China/US Joint Winter School &
3rd China/US Workshop on Novel Superconductors

19 – 27 January 2013

University of Hong Kong

A Density-Functional Study of the Electronic and Magnetic Properties of Tetragonal Copper Monoxide as a Proxy for High Temperature Superconductivity

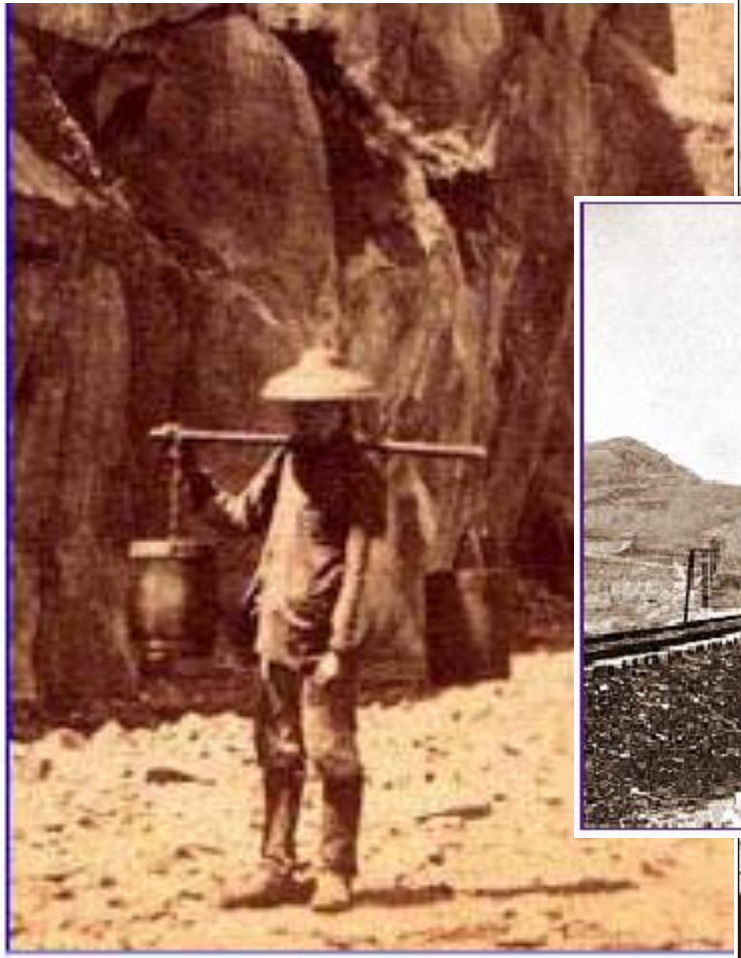
Paul M. Grant
W2AGZ Technologies
www.w2agz.com

AGING IBM PENSIONER

~ 10,000 years

“China/US Joint...”

~ 1,000 years




10 MILES
OF
TRACK, LAID
IN ONE DAY.
APRIL 28TH 1869

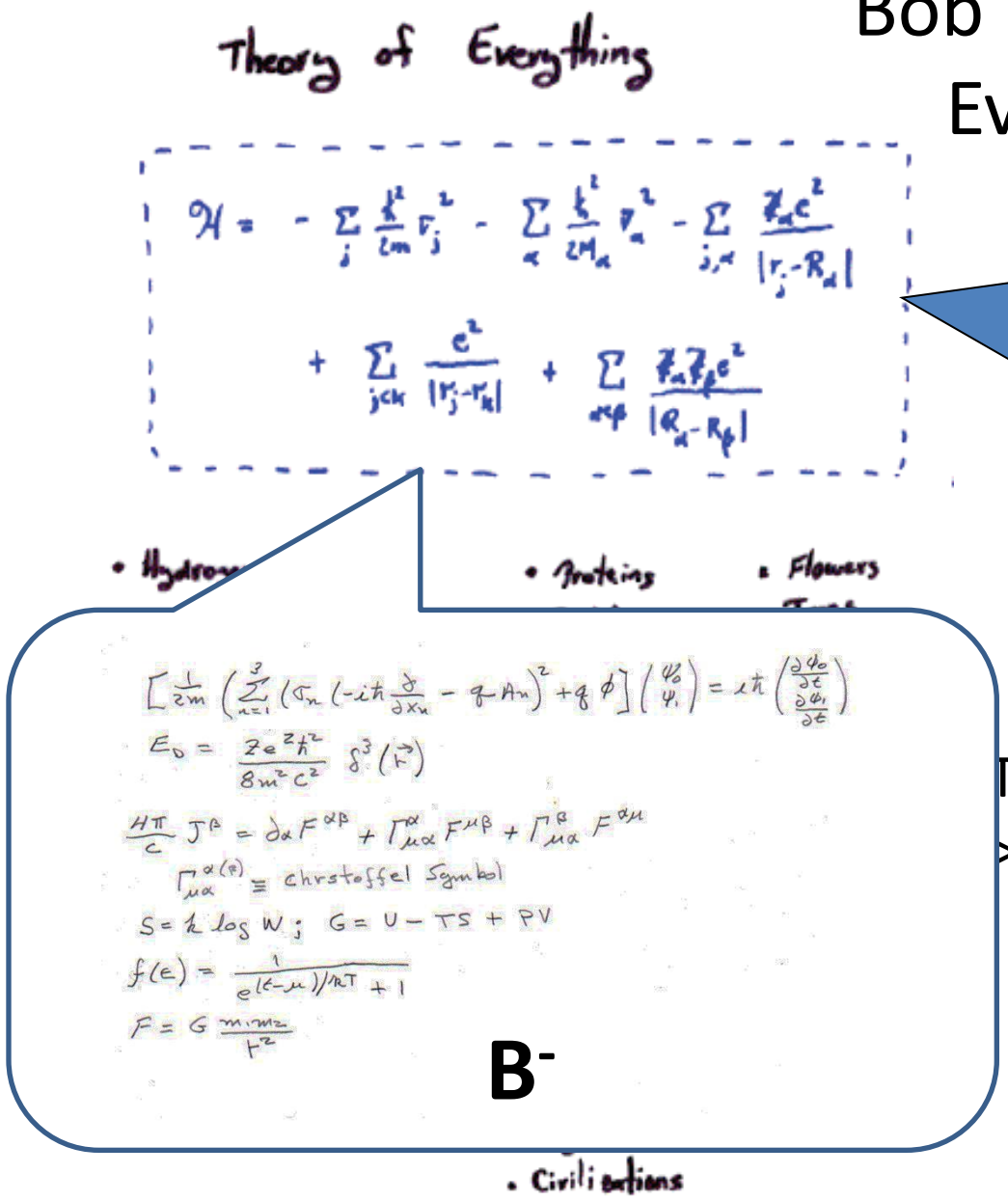
Zhu Jingwu

Yao Ming

Now Let’s Get Started!

Tools

Bob Laughlin's "Theory of Everything" (that matters)



Where's spin, Pauli and Darwin? Ya screwed up, Bob!
Oh yeah, how about Maxwell, Boltzmann, Gibbs, Fermi,…and finally, Newton's Apple.

The crunch comes when Σ_i with i >= 3 -> "thermodynamic limit."

"Van Vleck Catastrophe (1936)"

"Size Matters !"

Extended Hubbard Hamiltonian

Qualitative Description of the Physical Properties of Antiferromagnetic Insulators

$$H = \sum_{\langle ij \rangle,\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} n_{i\downarrow} n_{i\uparrow} + \frac{V}{2} \sum_{\langle ij \rangle,\sigma,s} n_{i\sigma} n_{js}$$

One-electron "band" term

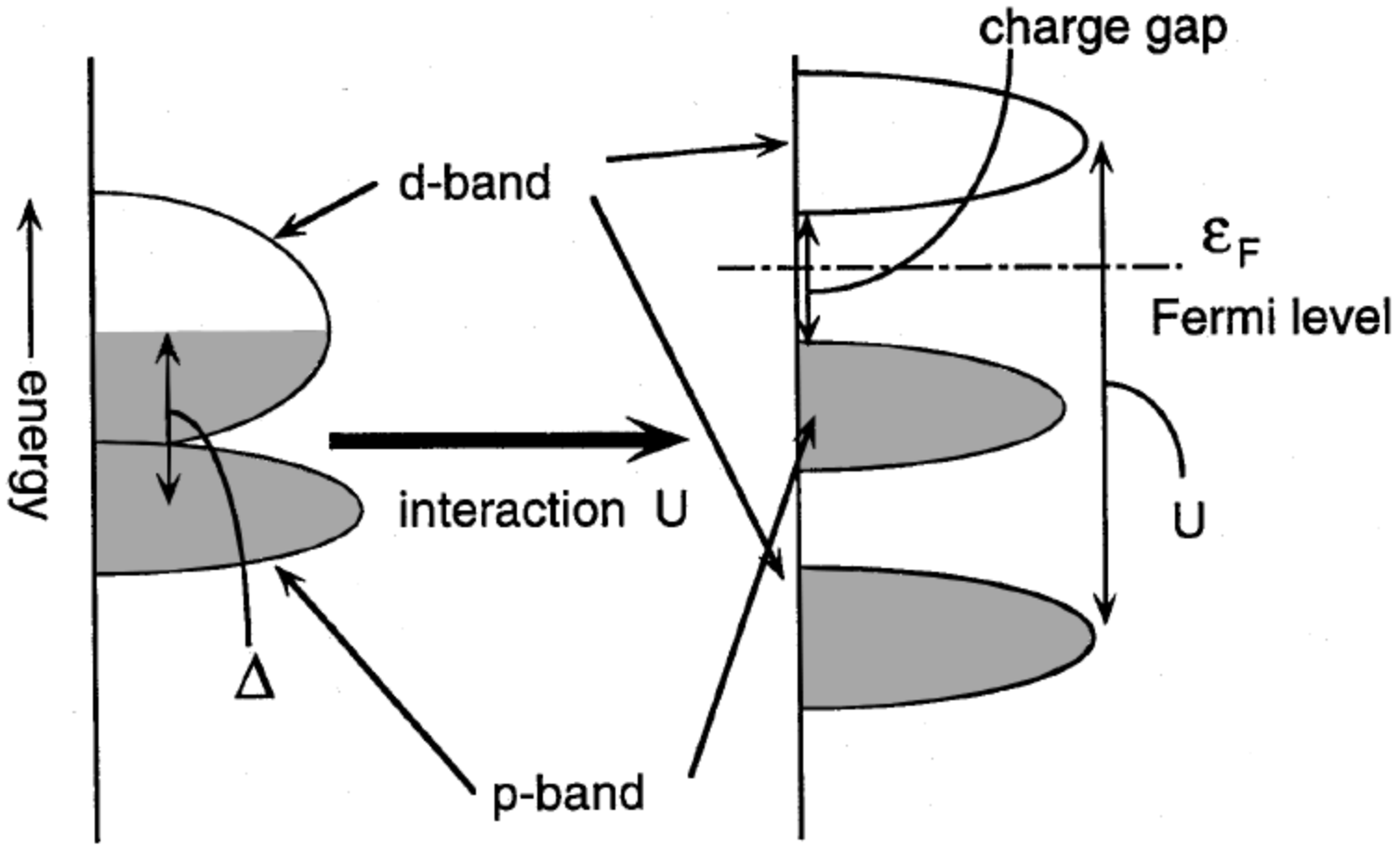
On-site "Hubbard" double occupation coulomb repulsion

Off-site repulsion

$$kT_N \approx 4t^2 / S^2 U$$

More Later!

Charge Transfer Insulator



After Imada, et al, RMP 70, 1039 (1998)

Density Functional Theory
Hohenberg – Kohn (NP Chemistry, 1998)

Kohn-Sham Equations (~1965)

$$(T + \hat{V} + V_H(n) + V_{xc}(n))\psi_i = \epsilon_i \psi_i$$

with charge density $n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$, i = combined $\mathbf{k}$ and band index,

f_i = occupancy of states, and orthonormality constraints $\langle \psi_i | \psi_j \rangle = \delta_{ij}$

Now minimize self-consistently:

$$E[\{\psi_i\}] = \sum_i f_i \langle \psi_i | T + \hat{V} | \psi_i \rangle + E_H + E_{xc}(n) + E_{ion-ion}$$

obtaining:

$$E = \sum f_i \langle \psi_i | T + \hat{V} | \psi_i \rangle + E_H + E_{xc}[n] + E_{ion-ion}$$

Looking into the future I expect that wavefunction-based and density-based theories will, in complementary ways, continue not only to give us quantitatively more accurate results, but also contribute to a better physical/chemical understanding of the electronic structure of matter. ***W. Kohn***

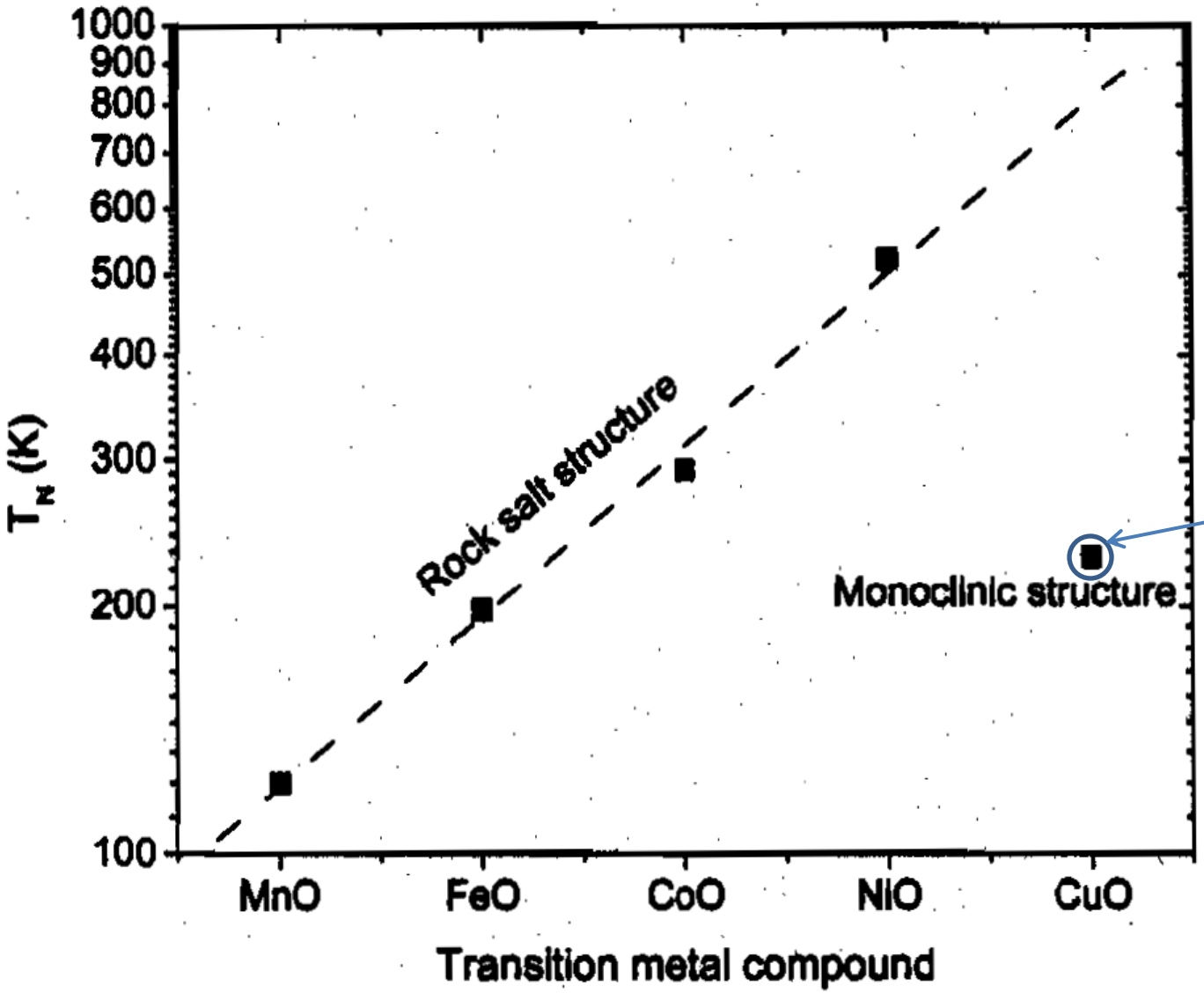
DFT & (LDA + U)

$$E_{\mathrm{LDA+U}}\left[n(\mathbf{r})\right] = E_{\mathrm{LDA}}\left[n(\mathbf{r})\right] + E_{\mathrm{HUB}}\left[\left\{n_m^{l\sigma}\right\}\right] - E_{\mathrm{DC}}\left[\left\{n^{l\sigma}\right\}\right]$$

- Implemented in LMTO by Anisimov, et al, JPCM 2, 3973 (1990)
  - Applied to rock salt NiO, MnO, FeO, CoO
- Plane-Wave Pseudopotential Implementation by Cococcioni and de Gironcoli, PRB 71, 035105 (2005)
  - Applied to rock salt FeO and NiO
- *But where is rock salt copper monoxide, CuO?*

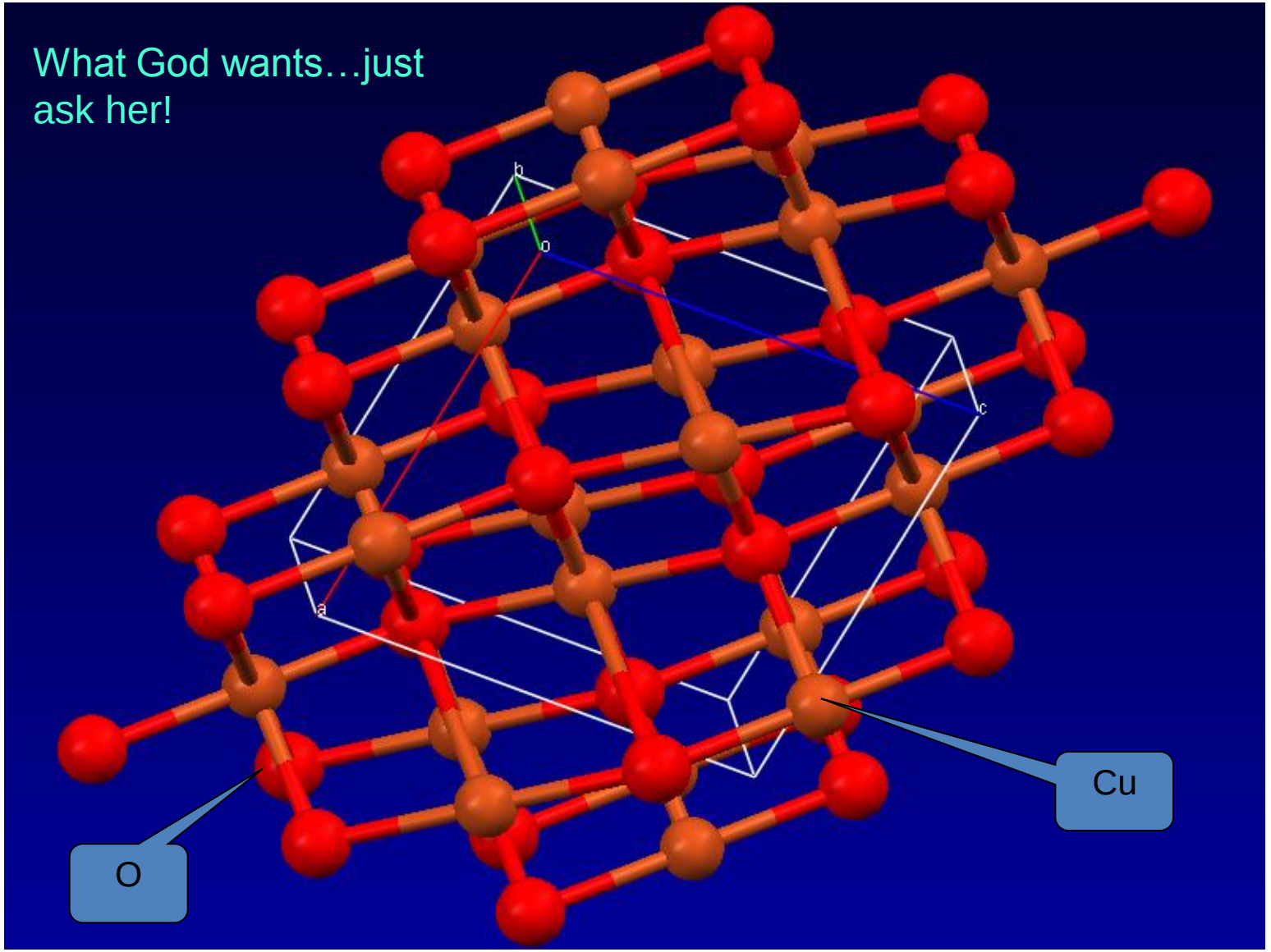
Copper Monoxide

Néel Temperature vs. TMO Atomic Number

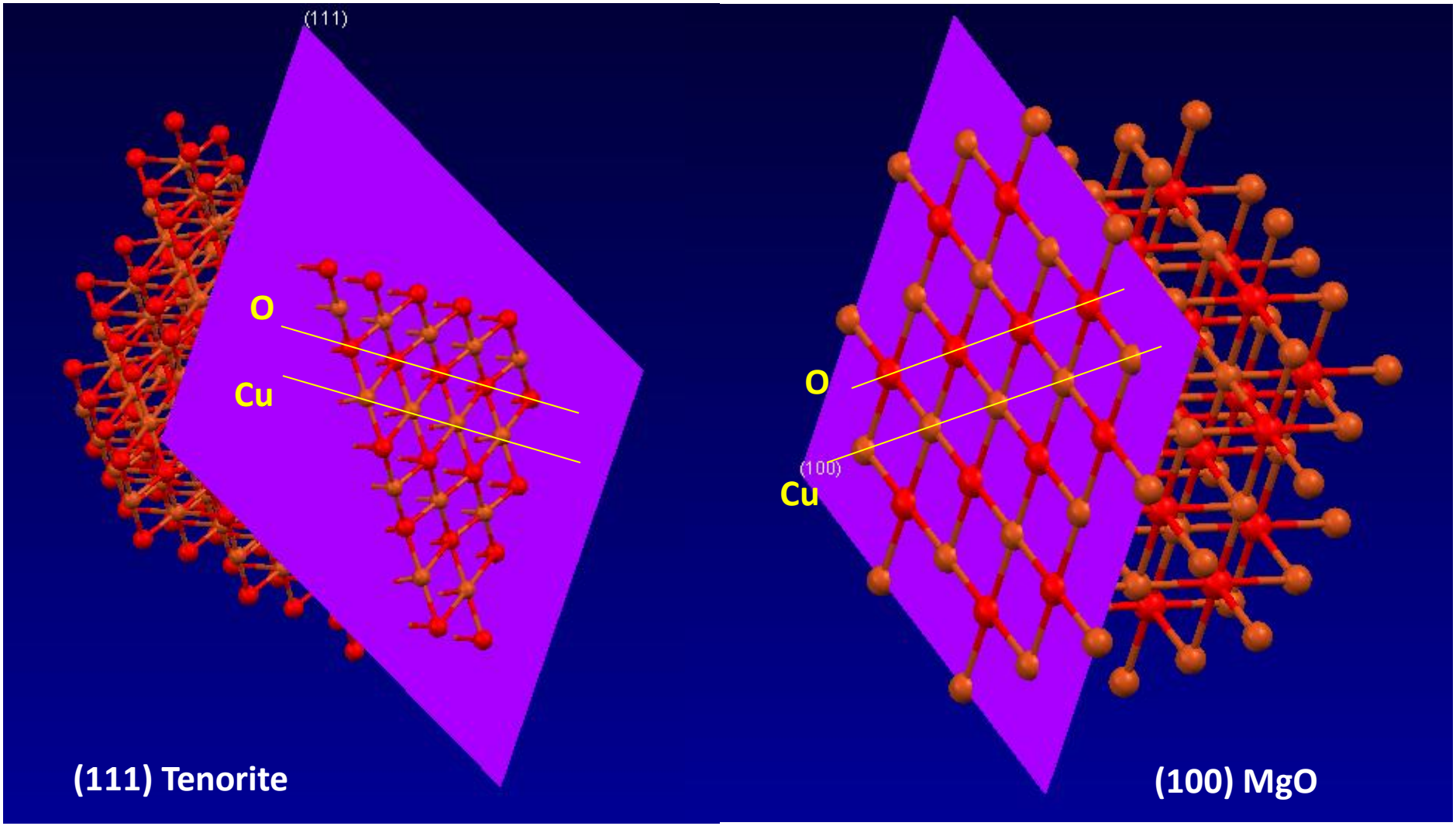


"Tenorite"
~225 K

Tenorite (Monoclinic CuO)



Comparison of Tenorite (111) to CuO – MgO Proxy (100)

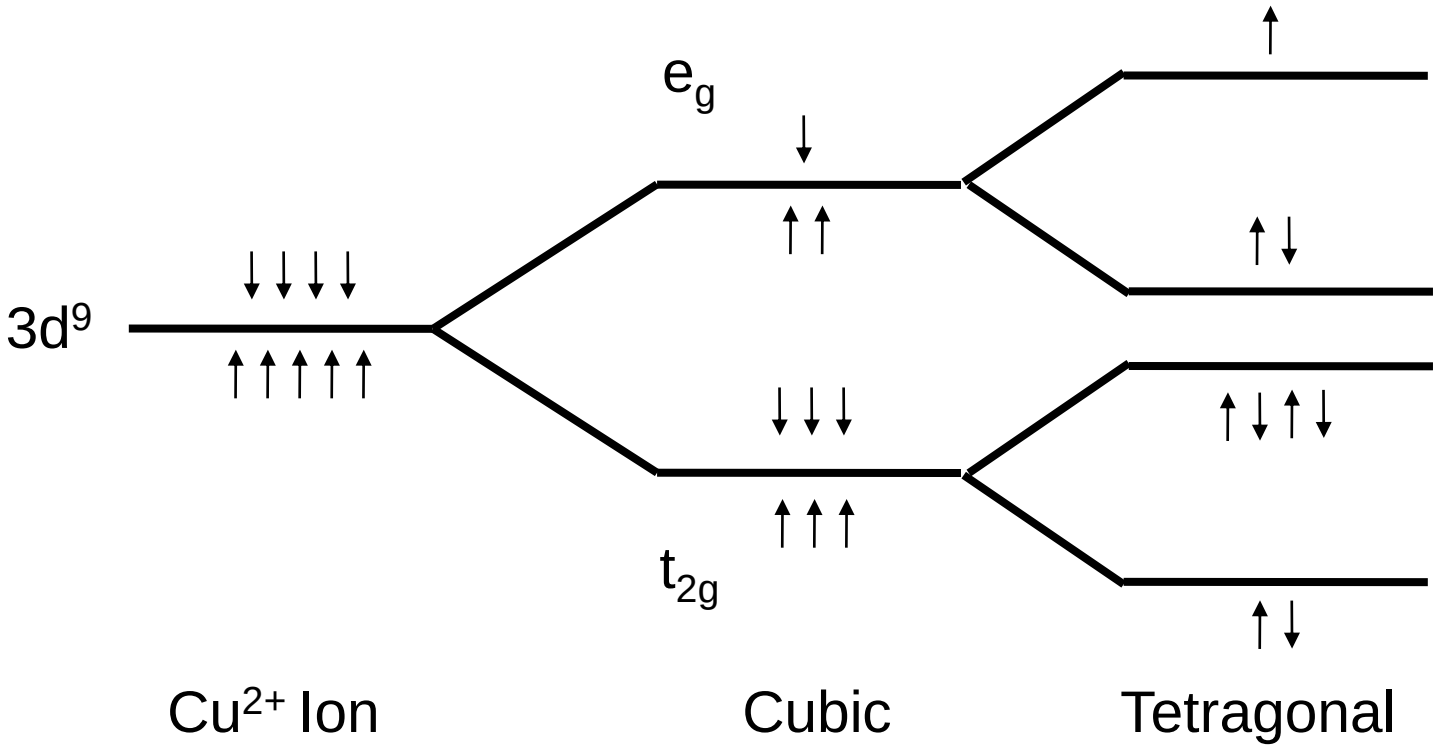


Anthologies (CuO rs/tet fsc)

- Experimental
  - Siemons:
    - *"Tetragonal CuO: End Member of the 3d Transition Monoxides,"* Siemons, et al., PRB **79**, 195122 (2009).
- Computational
  - Grant:
    - *"Electronic Properties of Rocksalt Copper Monoxide: A Proxy Structure for High Temperature Superconductivity,"* Grant, JOP:CS **129**, 012042 (2008).
  - Franchini:
    - *"Hybrid Density-Functional Calculations of the Electronic and Magnetic Structure of Tetragonal CuO,"* Chen, et al., PRB **80**, 094527 (2009).
    - *"Thickness Dependent Structural and Electronic Properties of CuO Grown on $SrTiO_3$(100): A Hybrid Density Functional Theory Study,"* Francini, et al., JOP:CM 23, 045004 (2011).
  - Cococcioni:
    - *"First Principles Study of Electronic and Structural Properties of CuO,"* Himmetoglu, et al., arXiv:1107:4399v1 (2011).
      (This is a great paper...see Acknowledgements...and estimate of T_N)
- What's Next?:
  - Geballe:
    - "Optimal T_C of Cuprates: The Role of Screening and Reservoir Layers," Raghu, et al., PRB 86, 094506 (2012).

      (I suspect this model/assertion may be "DFT testable")

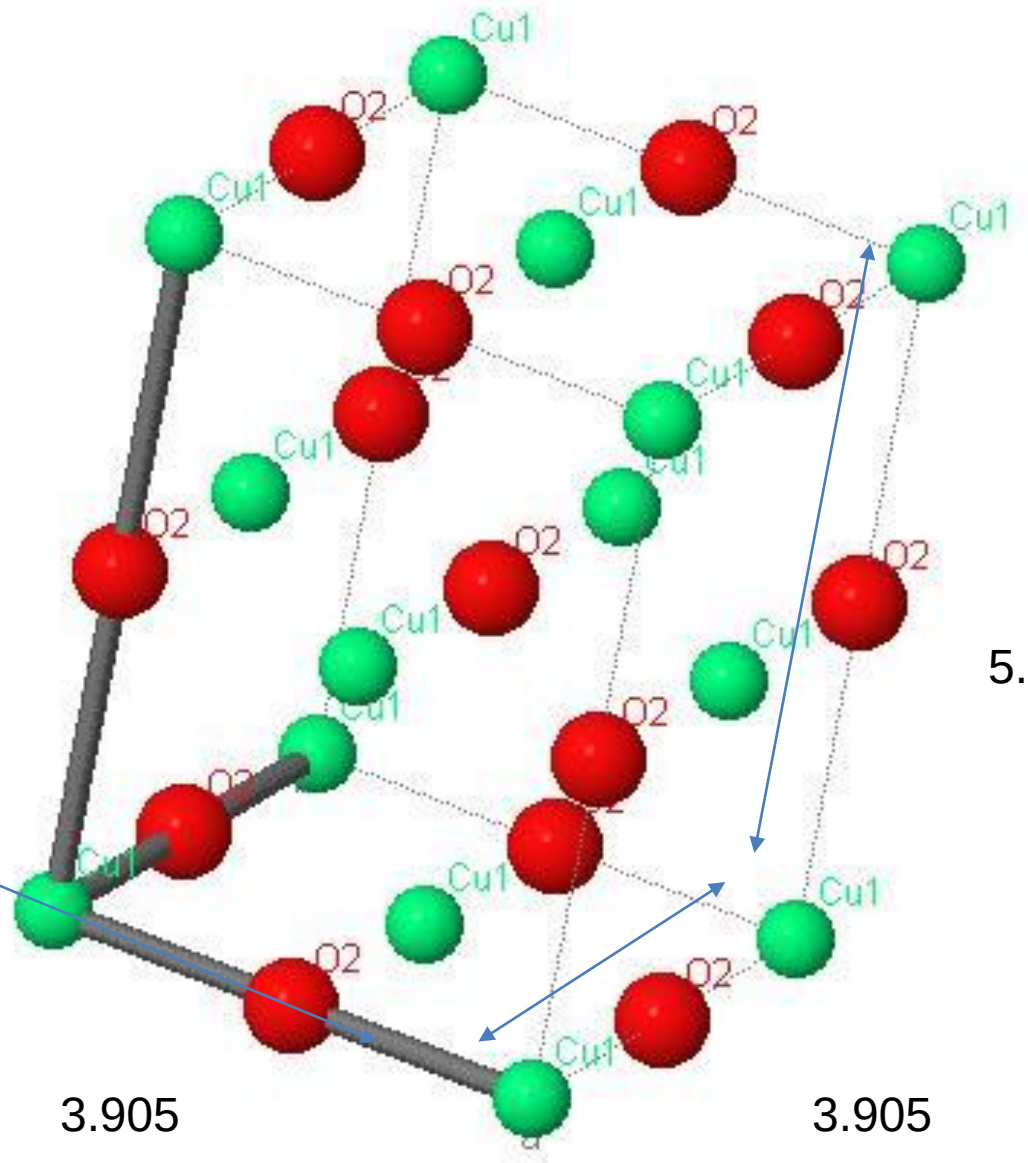
Cu2+ 3d Multiplet Splitting (Tetra)



Tetragonal CuO

Fm-3m
a=3.905Å
b=3.905Å
c=5.320Å
α=90.0°
β=90.0°
γ=90.0°

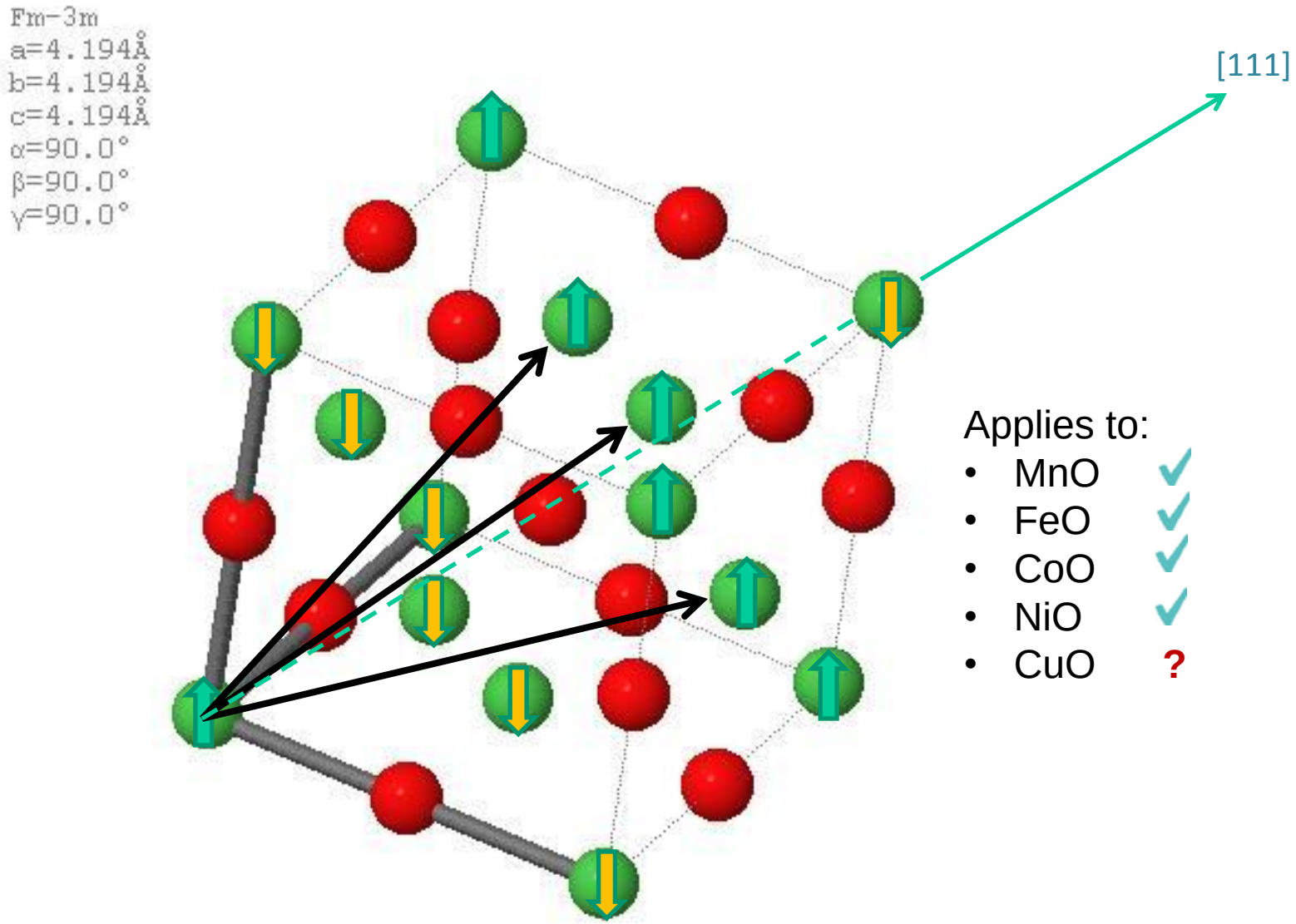
c/a = 1.36



Measurements (Wolter Siemons)

- 2-4 ML epi on STO
- No Fermi Edge
- No Exchange Bias on ferro-SRO (Tc ~ 100-150 K)

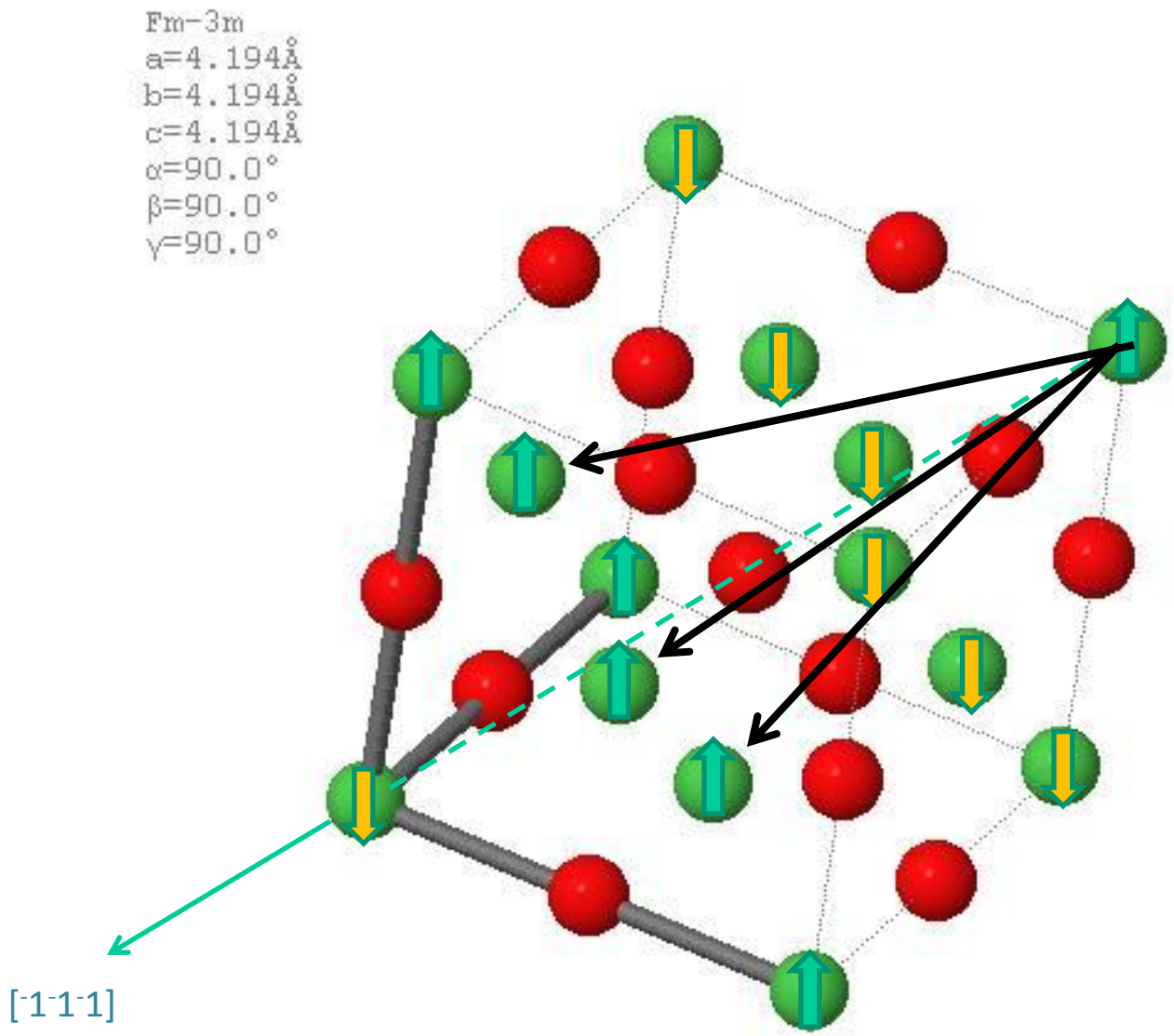
Proto-TMO AF-II Rocksalt Unit Cell



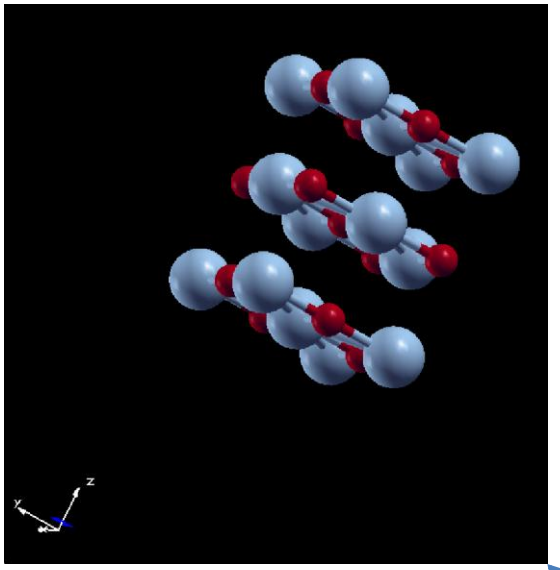
Applies to:

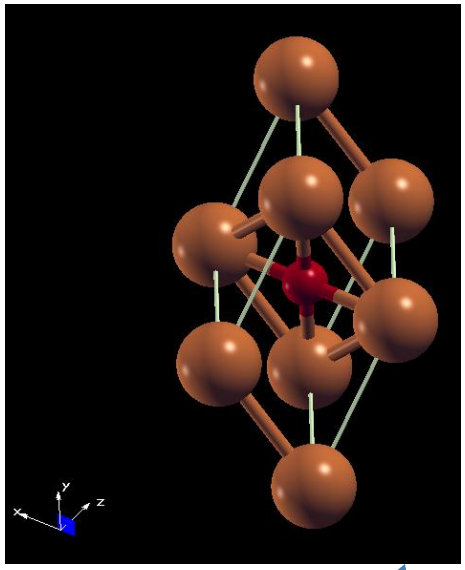
- MnO ✓
- FeO ✓
- CoO ✓
- NiO ✓
- CuO ?

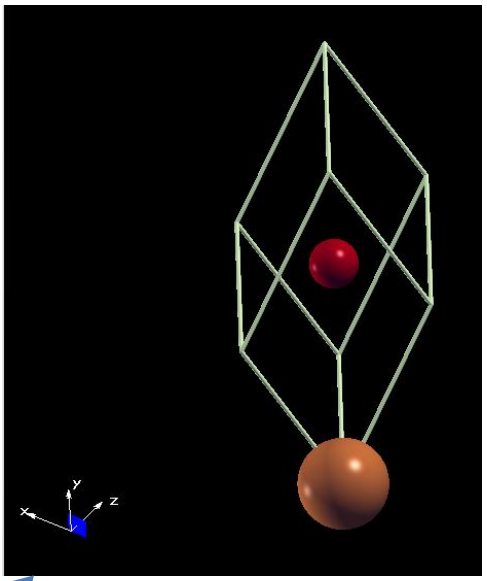
Proto-TMO AF-II Rocksalt

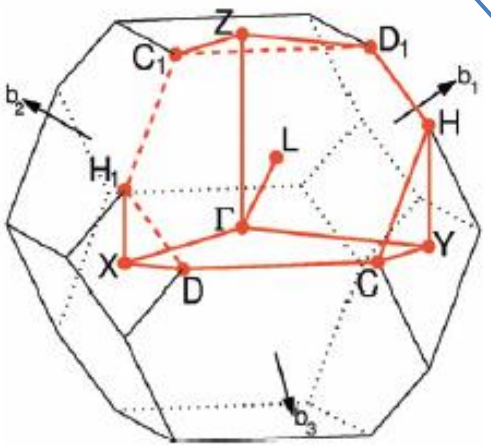


“Zone-ology” of “nm_Tet-CuO”









Conventional lattice
$\mathbf{a}_1 = (a, 0, 0)$
$\mathbf{a}_2 = (0, b, 0)$
$\mathbf{a}_3 = (0, 0, c)$

Primitive lattice
$\mathbf{a}_1 = (0, b/2, c/2)$
$\mathbf{a}_2 = (a/2, 0, c/2)$
$\mathbf{a}_3 = (a/2, b/2, 0)$

Actually, “Tet-CuO” is really “Ortho-fcc CuO” with a = b

oh...btw...the red balls are O

Fig. 10. Brillouin zone of $ORCF_2$ lattice. Path: Γ–Y–C–D–X–Γ–Z–D_1–H–$C|C_1$–$Z|X$–$H_1|H$–$Y|L$–Γ. An example of band structure using this path is given in Fig. 34.

W. Setyawan, S. Curtarolo / Computational Materials Science 49 (2010) 299–312

So...

Let's "Shut up and start calculating."

- David Mermin, Cornell, as quoted by yours truly, (Nature 4 August 2011)

Tools

QUANTUM-ESPRESSO Suite of Codes

DFT (LDA+U) plus electron-phonon

Graphics by Tone Kolalj (XCrysDen)

www.quantum-espresso.org

"Dial-in" Parameters

$G^2 = 40$ Ry $\rho = 320$ Ry

Convergence $\leq 10^{-6}$ Ry

"Smearing" = Methfessel-Paxton

Psuedopotentials: Ultrasoft, XC = Perdew-Zunger

Cu: $3d^9 4s^2$ O: $2s^2 2p^4$

Hardware

3.33 GHz Intel Core i7 – 12 GB+

Tetragonal Rocksalt CuO

Fm-3m
a=3.905Å
b=3.905Å
c=5.320Å
α=90.0°
β=90.0°
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Measurements (Wolter Siemons)

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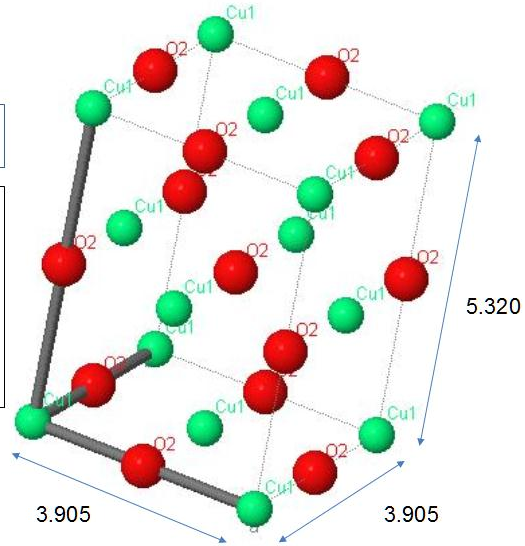
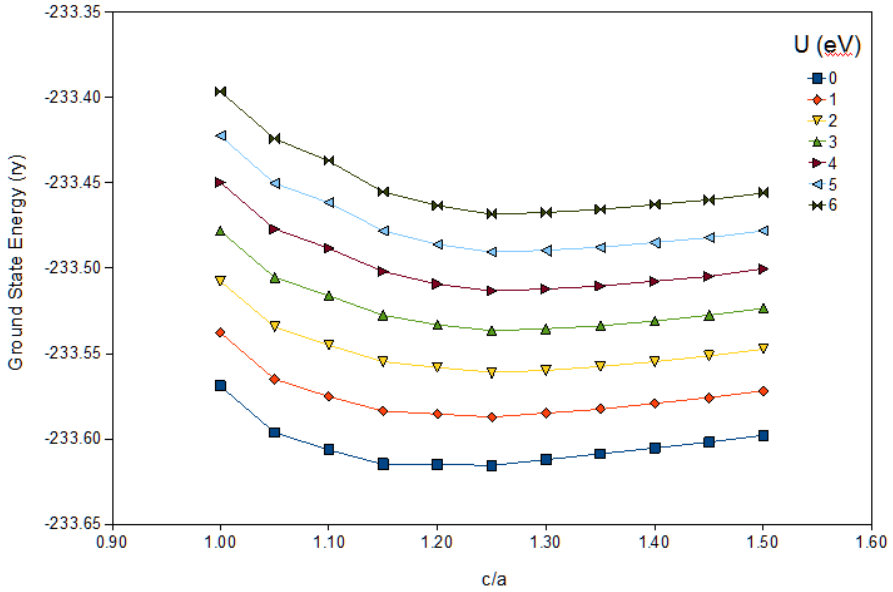
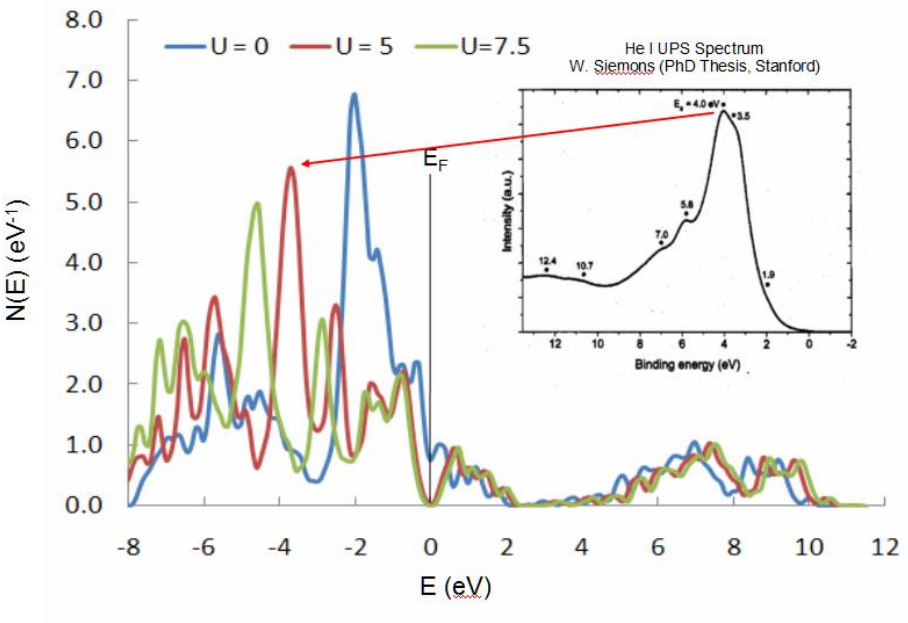


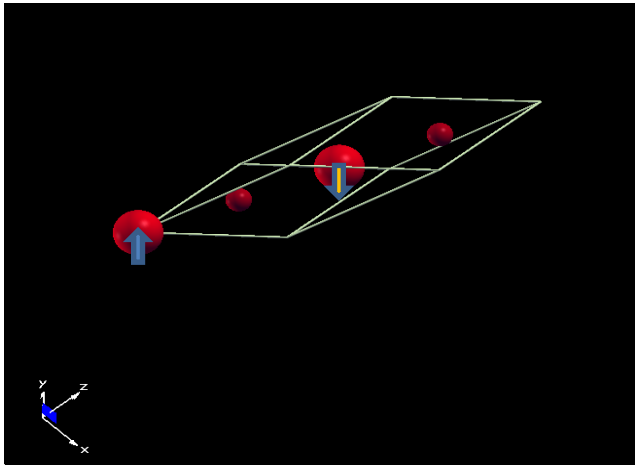
Ground State Energy vs c/a & U(ev)



t-CuO Density-of-States



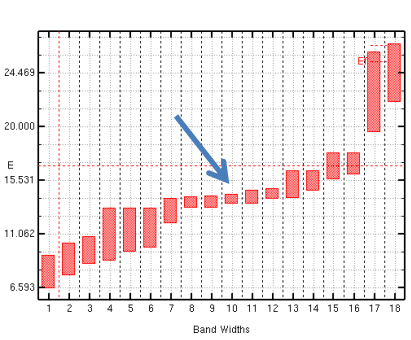
First Efforts

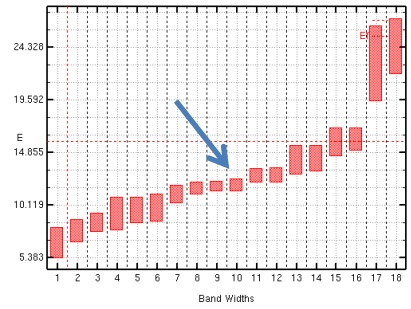


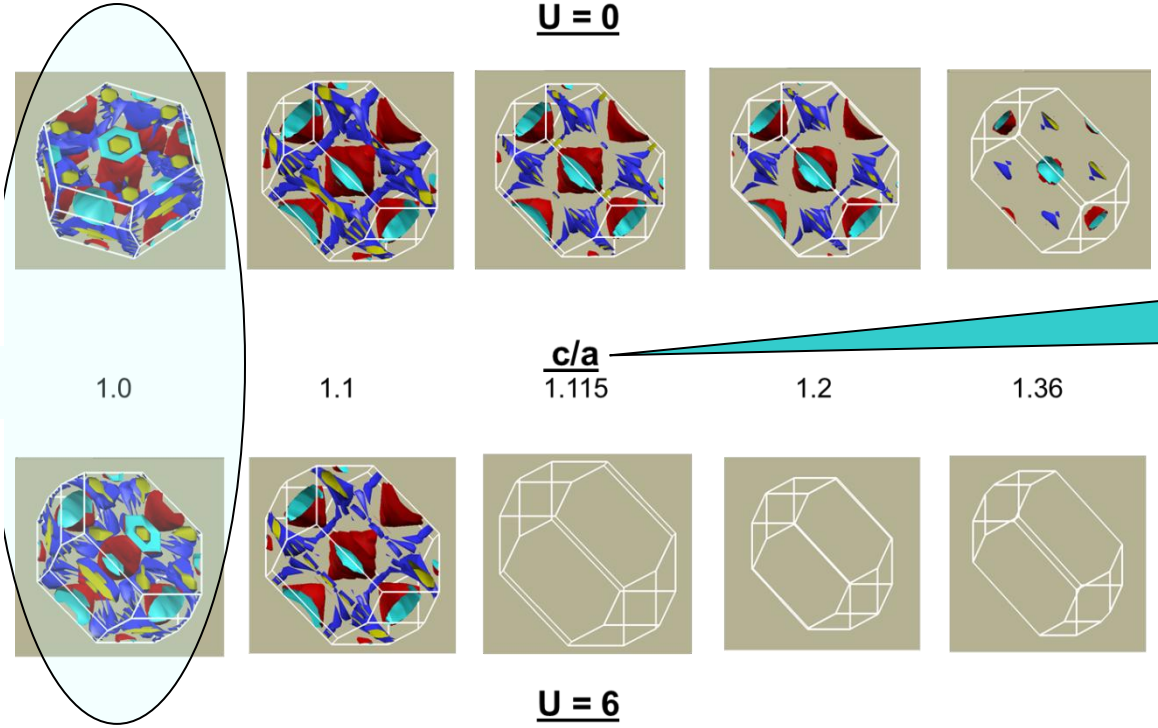
TMO Asymmetric Type II
af-CuO Cell

LDA+U Calcs

Grant, IOP-CS 129 (2008) 102042
(Click Here)



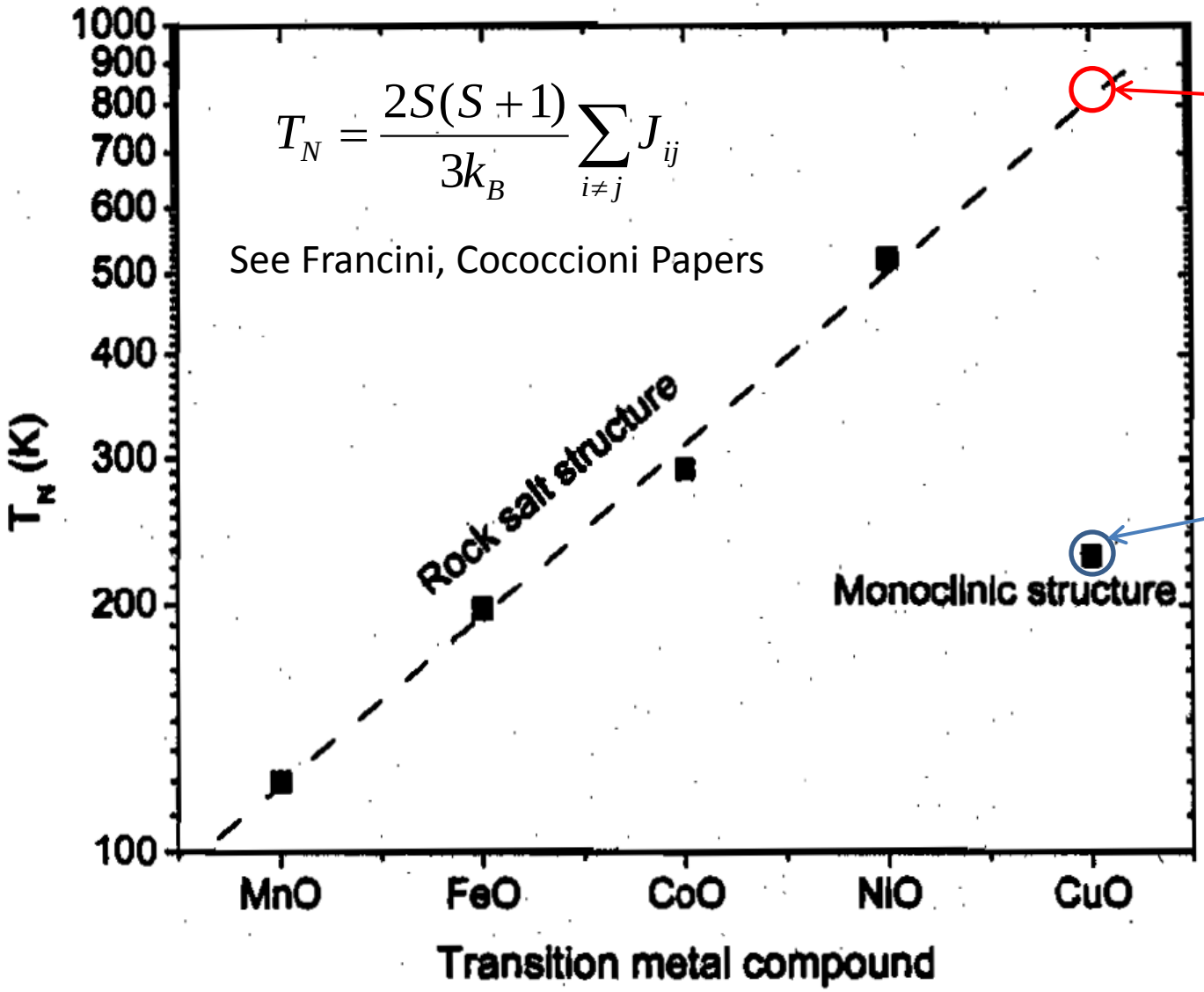




Tetragonal Distortion

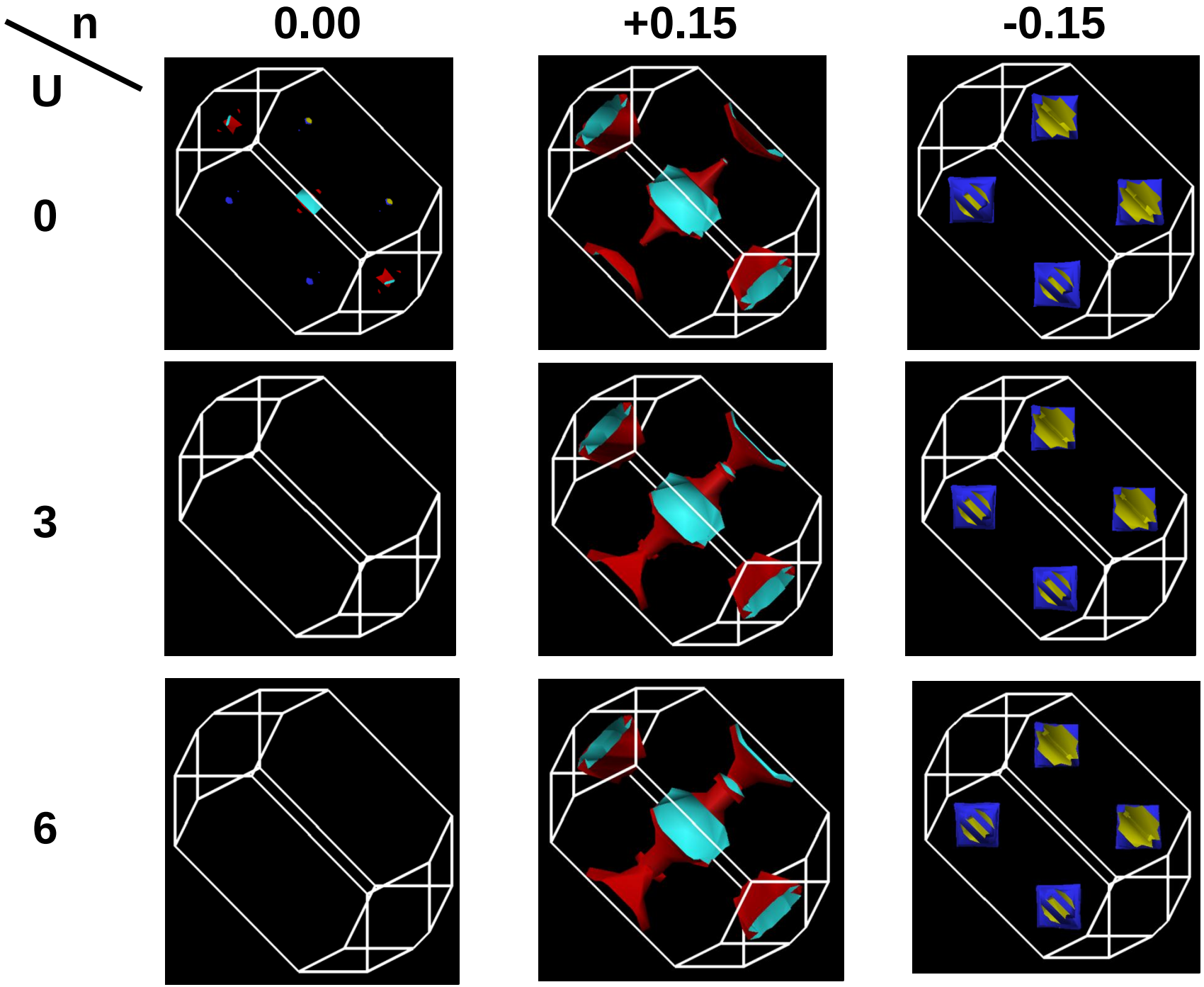
Siemons, et al, PRB 79 (2009) 195122
(Click Here)

Néel Temperature vs. TMO Atomic Number



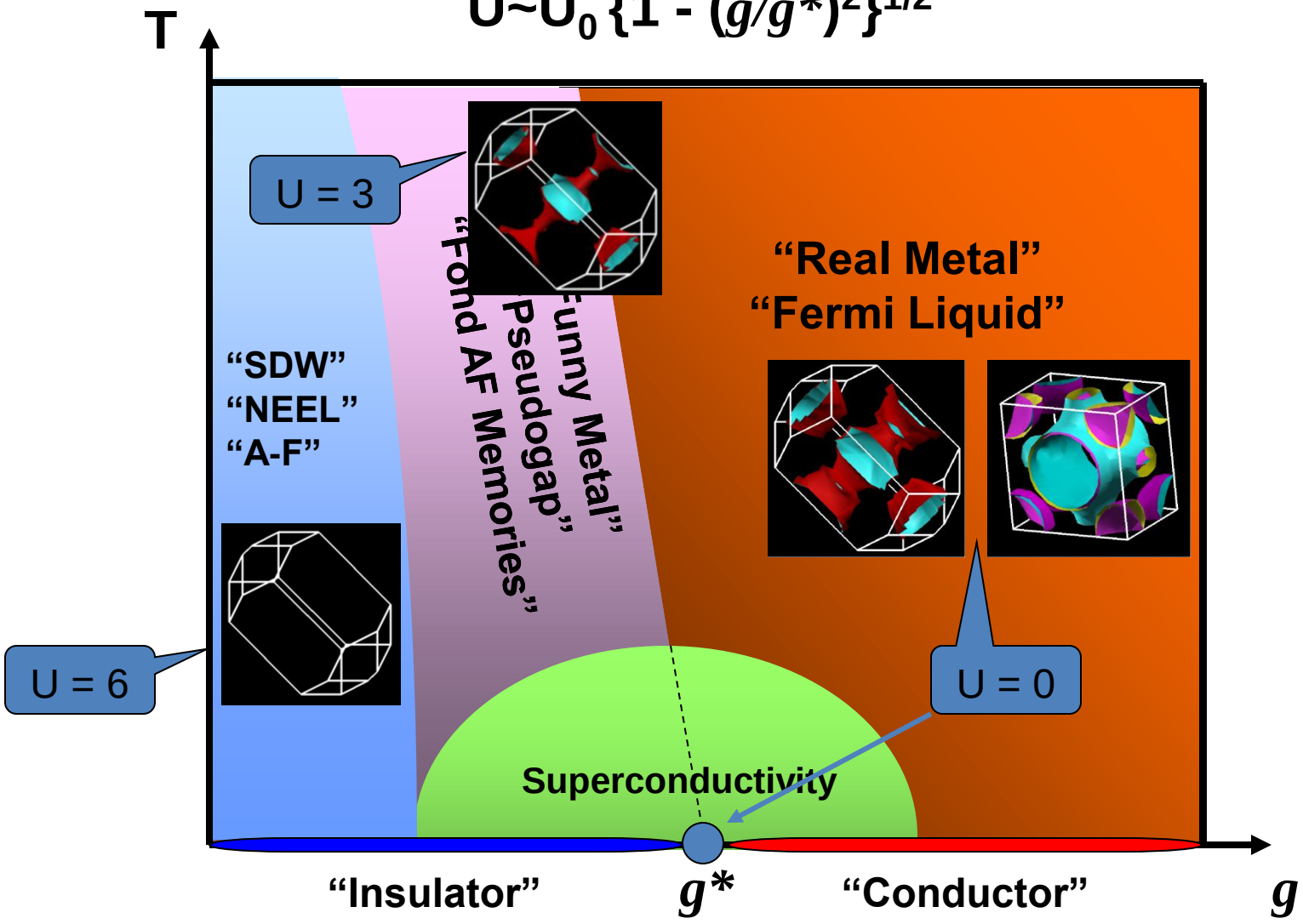
"Face-Centered, Rock Salt CuO" ~850 K (wow!)

"Tenorite" ~225 K


n
U
0.00
+0.15
-0.15
0
3
6

The Colossal Quantum Conundrum

$$U \sim U_0 \{1 - (g/g^*)^2\}^{1/2}$$



Somewhere in here there has to be "BCS-like" pairing!

Shakes or Spins or Both?

Are They Copacetic, Competitive…or…

…just another Conundrum?

What formalism is the HTSC analogy to Migdal-Eliashberg-McMillan?

(In other words, how do I calculate the value of the BCS gap?)

- Original Strong Coupling, Eliashberg *(JETP, 1960), McMillan (PR, 1968)*
- Generalized Linhard Response Function (RPA + fluctuations) *Hu and O'Connell (PRB 1989)*
- Dielectric Response Function *Kirznits, Maximov, Khomskii (JLTP 1972)*

McMillan Strong Coupling

(Computationally implemented by Wierzbowska, et al., cond-mat/0504077, 2006)

$$T_c = \frac{\Theta}{1.45} \exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right]. \qquad (18)$$

$$\lambda = 2\int \frac{d\omega\, \alpha^2(\omega) F(\omega)}{\omega} = \frac{N(0)\langle \mathcal{I}^2\rangle}{M\langle\omega^2\rangle}, \qquad (23)$$

$$\alpha^2(\omega) F(\omega) = \int_S \frac{d^2p}{v_F} \int_{S'} \frac{d^2p'}{(2\pi\hbar)^3 v_{F'}} \sum_\nu g_{pp'\nu}{}^2 \delta(\omega-\omega_{p-p'\nu}) \Big/ \int_S \frac{d^2p}{v_F}, \qquad (19)$$

where the integral $\int d^2p$ is taken over the Fermi surface and the electron-phonon matrix elements are given by[14]

$$g_{pp'\nu} = (\hbar/2MNV\omega_{p-p'\nu})^{1/2} \mathcal{I}_\nu(p, p'), \qquad (20)$$

where $\mathcal{I}_\nu(pp')$ is the electronic matrix element of the change in the crystal potential $\mathfrak{U}$ as one atom is moved:

$$\mathcal{I}_\nu(pp') = \int \psi_p{}^*(\varepsilon_{p-p'\nu} \cdot \nabla\mathfrak{U})\psi_{p'} d\mathbf{r}. \qquad (21)$$

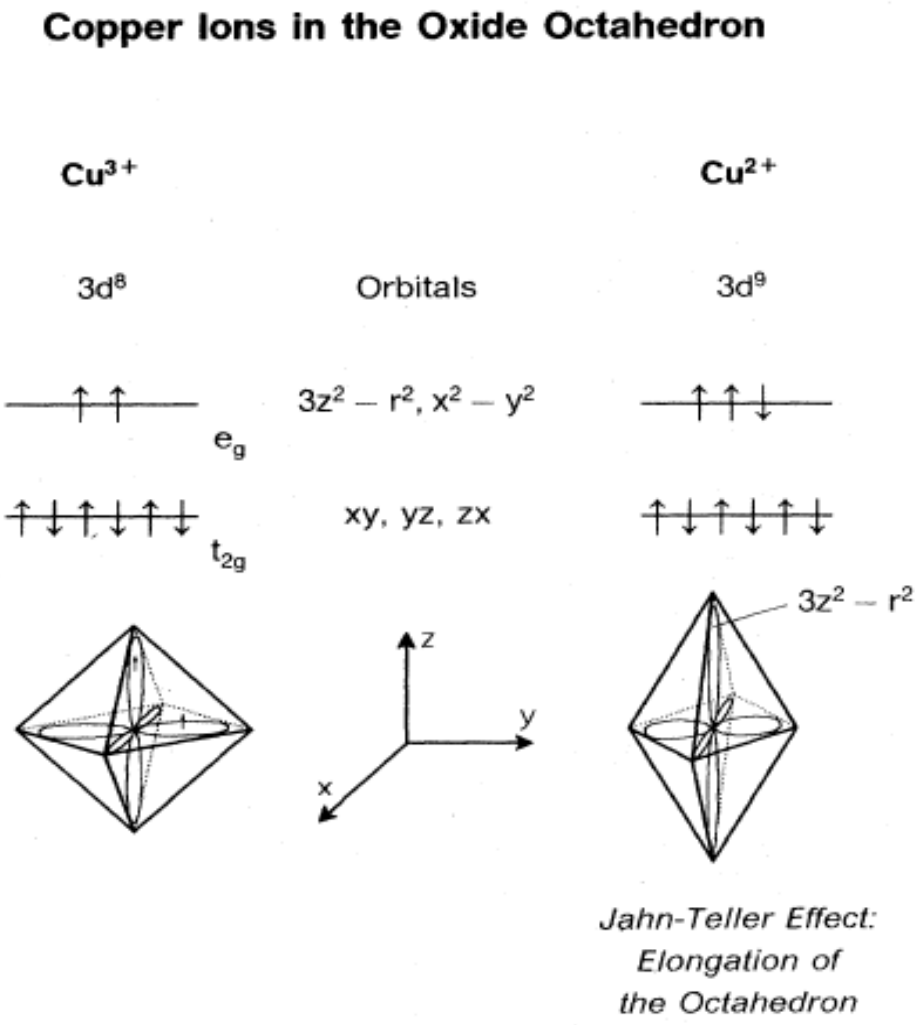
What's the HTSC equivalent?

Well!
What do I "move?"

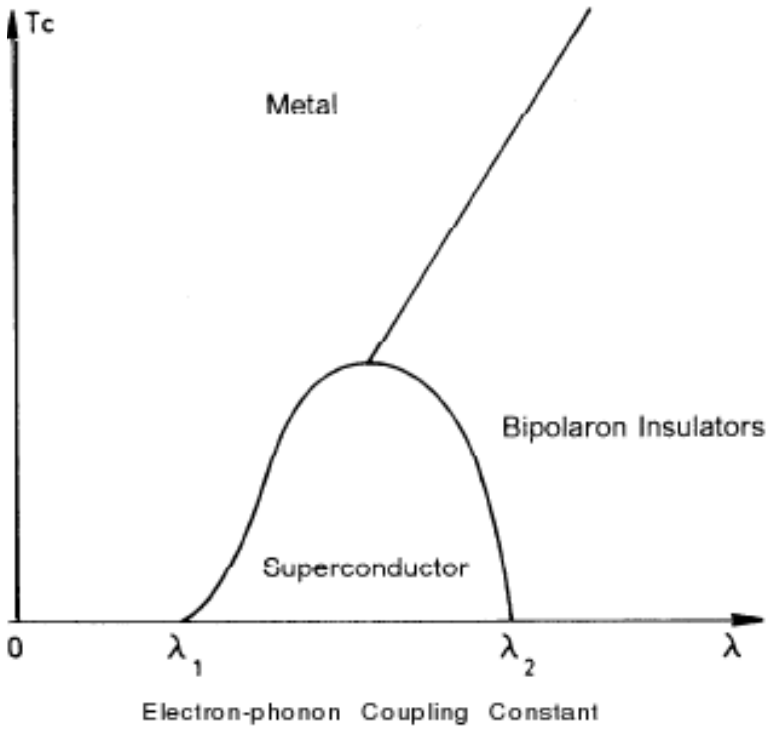
Phonons?

(Ask Alex M.)

Bednorz-Mueller Nobel Lecture



Jahn-Teller Effect: Elongation of the Octahedron

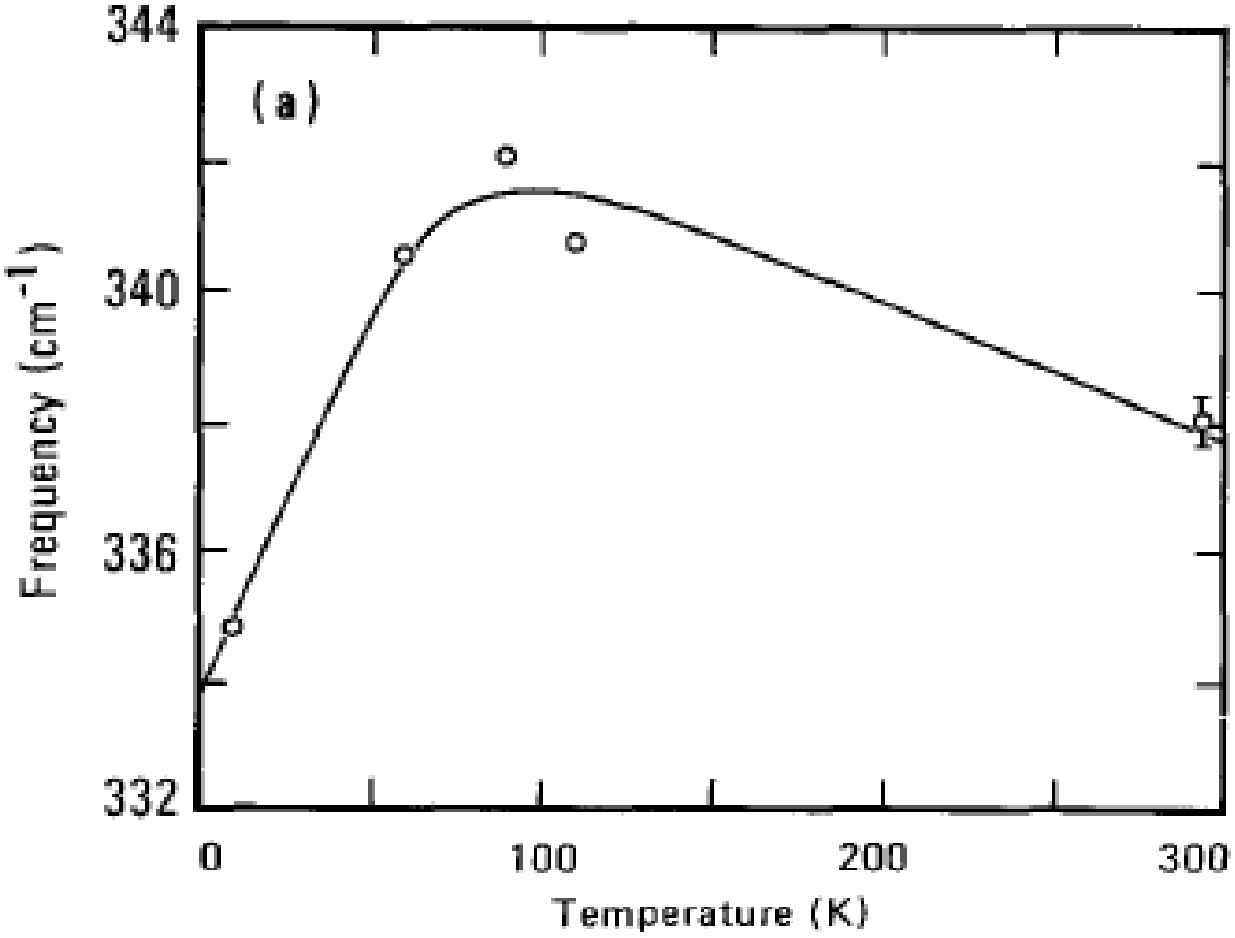


After Chakravarty, (1979)

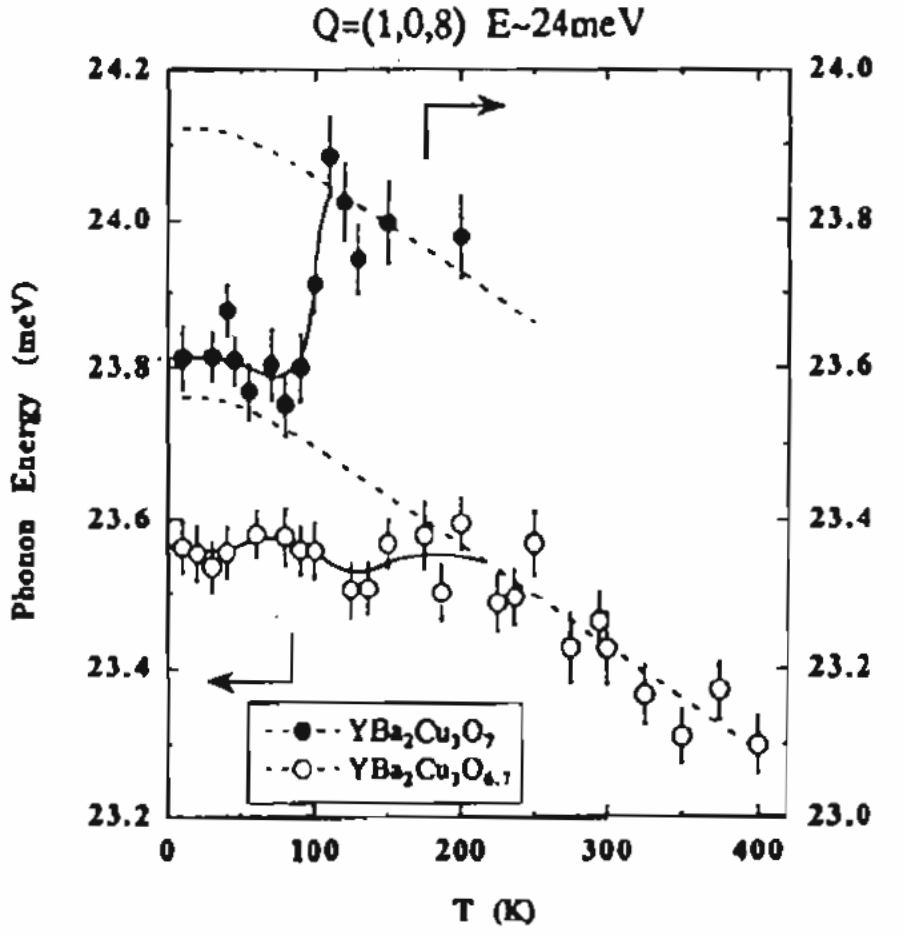
Indeed, they're there!

Macfarlane, Rosen, Seki, SSC 63, 831 (1987)

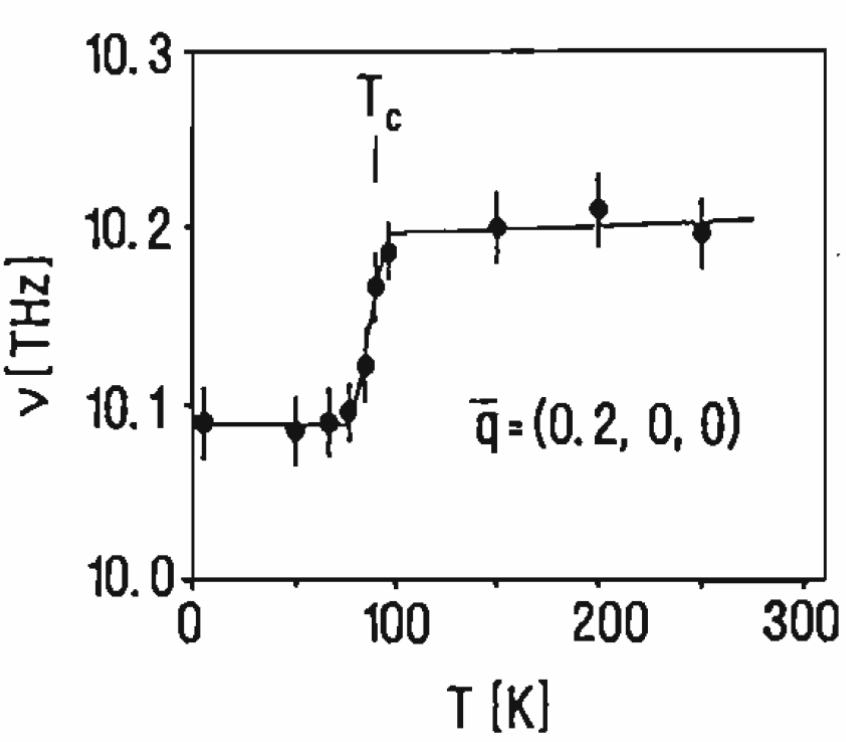
Raman Spectroscopy of YBCO



More Evidence



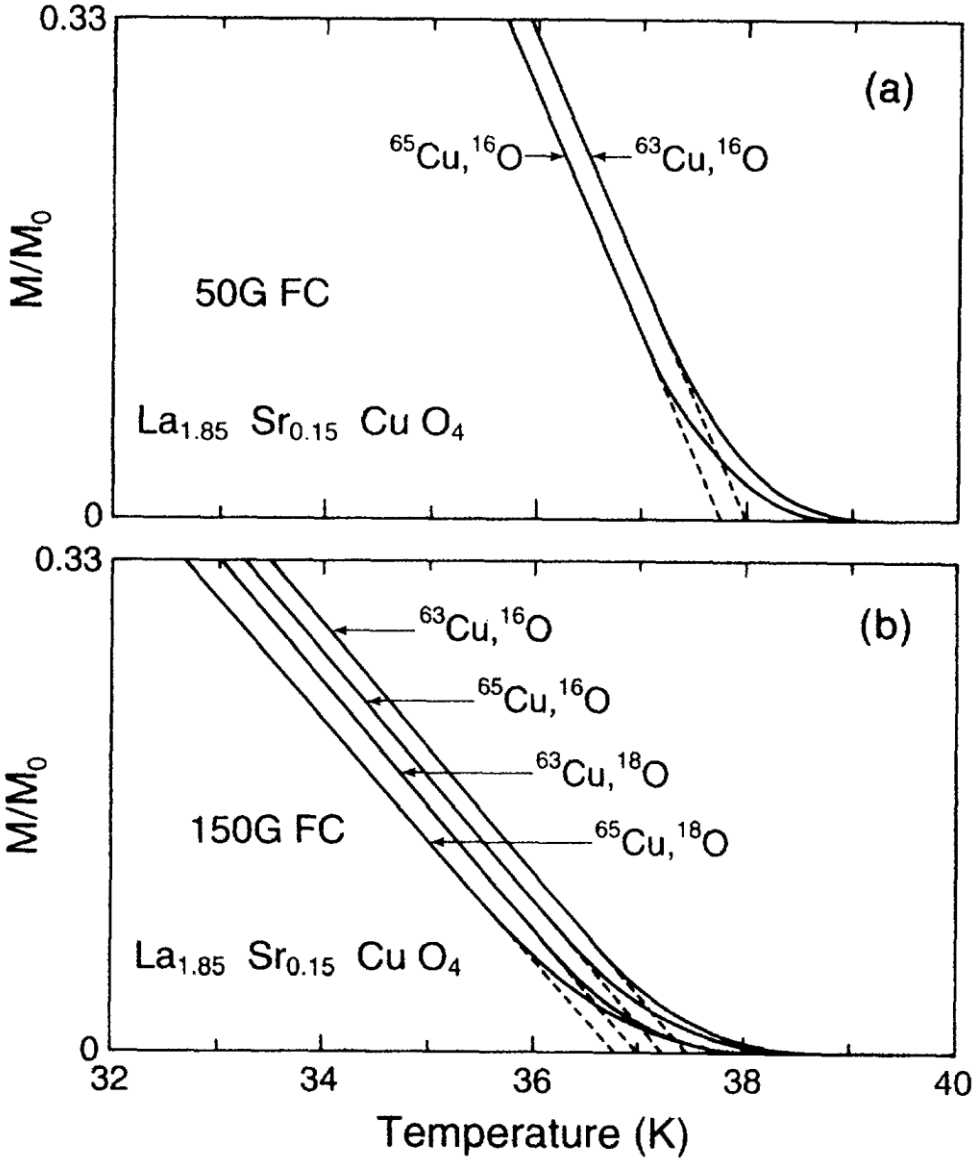
Harashima, et al., Physica C263, 257 (1996)



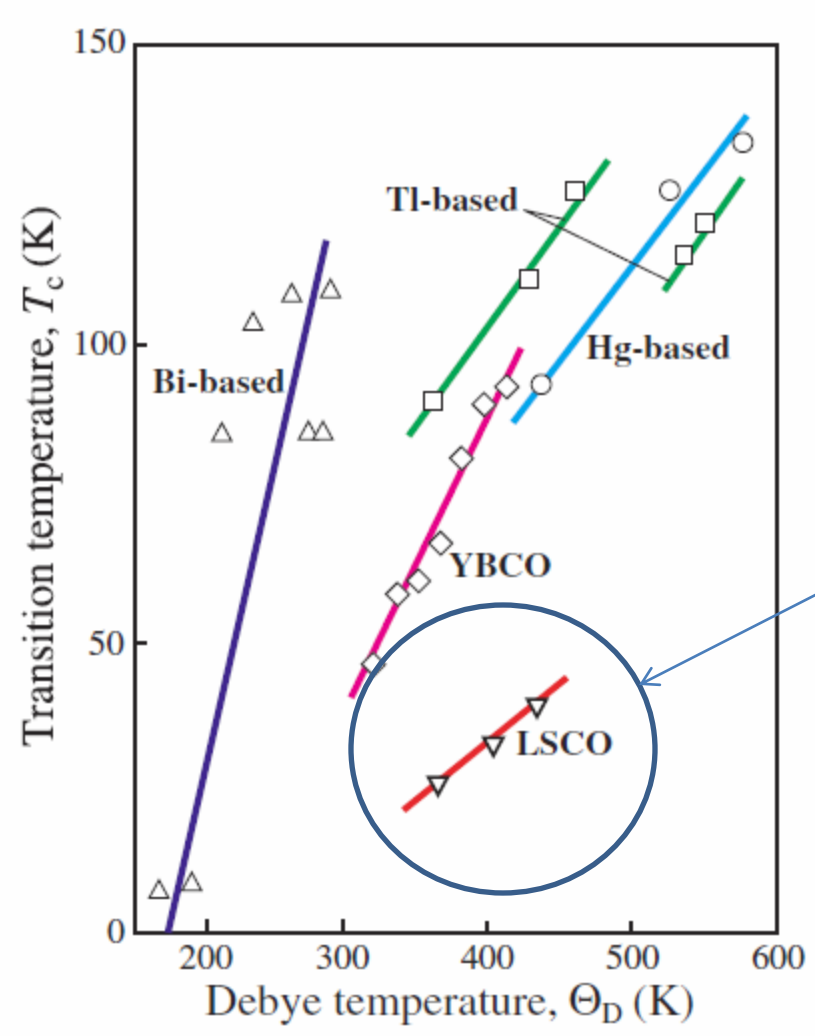
Pyka, et al., PRL 70, 1457, (1993)

Copper and Oxygen Isotope Effects in $La_{2-x}Sr_xCuO_4$

J. P. Franck,[1] S. Harker,[1] and J. H. Brewer[2]



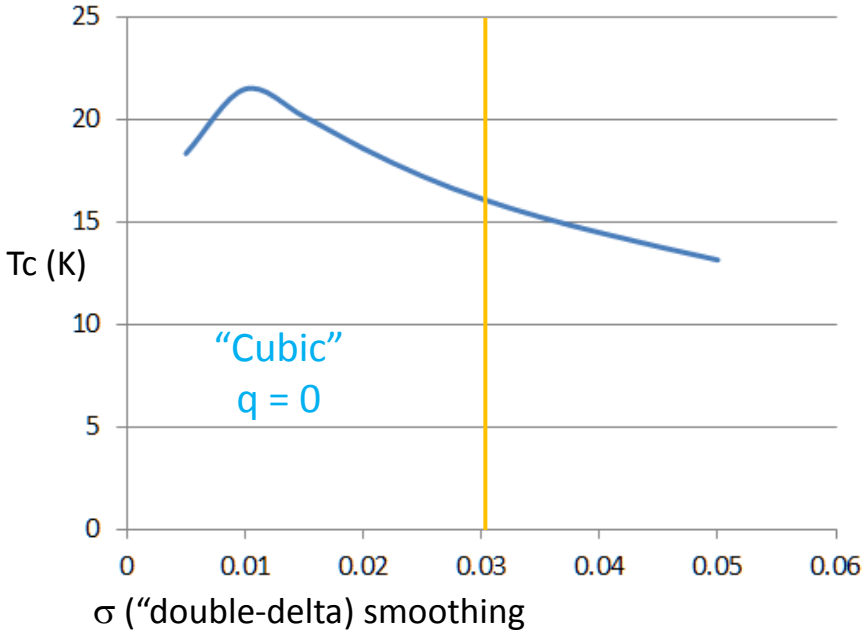
Finally, T_C scales (roughly) with Θ_D

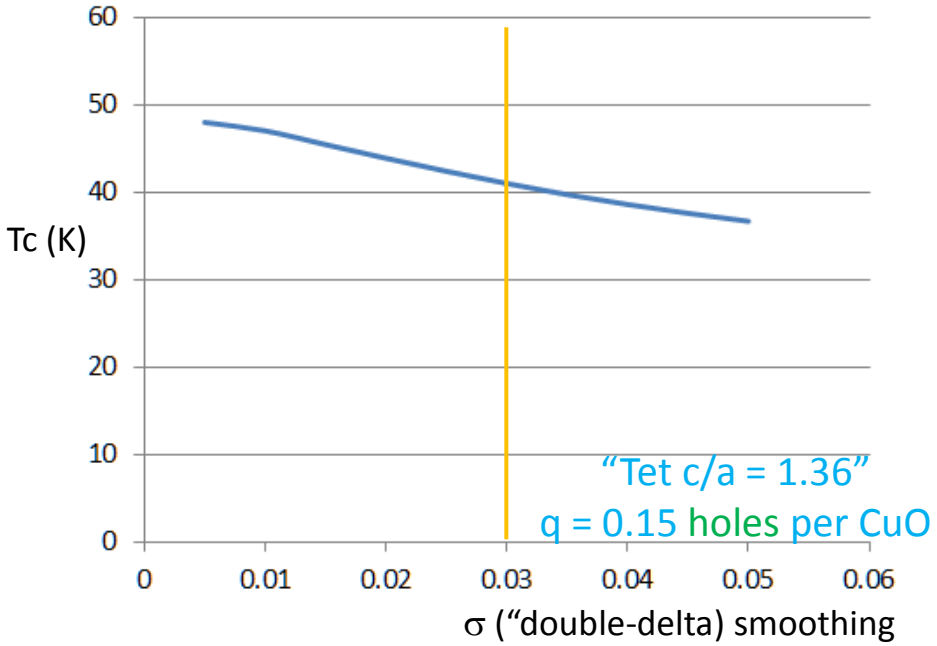


Nota Bene!

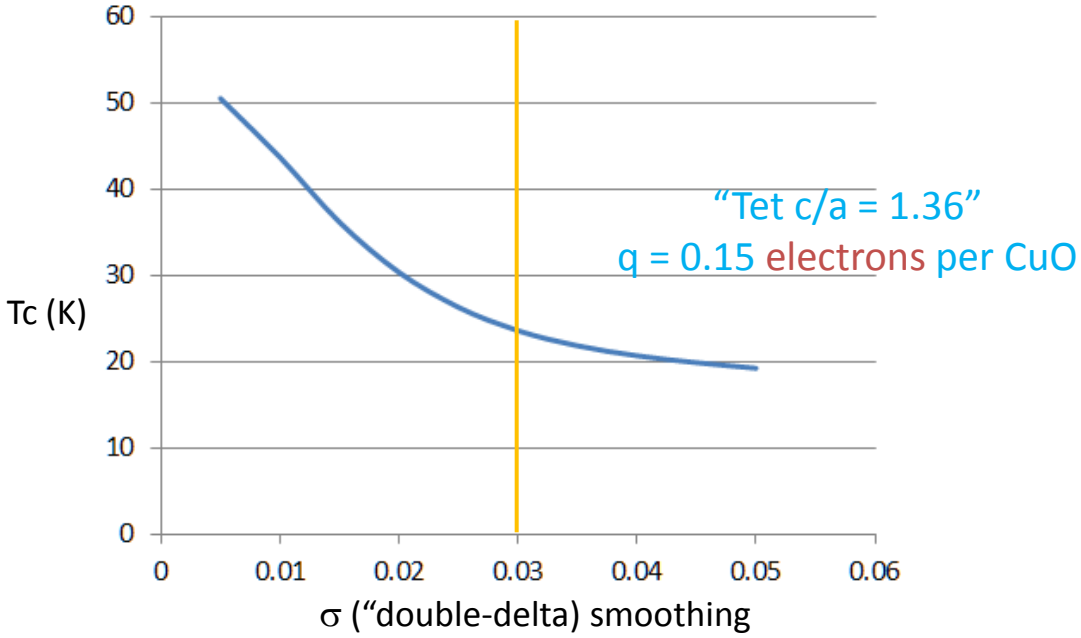
Ledbetter, Physica C 235, 1325 (1994)

The Grand(t) Summary: (EM, $\Theta_D \approx 440$ K, $\mu^* \approx 0.05$)

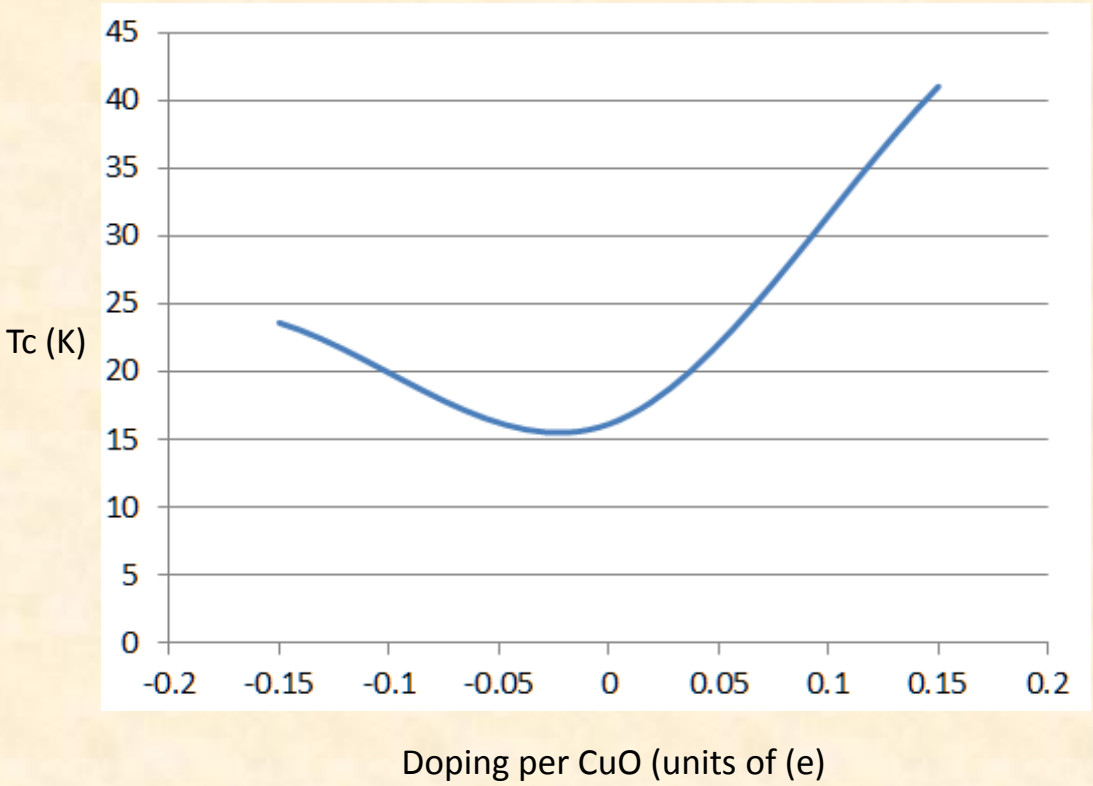




Note Differences in Tc Scale



Conclusions

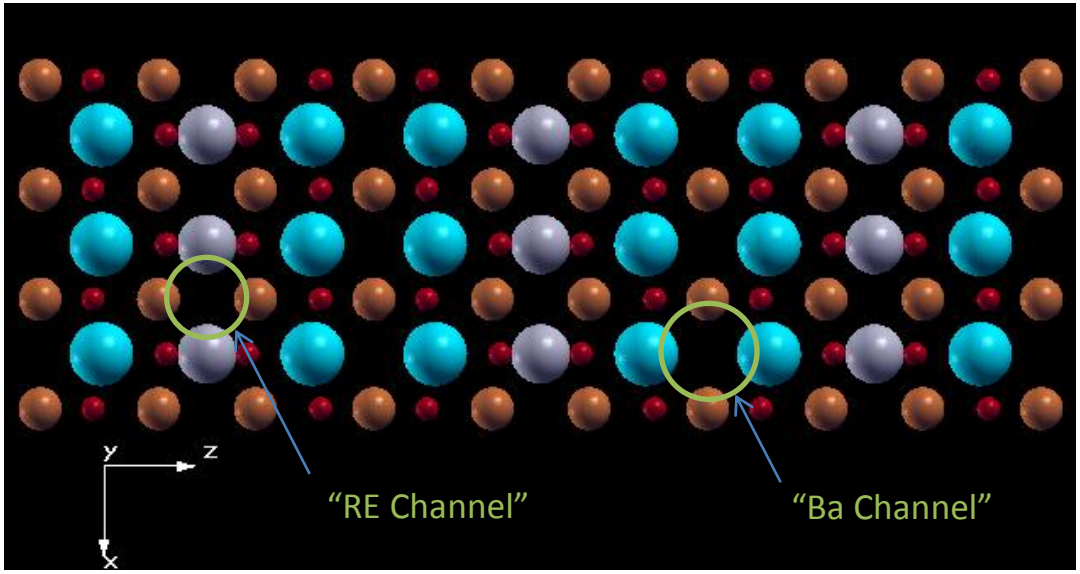


- Phonons can yield “credible” values of Tc in the cuprates
- Holes are better than electrons
- Can’t account for higher Tc’s in “1-2-3 +” layered compounds (Yet...check out Raghu, et al.)

Computers and the Study of Proxy Structures may finally resolve the mystery of High-Tc...a Future NP for someone in the audience...much younger than me!

The End

Well...almost...



Come See Me in Baltimore!

Possibilities for Observation of Quantum Transport in $(RE)Ba_2Cu_3O_{7-y}$ Perovskites

R43.00003
2:54 PM, Wednesday, 3/20/2013
Hilton Ballroom 2

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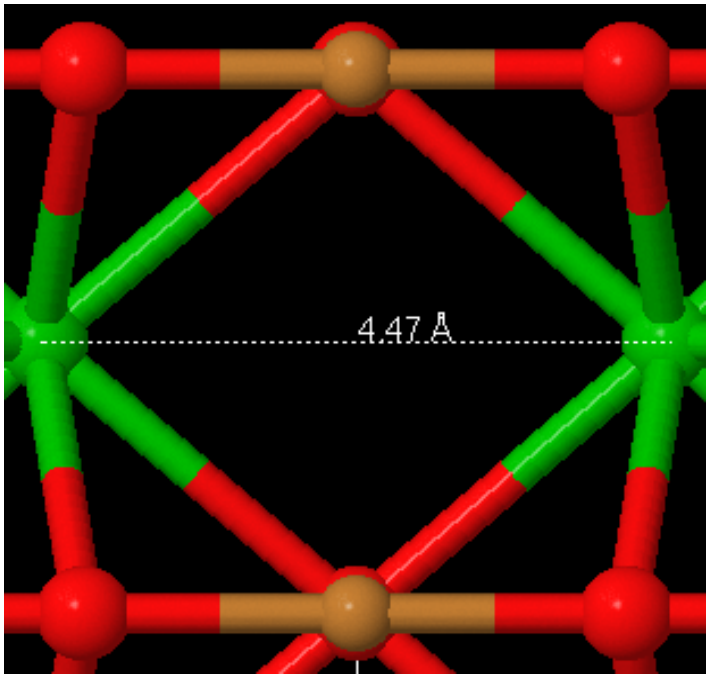

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