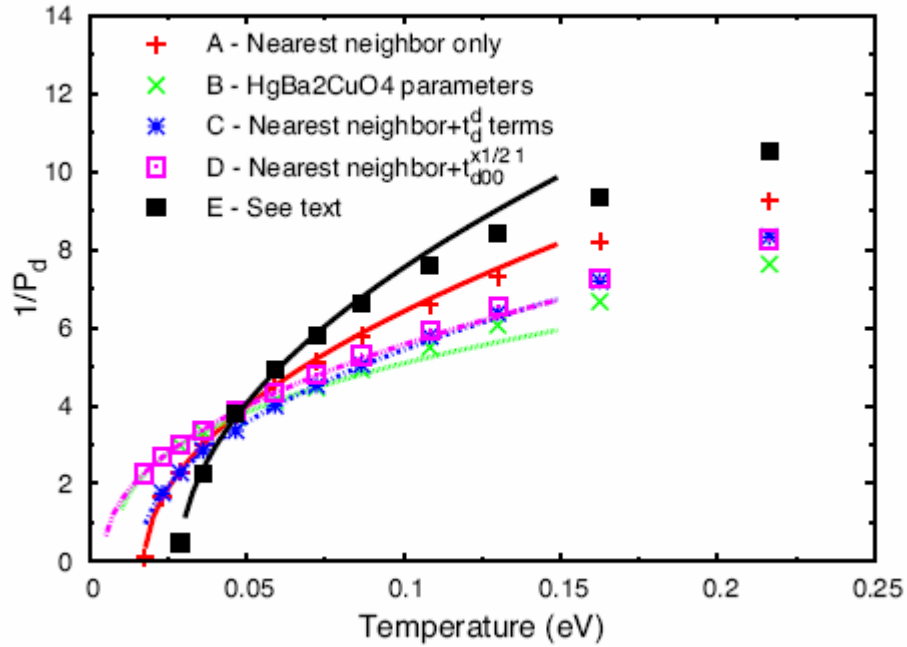
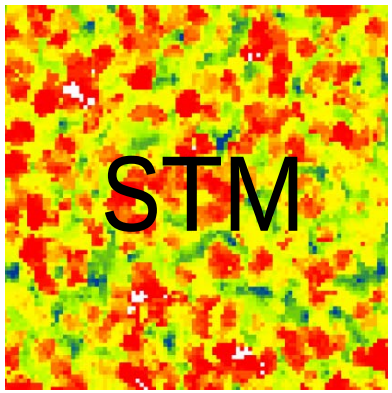


FIG. 2: (Color online) Calculated in-layer hoppings for five single-layer cuprates with different $T_{c\,\max}$.



Combining ‘DFT+’ with experiments



DFT

engineer new materials optimizing displacements

X-ray

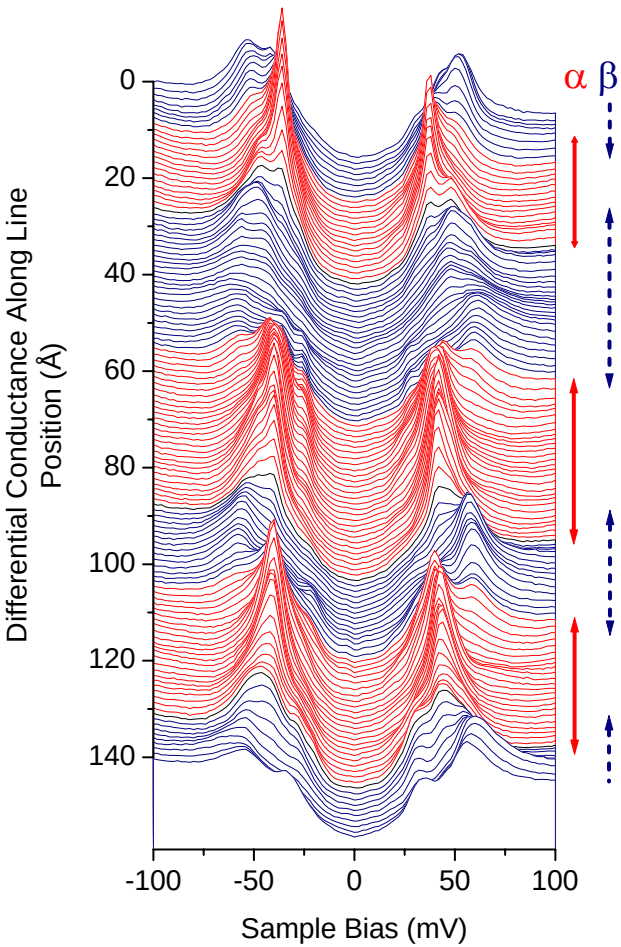
pairing theory

measure correlations of pairing with spatial perturbations

determine actual atomic displacements

figure out how to make a higher temperature superconductor

Nanoscale Inhomogeneity in BSCCO-2212



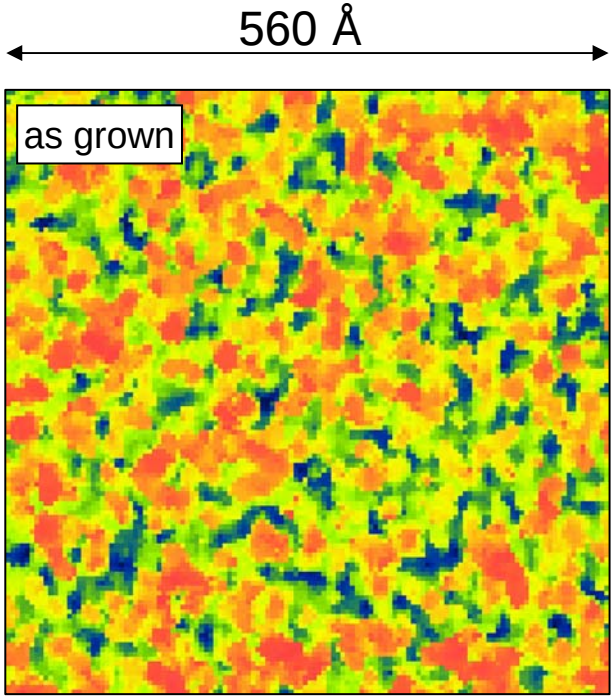
Cren *et al.* 2001

Pan *et al.* 2001

Lang *et al.* 2002

Howald *et al.* 2002

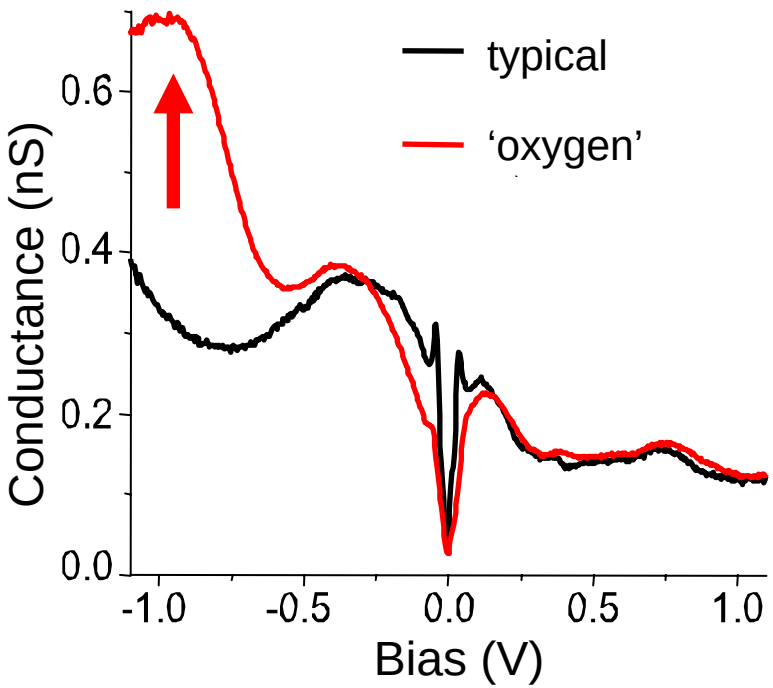
Δ map

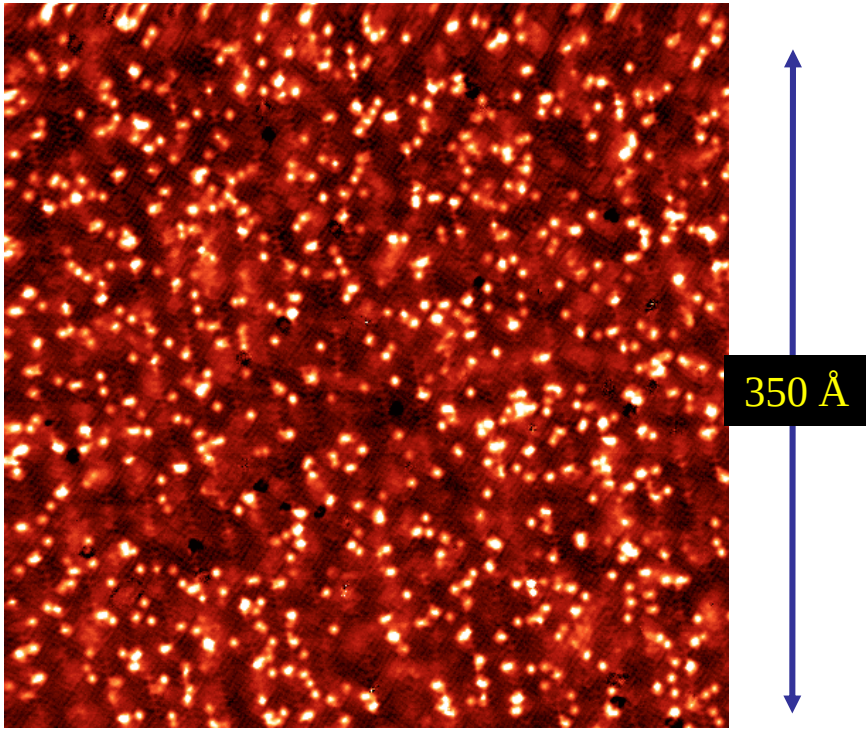


Spectral gap in LDOS varies by factor of 2-3 over distances 20-30 Å

A.A.A. : "can you please make the resolution *less*?"

Out-of-plane defects, e.g. interstitial oxygen





-960meV LDOS map

-960mV peak with 300meV FWHM

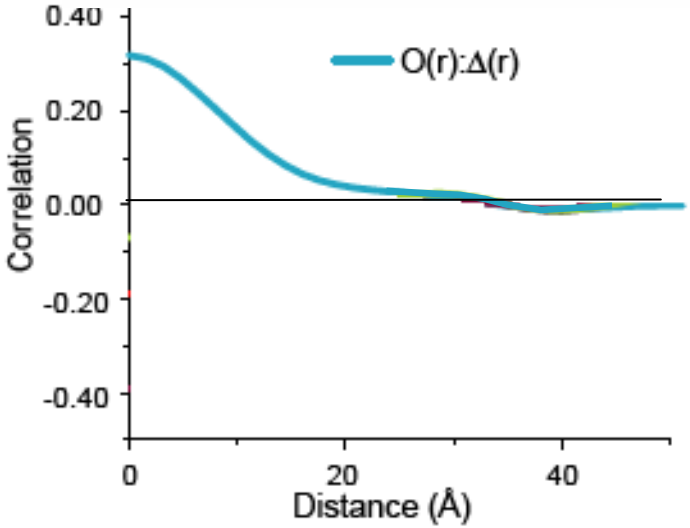
K. McElroy *et al* Science 05

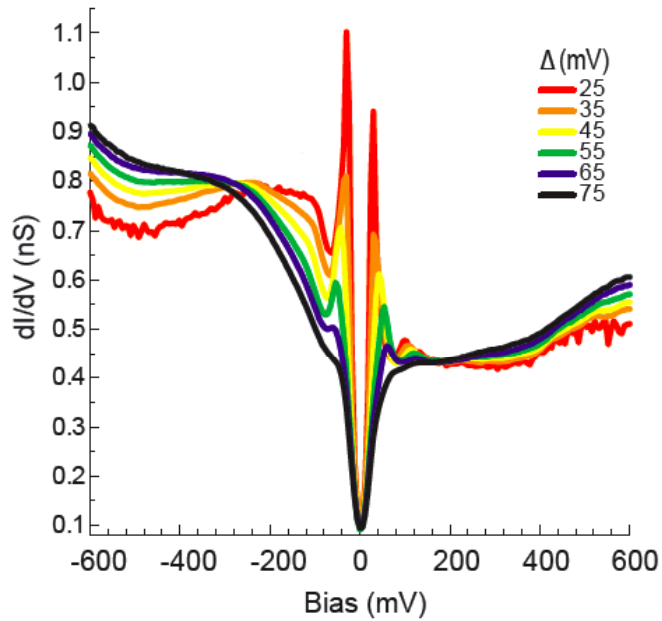
Relation: spectra ↔ oxygen dopants

Fantastic possibility to correlate dopants and energy gap!

K. McElroy *et al.*, 2005

$$C_{fg}(j) = \frac{1}{N}\sum_i \frac{\langle \delta f(i)\delta g(i+j)\rangle}{\sqrt{\langle \delta f\rangle\langle \delta g\rangle}}$$





Oxygen ↔ gap *positively* correlated

contradicts local doping picture

Charge modulations almost disappear when integrated up to -900meV

Simple disorder model(s)

conventional impurity potential

Mean field Hamiltonian for inhomogeneous d-wave superconductor (BdG):

$$H = \sum_{k\sigma} \varepsilon_k c^+_{k\sigma} c_{k\sigma} + \sum_{i\sigma} V_i c^+_{i\sigma} c_{i\sigma} + \sum_{\langle ij \rangle} \left(\Delta_{ij} c^+_{i\uparrow} c^+_{j\downarrow} + H.c. \right)$$

with: $\varepsilon_k = -2t\left(\cos k_x + \cos k_y\right) - 4t' \cos k_x \cos k_y - \mu$ t'=-0.3t, μ=-1.0t

(d-wave ground state $\Delta_{\mathbf{k}} \sim \cos k_x - \cos k_y$ in homogeneous case)

Self-consistency condition for order parameter: $\Delta_{ij} = g_{ij} \left\langle c_{i\uparrow} c_{j\downarrow} - c_{i\downarrow} c_{j\uparrow} \right\rangle$

Allow for dopant-modulated coupling constant:

How could O-dopants modulate pair interaction?

Previous works on spatial modulations of pair interactions by impurities, grain boundaries, ...:

H. Suhl et al 1962
A.I. Larkin 1970
Weinkauf Zittartz 1975
I. N. Khlyustikov and A. I. Buzdin 1987

(modulation of e-ph couplings by impurities or interfaces)

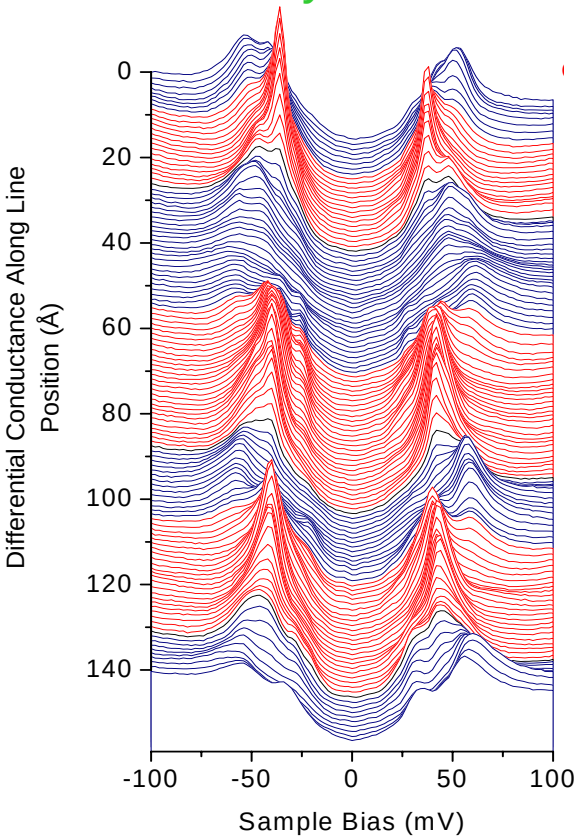
For HTS, maybe similar, or possibly:

atomic-scale modulation of local electronic structure which affects pairing via exchange of electronic excitation

Nunner et al 2005, J.-X. Zhu 2006, Maska et al 2007: modulation of J

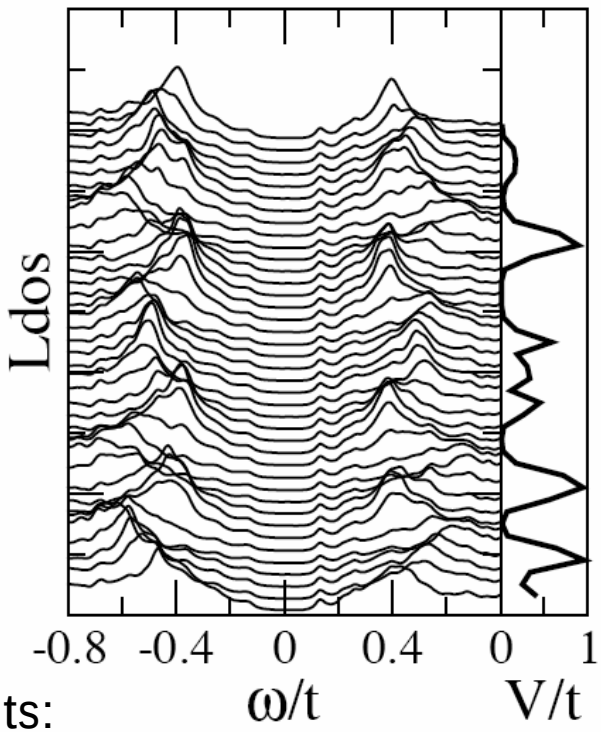
Atomic scale pairing disorder

McElroy et al 2005

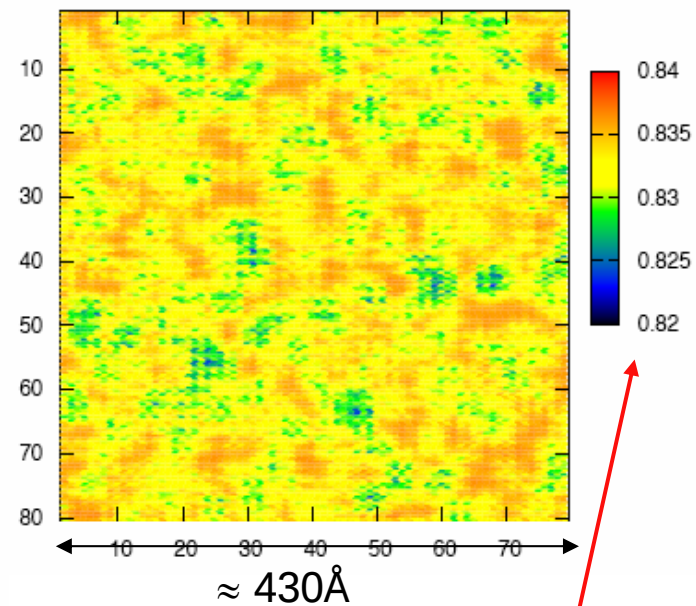


Theory: Nunner et al 2005

Ldos along line-cut (BdG)



Charge



Note small scale

Results:

- Homogeneous low-energy Ldos ✓
- Positive correlation: dopants ↔ gap magnitude ✓
- Anti-correlation: “coherence” peak height ↔ gap magnitude ✓
- Small charge modulations ✓

Can STM tell us about *local causes* of pairing?

Logic:

- O dopants enhance pairing *locally* around themselves
- Find out what O dopants do to local electronic structure
- See how these changes affect models of pair interaction

Part of more general program:

Systematic investigation of *local* perturbations which correlate positively with superconducting gap: constrain pair theories

Grand challenge for theory: give up old prejudice that atomic scale information is irrelevant for superconductivity

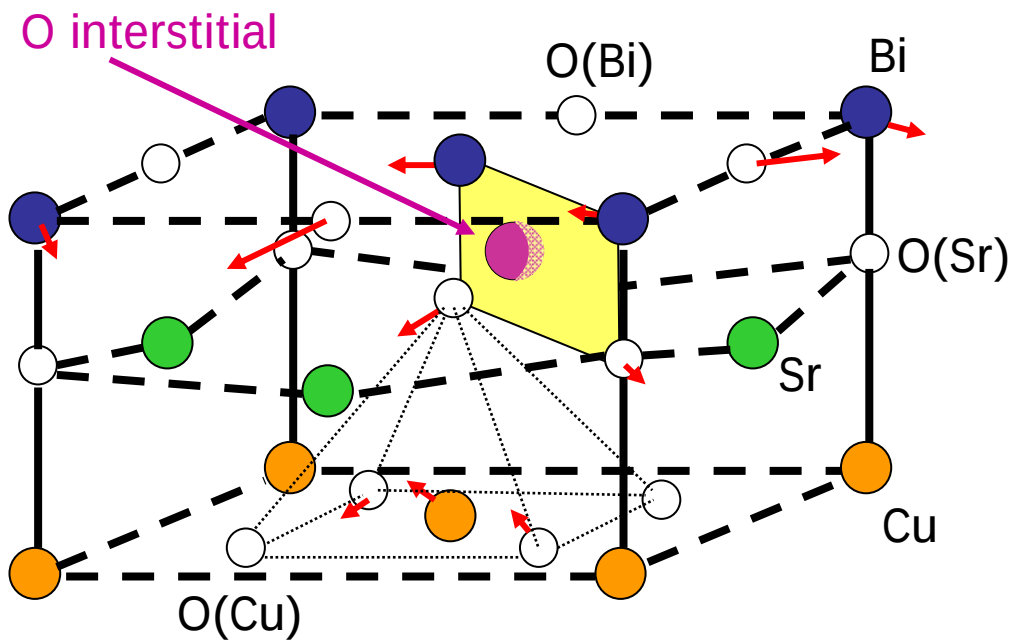
DFT calculations of O interstitials: structure

Calculations performed by Y. He and H-P Cheng, U. Florida

DFT good for calculations of high-energy (impurity) states, structure

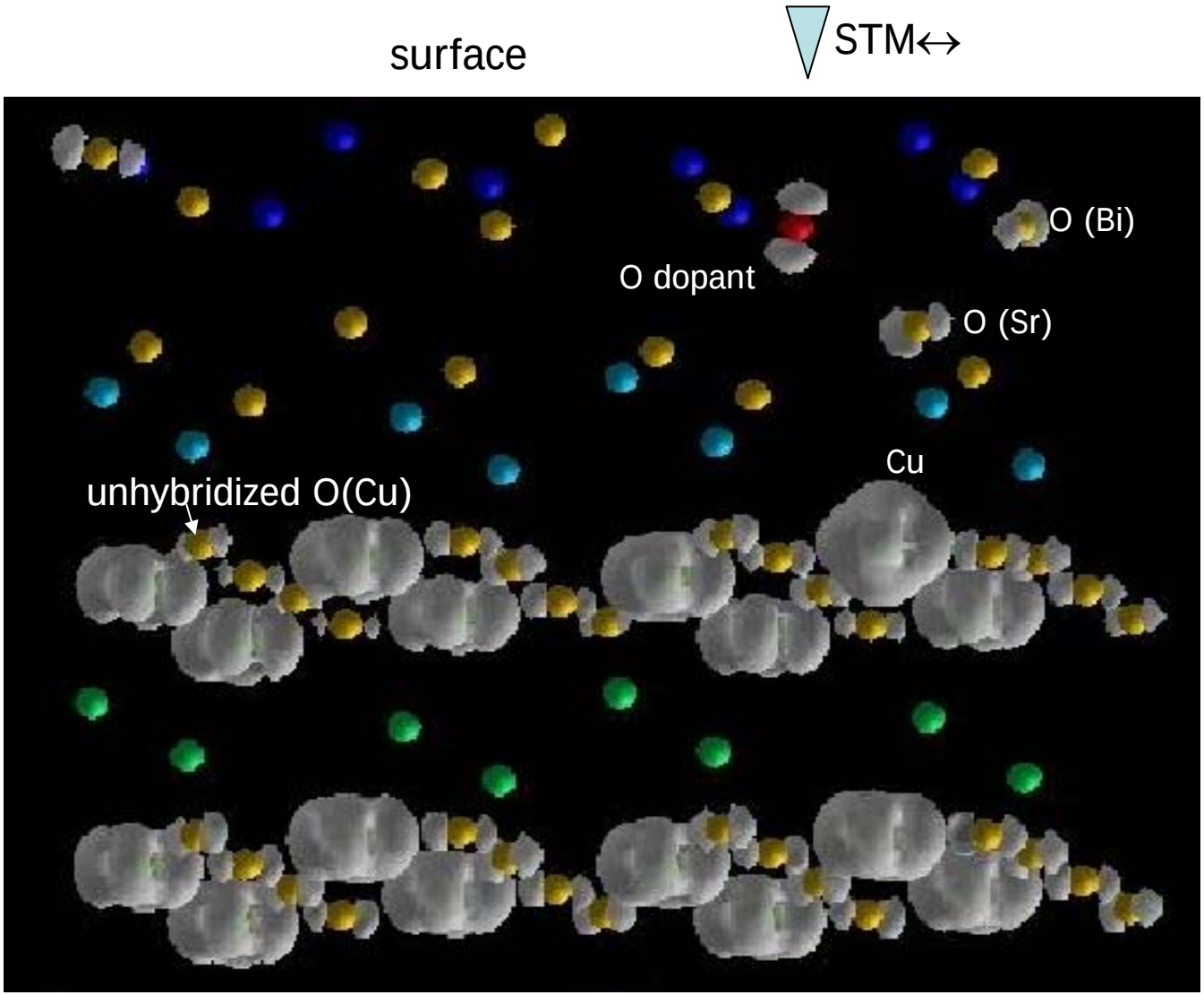
#	Location (Å)	Energy (eV)
1	1.09,1.09,-0.83	-6.560172
2	2.11,0.00,-0.38	-3.914803
3	2.59,0.00, -0.38	4.378865
4	2.59,0.00,-4.81	14.968390

Stable positions of O interstitial, energies relative to crystal w/o interstitial



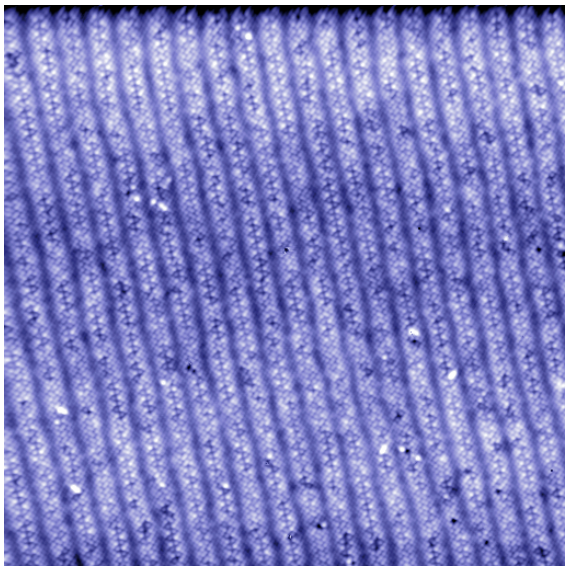
Interstitial creates unhybridized O $2p_z$ state at –1eV

$$\int_{-0.9eV}^{1.1eV} d\varepsilon\, \rho(\mathbf{r},\varepsilon)$$

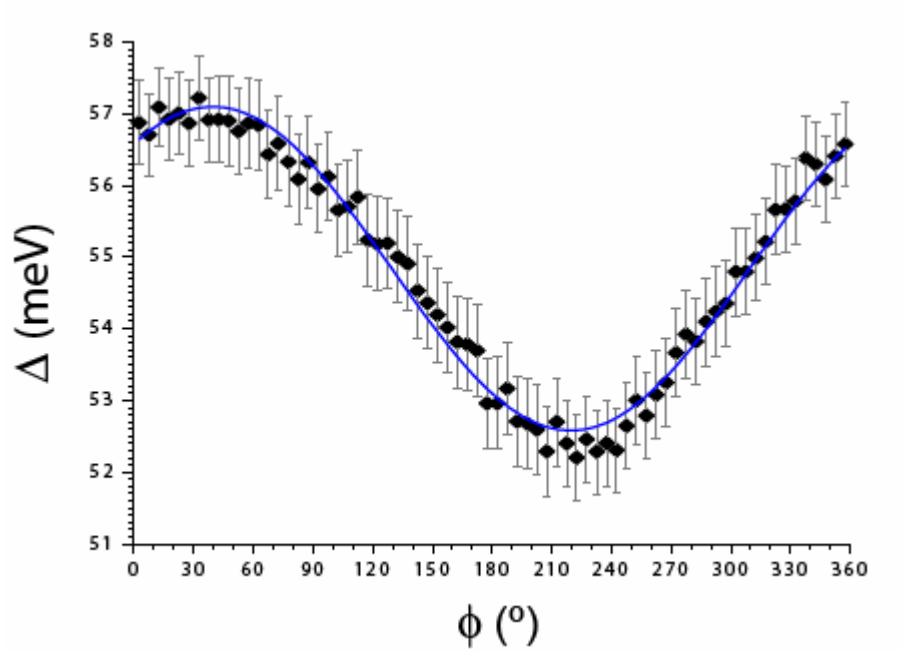


BSCCO "supermodulation" also correlates with gap (pairing?)

Bi-2212 topograph (Davis group)



BSCCO-2212 supermodulation correlates with gap (Slezak et al 07)

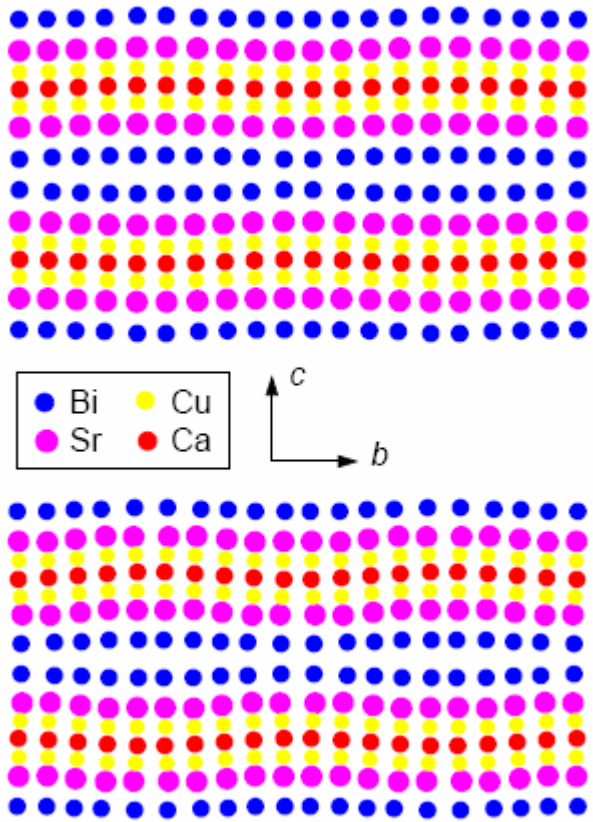


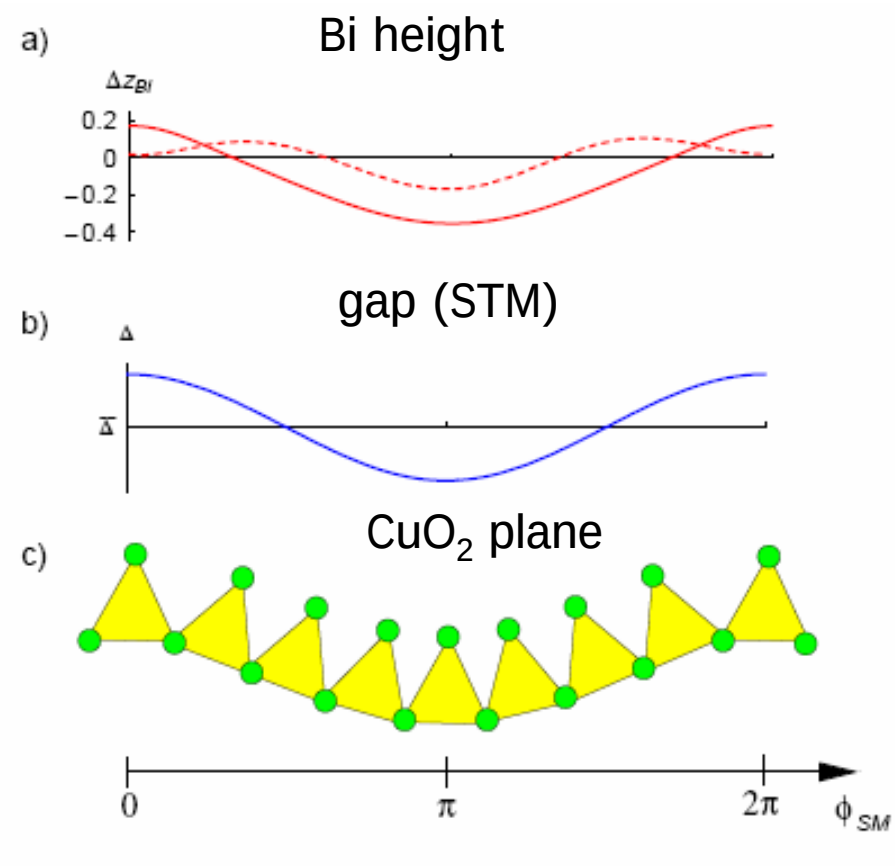
DFT calculations of supermod structure agree with x-ray data!

He et al arXiv:0709.0662

DFT

x-ray
(Levin etal
1994)



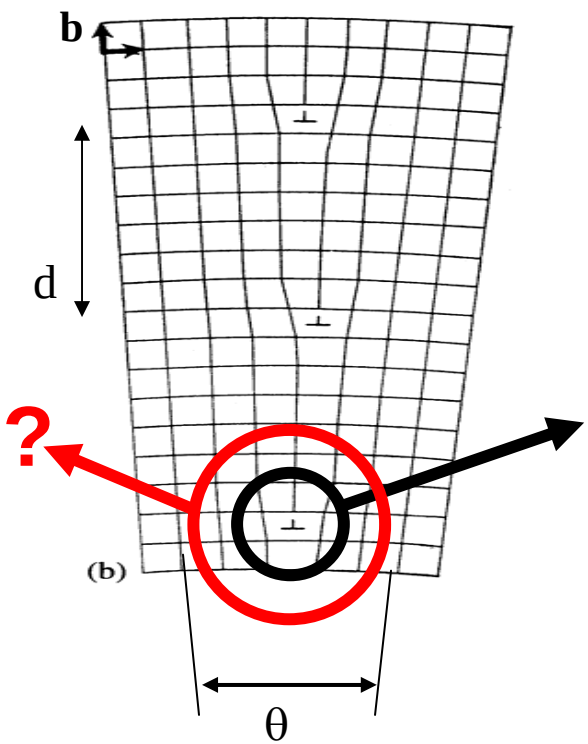


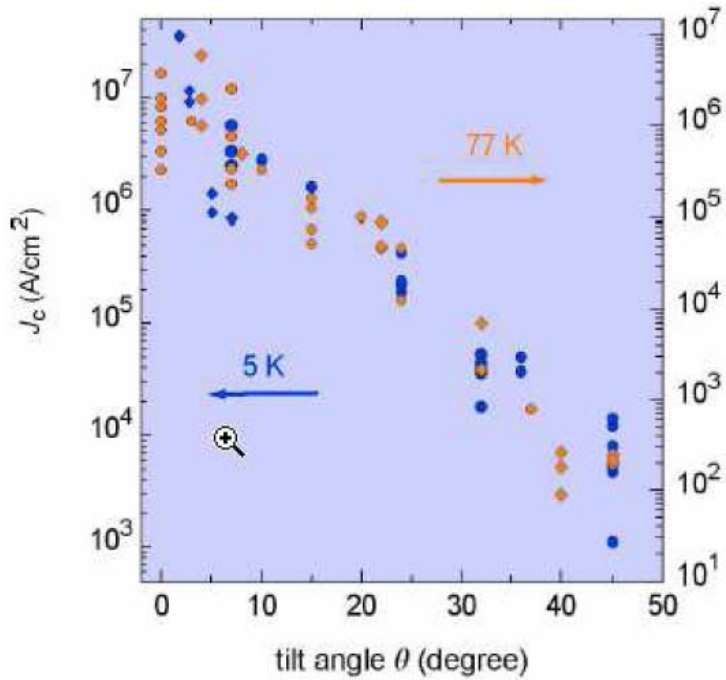
same displacement of apical oxygen sideways as in O defect case correlates positively with gap!

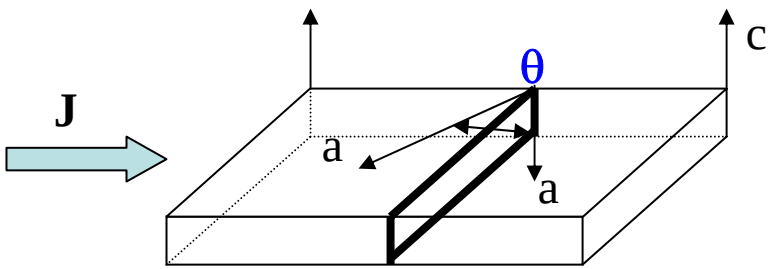
Combining "DFT+" and calculations of critical current to solve grain boundary problem?

D. Dimos, P. Chaudhari, J. Mannhart, PRB 41, 4038 (1990); R. Gross (1994); N.F. Heinig et al., APL, 69, 577 (1996)

$$J_c(\theta) = J_0 \exp(-\theta/\theta_0)$$





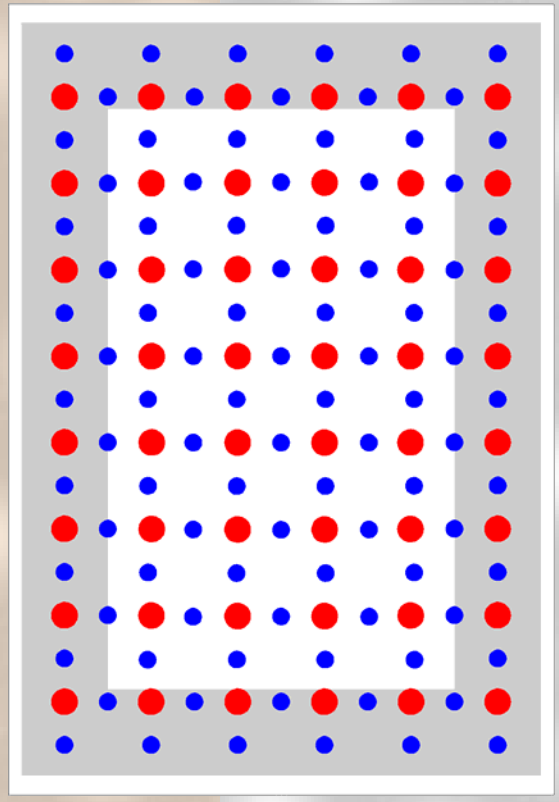


Conclusion – strong texture is needed!

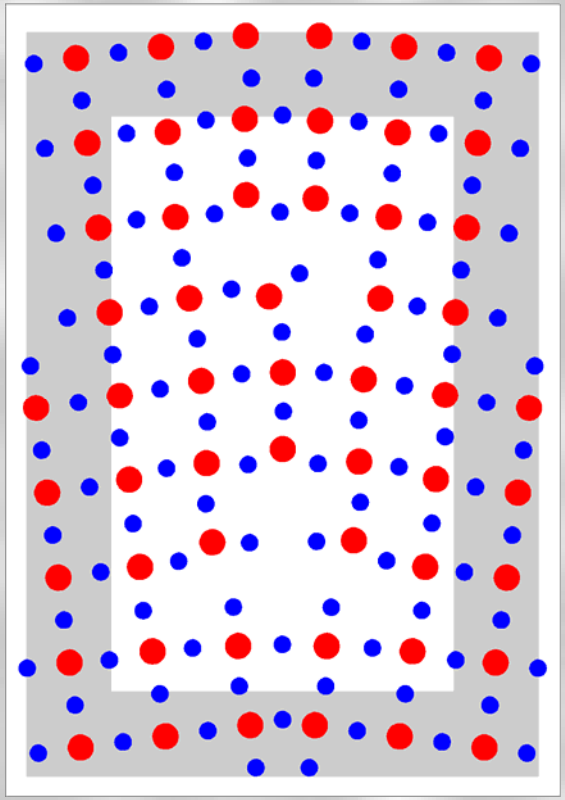
Approach in PH group: 1) reconstruct CuO_2 plane using MD simulation (à la Zhang and Catlow 1992)

Molecular dynamics approach

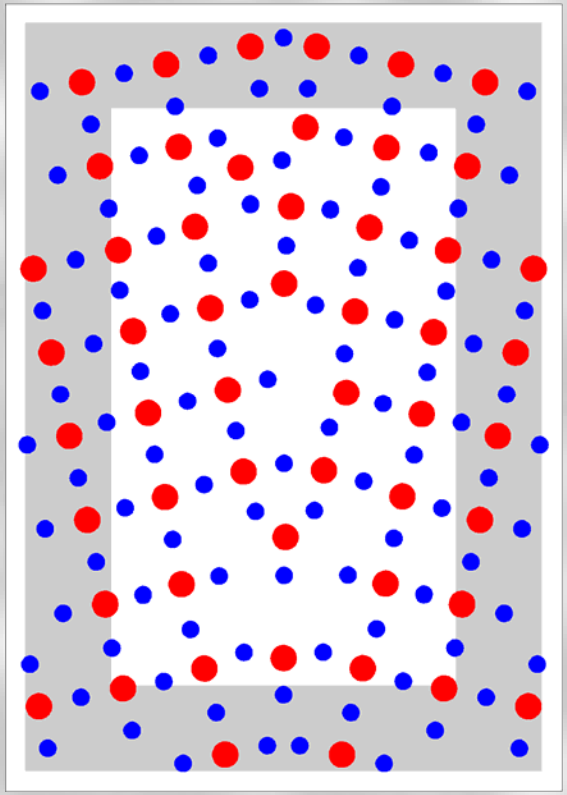
Final structures



0°

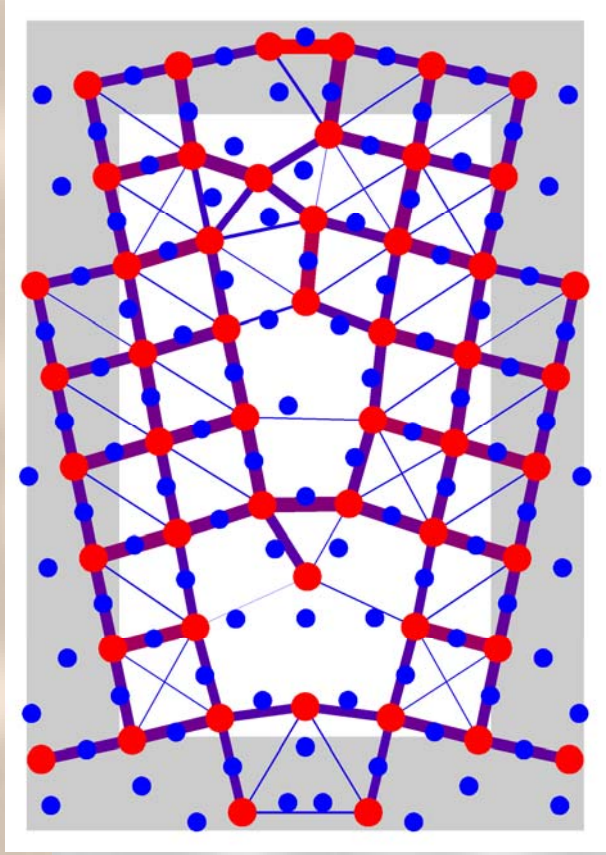


15°

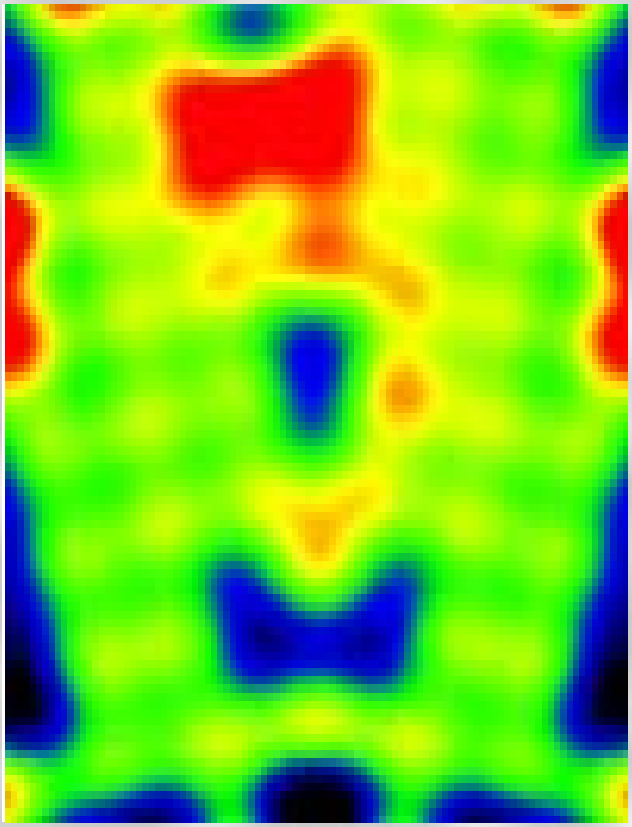


24°

2) Calculate hoppings in grain boundary via overlap of Cu 3d and O2p orbitals, include charging of defects



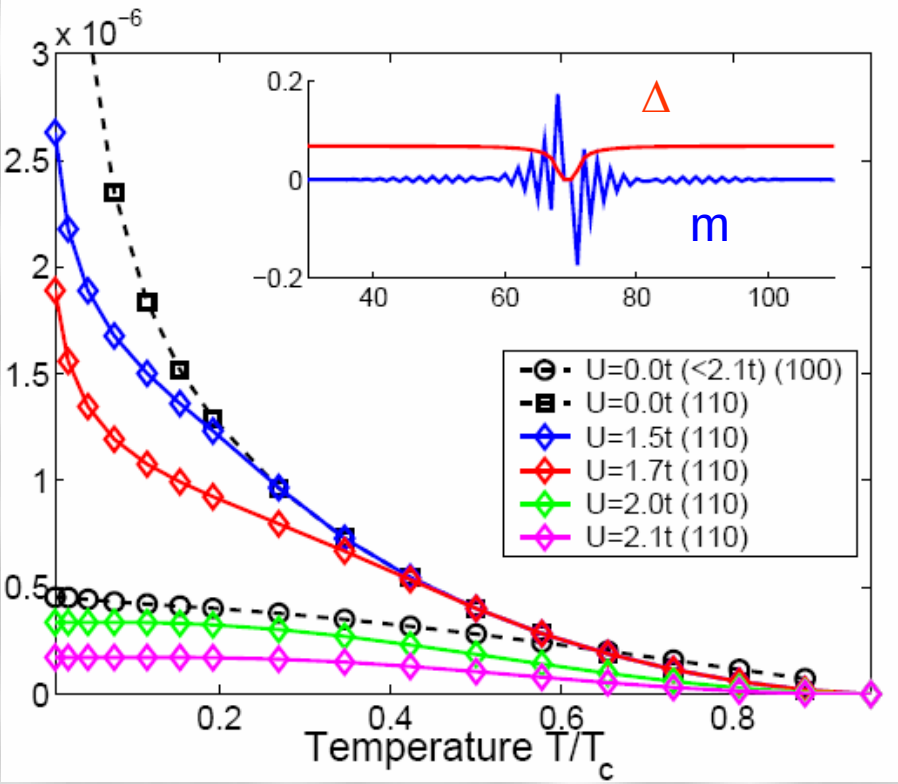
hopping map



charge density map

3) Use hopping and electrostatic potentials thus determined in Bogoliubov-de Gennes calculation of critical current $J_c(\theta)$ including d-wave order parameter and Hubbard U

110 junction with magnetic correlations in leads
(Andersen et al 2008)



Next: DFT+ calculations of grain boundaries ?

Conclusions

higher standard needed to make materials-specific predictions, to aid discovery or engineering of new, higher T_c compounds

- Most important theory and simulation problems remaining in HTS physics/materials science will require large-scale computers from here on

- Progress is being made in:

  - refining of electronic structure methods towards true *ab initio* method to study correlated systems (LDA+U, GW, CDMFT...)

  - calculating pairing interactions accurately within effective models

  - downfolding electronic structure to determine parameters of effective models

  - understanding and using data on inhomogeneity to study pairing