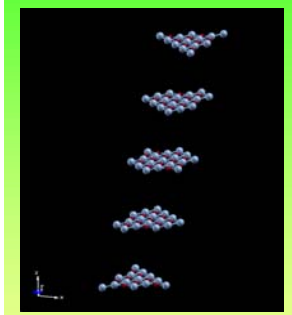
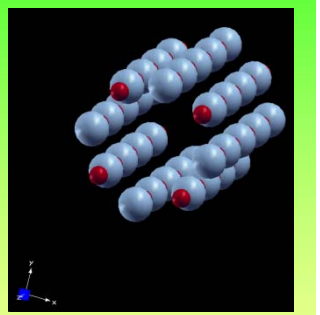
A DFT (LDA+U) Study of the Electronic Properties of Square-Planar Coordinated Copper Monoxide Structures





Paul M. Grant

IBM Research Staff Member, Emeritus

Aging IBM Pensioner

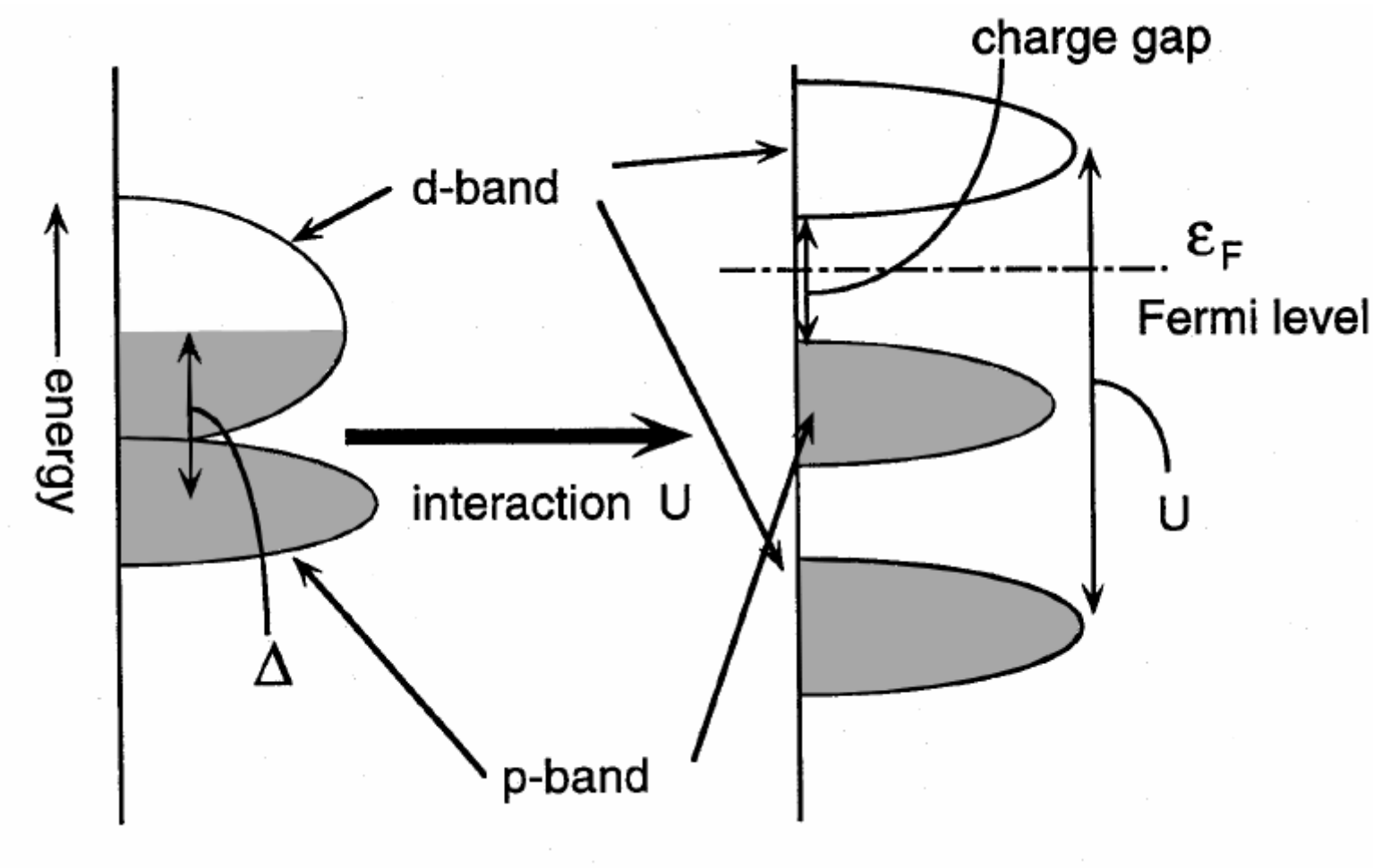
Financial Support From:

IBM Retiree Pension Fund Prior to 1990

MRS Spring Meeting
Moscone (West) Convention Center
25-29 April 2011, San Francisco, CA

Session VV4.2 Room 2020
9:00 AM
Tuesday, 26 April 2011

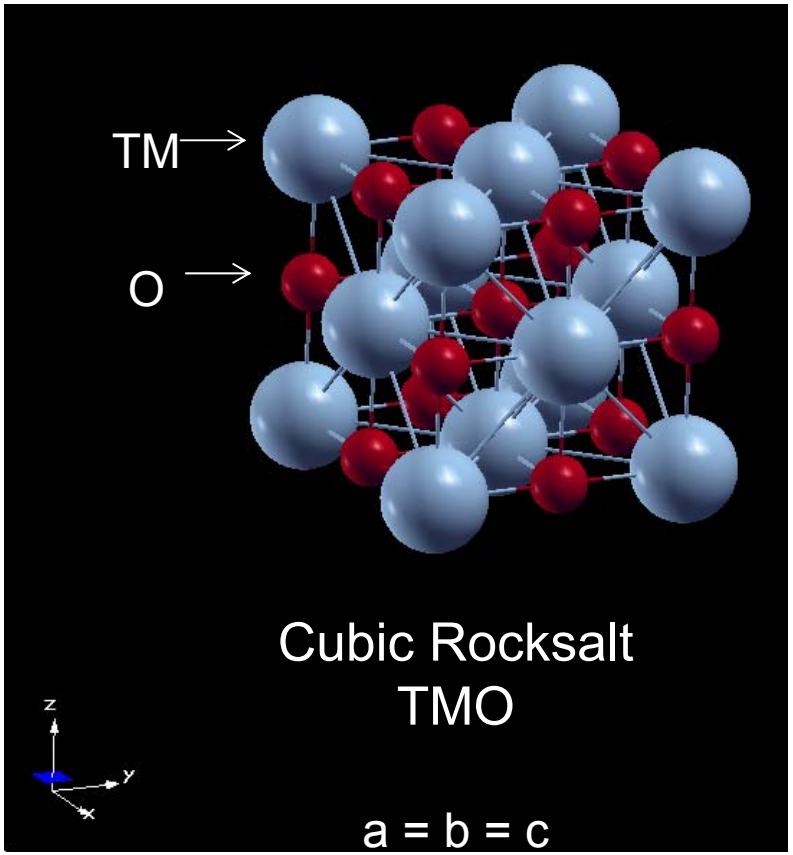
Transition Metal Oxides
"Should be Metals, But Aren't"
(Charge Transfer Insulators, Instead)

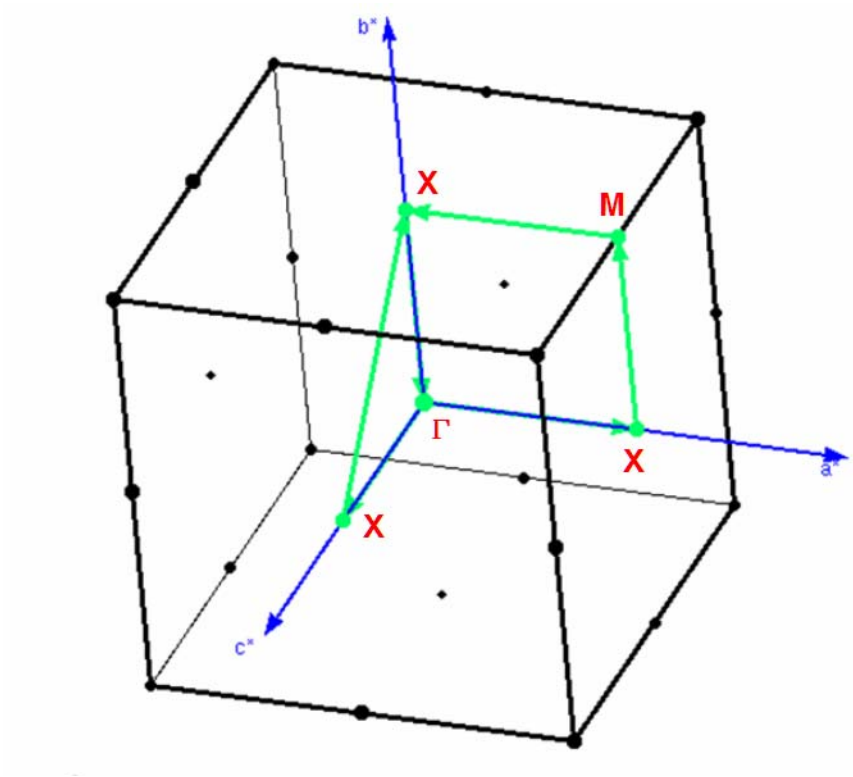


After Imada, et al, RMP 70, 1039 (1998)

Cubic Rocksalt TMOs

Direct and Reciprocal Lattices





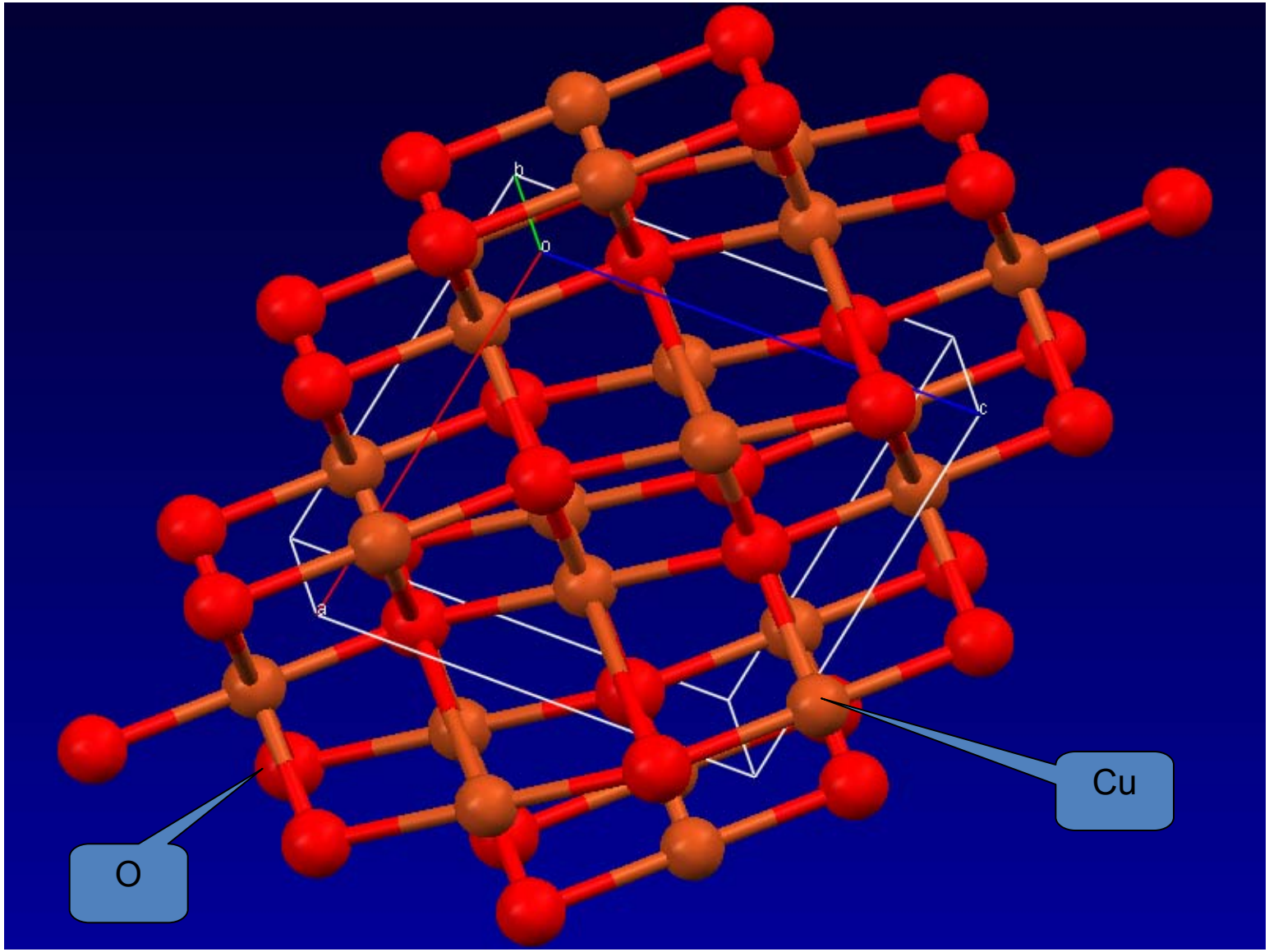
Cubic Rocksalt Divalent TMOs

TMO	3d Config	Properties
MnO	5	MH-CTI (5.6)
FeO	6	MH-CTI (5.9)
CoO	7	MH-CTI (6.3)
NiO	8	MH-CTI (6.5)
CuO	9	***XX Doesn't Exist!***

See Imada, Fujimore, Tokura, RPM 70 (1988)

Why Not?

Tenorite (Monoclinic CuO)



Can Application of DFT (LDA+U) Help Unravel the Cubic Rocksalt CuO Enigma?

...Let's see...

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 NiO, MnO, FeO, CoO and La_2CuO_4
- Plane-Wave Pseudopotential Implementation by Cococcioni and de Gironcoli, PRB 71, 035105 (2005)
  - Applied to FeO and NiO
  - Download open-source package from http://www.pwscf.org

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

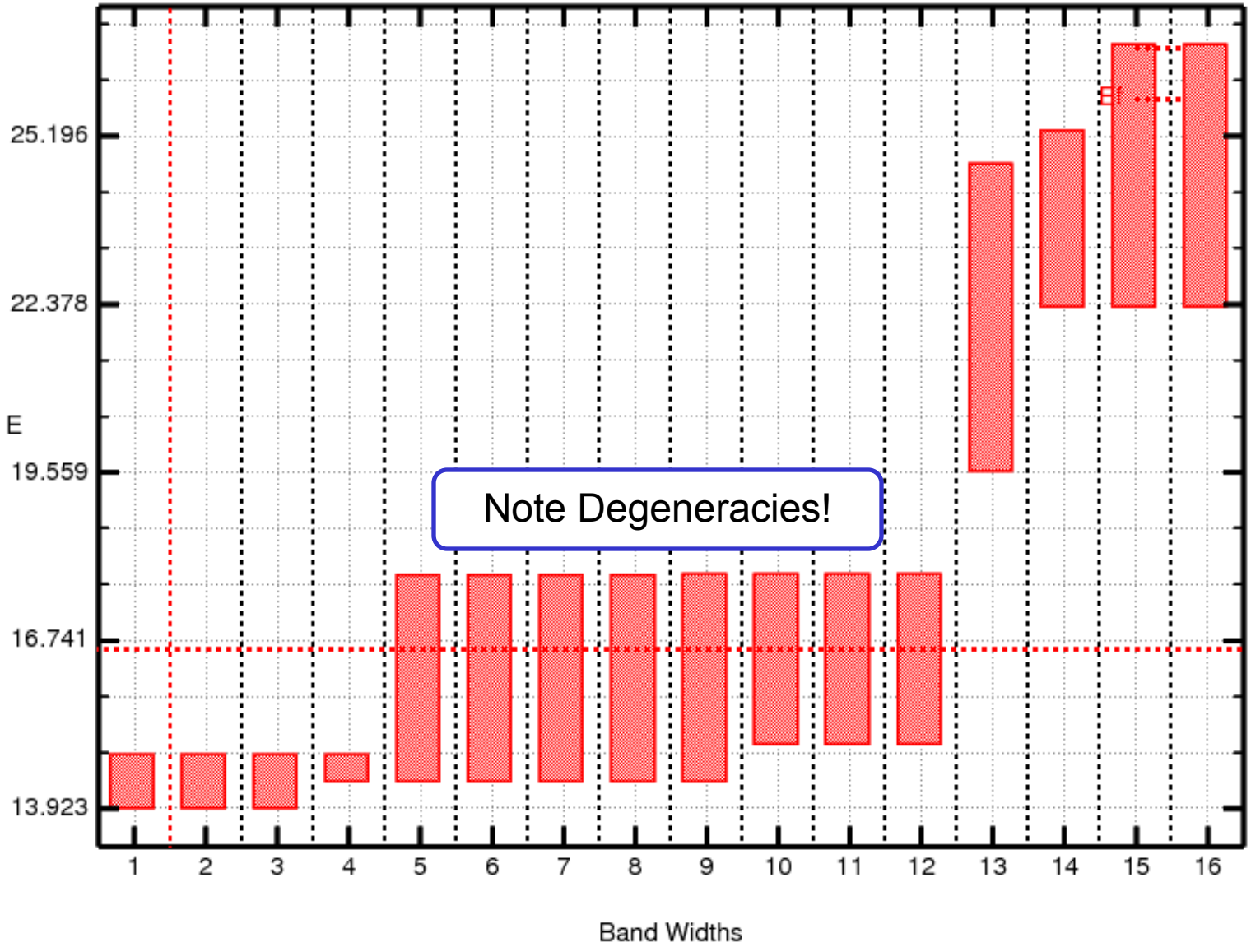
Psuedopotentials: Ultrasoft, XC = Perdew-Zunger

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

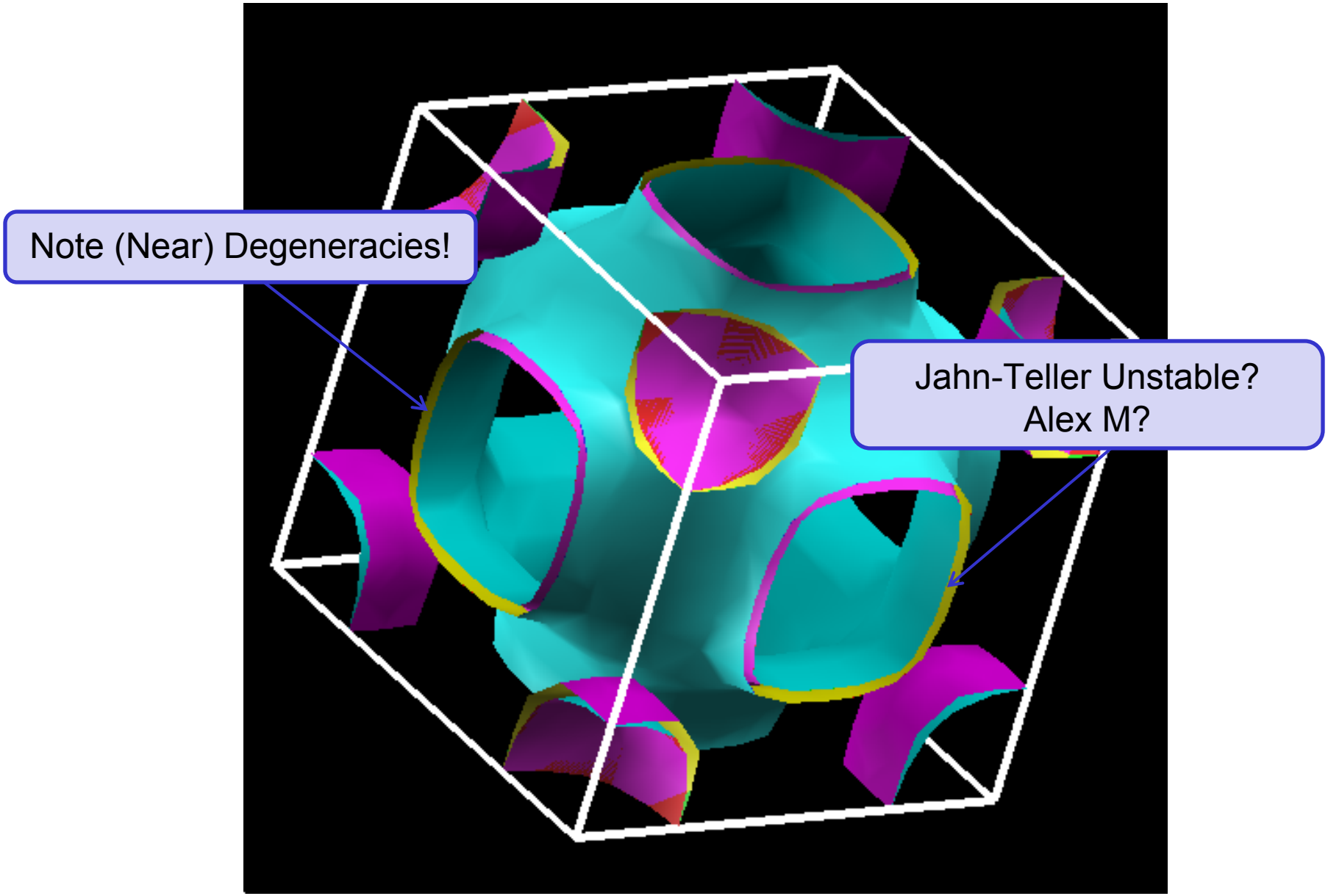
Hardware

3.33 GHz Intel Core i7 – 12 GB+

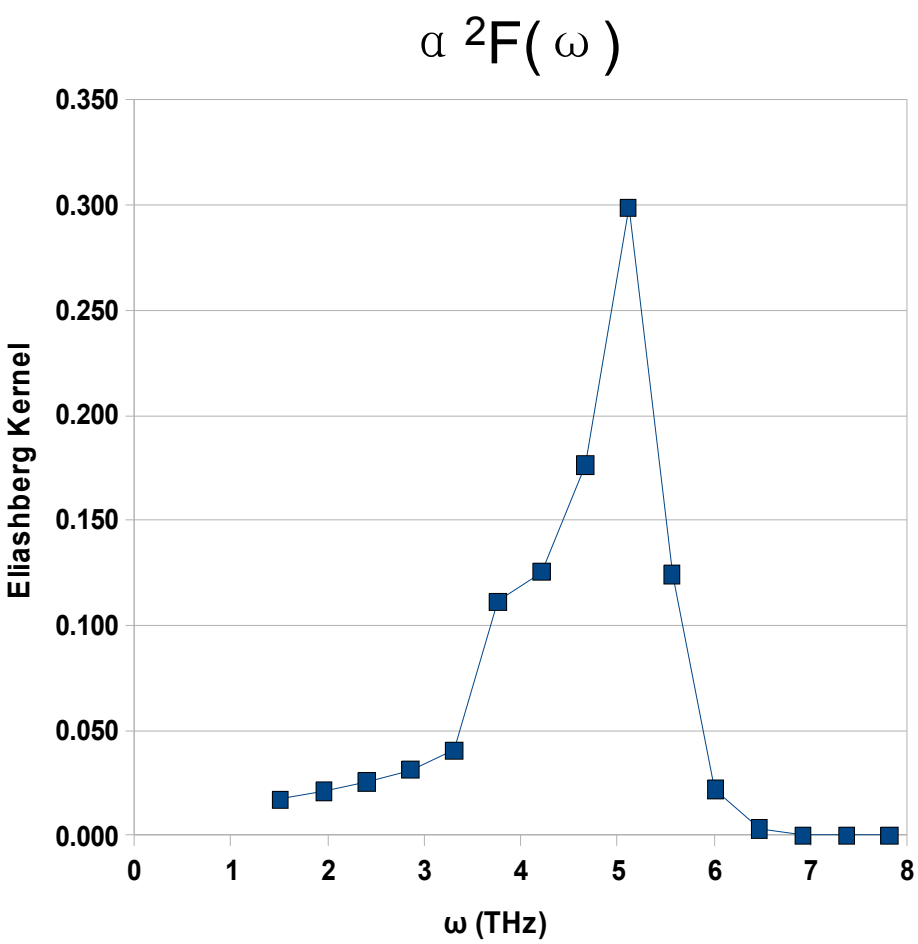
Rocksalt CuO Band Widths



Rocksalt CuO Fermiology (Combined)



Non-Magnetic Cubic Rocksalt CuO
-- Electron-Phonon Properties --



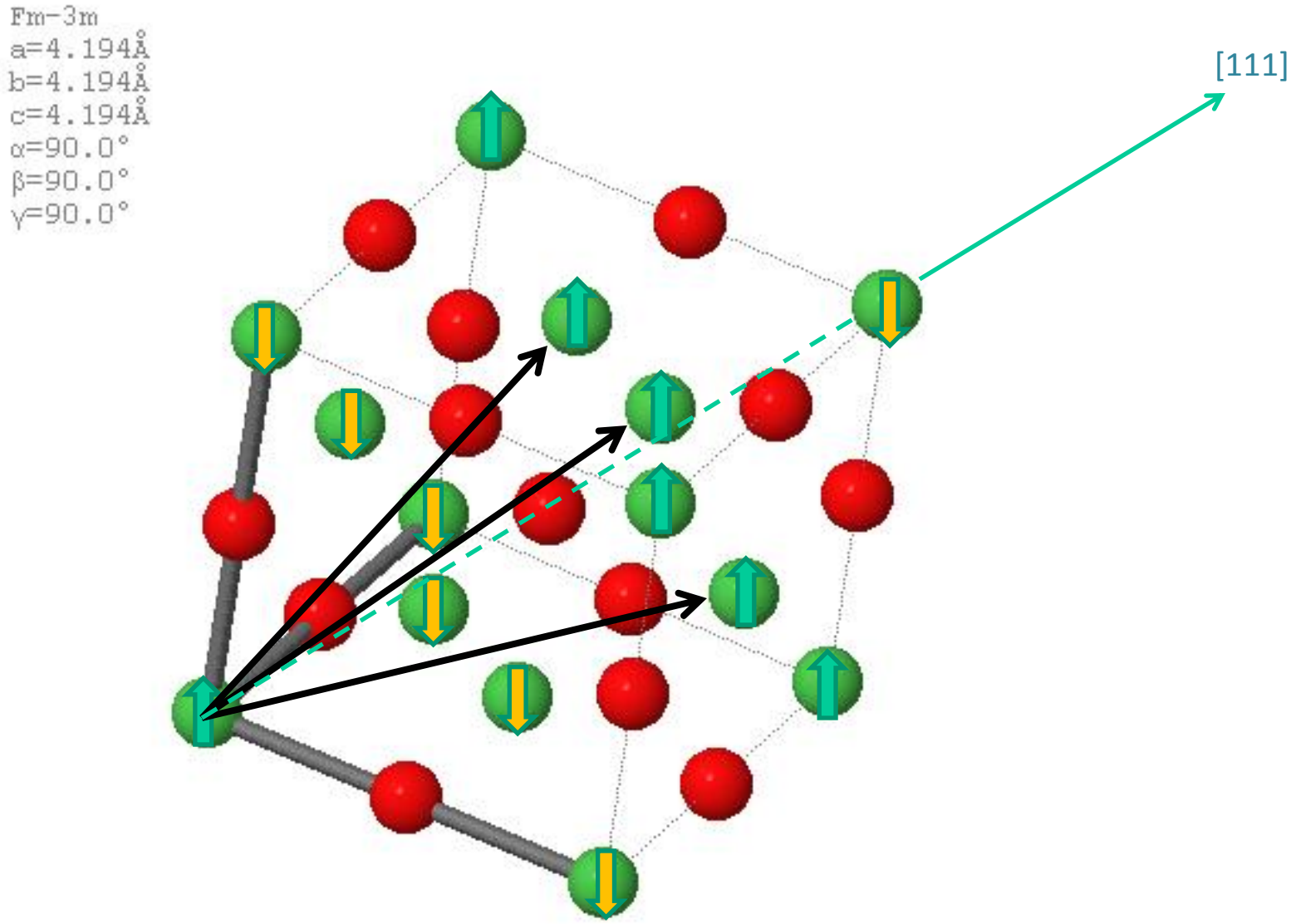
σ = 0.04

- λ ~ 0.6 – 0.7
- Other sc's…

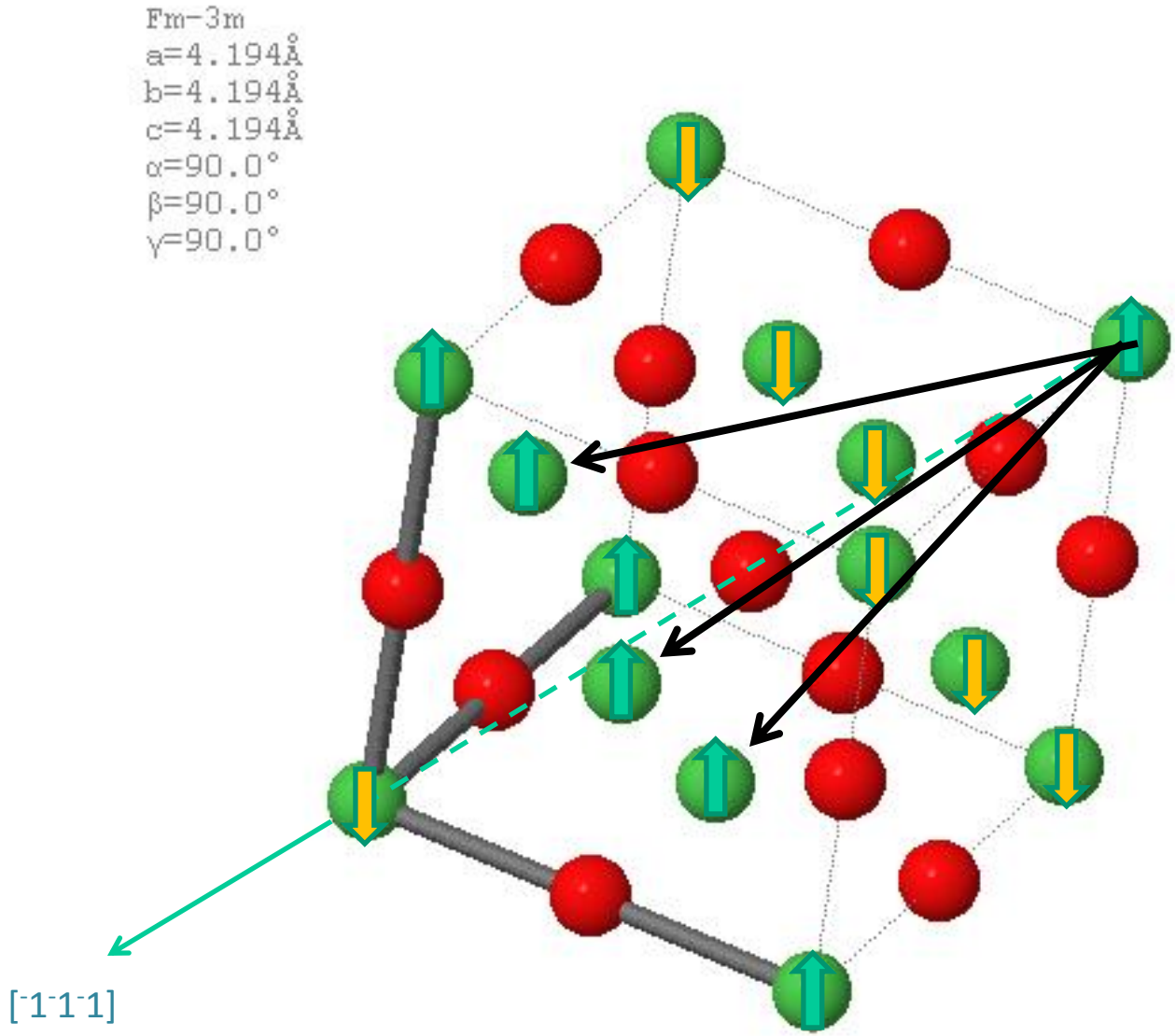
$$T_C = a\Theta e^{-\frac{1}{\lambda-\mu^*}} \qquad \lambda k\Theta \ll E_F$$

	T_C (K)	λ	μ*
K_3C_{60}	16.3	0.51	-
Rb_3C_{60}	30.5	0.61	-
Cs_3C_{60}	47.4	0.72	-

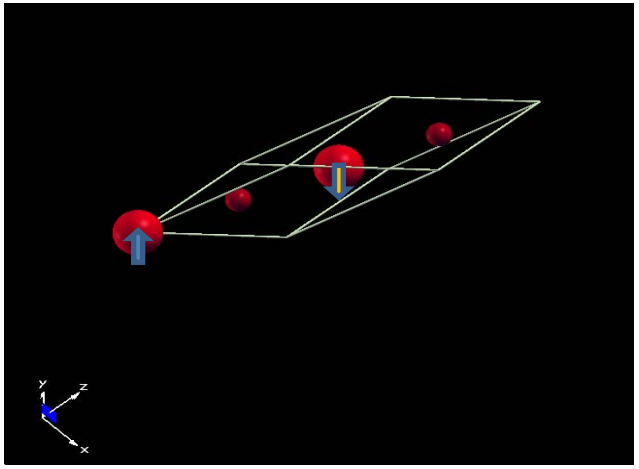
Proto-TMO AF-II Rocksalt



Proto-TMO AF-II Rocksalt



The Answer(s) !

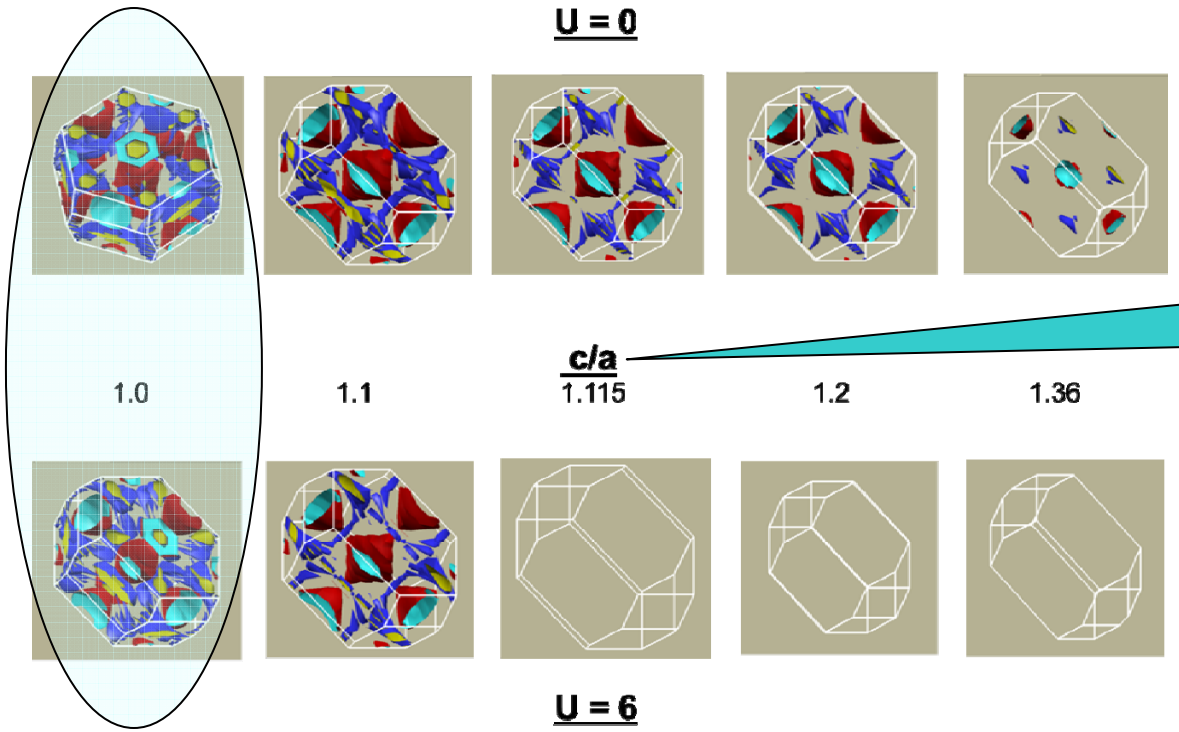


TMO Asymmetric Type II
af-CuO Cell

LDA+U Calcs

Grant, IOP-CS 129 (2008) 102042

Siemons, et al,
PRB 79 (2009)
195122



Tetragonal
Distortion

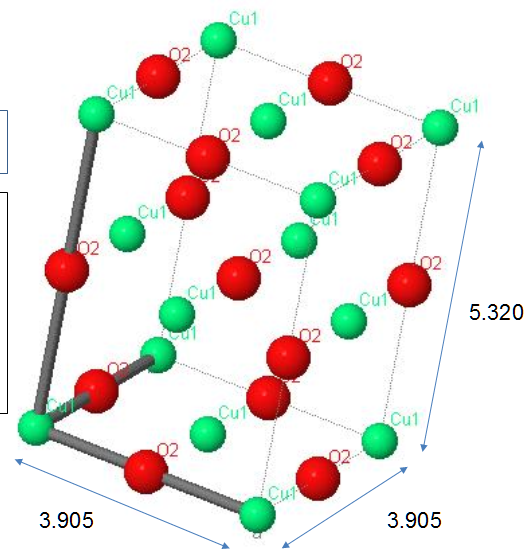
Tetragonal Rocksalt CuO

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

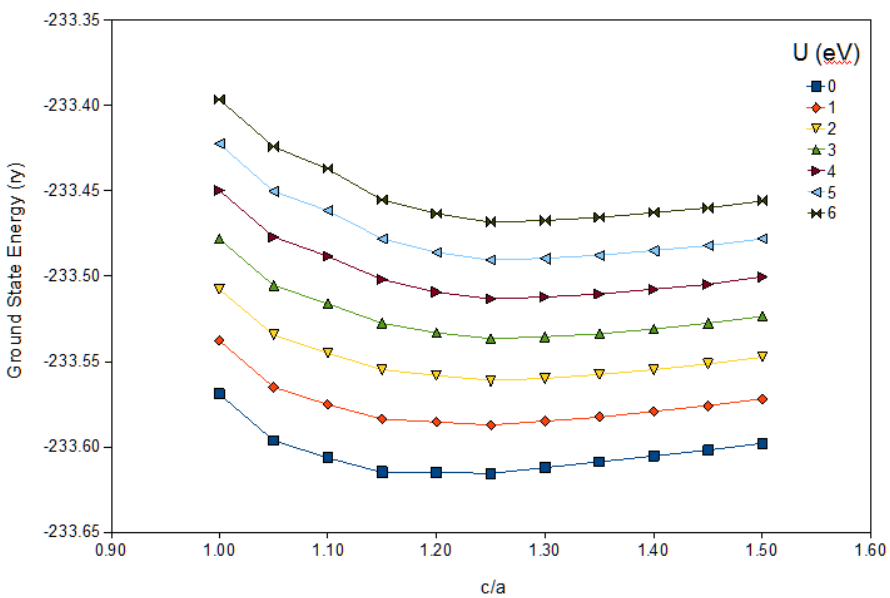
c/a = 1.36

Measurements (Wolter Siemons)

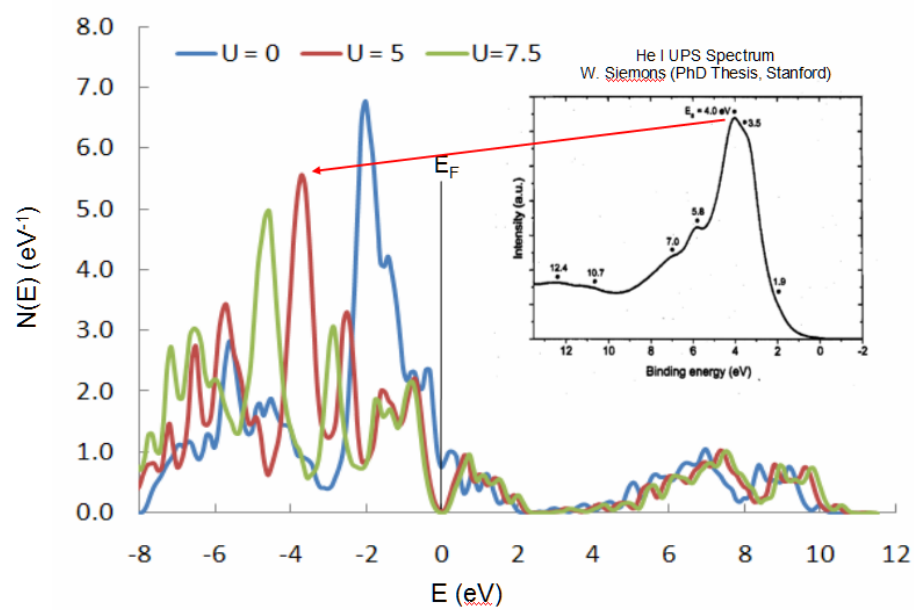
- 2-4 ML epi on STO
- No Fermi Edge
- No Exchange Bias on ferro-SRO (Tc ~ 100-150 K)



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



t-CuO Density-of-States



References

The International Conference on Theoretical Physics 'Dubna-Nano2008' IOP Publishing
Journal of Physics: Conference Series **129** (2008) 012042 doi:10.1088/1742-6596/129/1/012042

Electronic properties of rocksalt copper monoxide: A proxy structure for high temperature superconductivity

Paul M. Grant*
W2AGZ Technologies

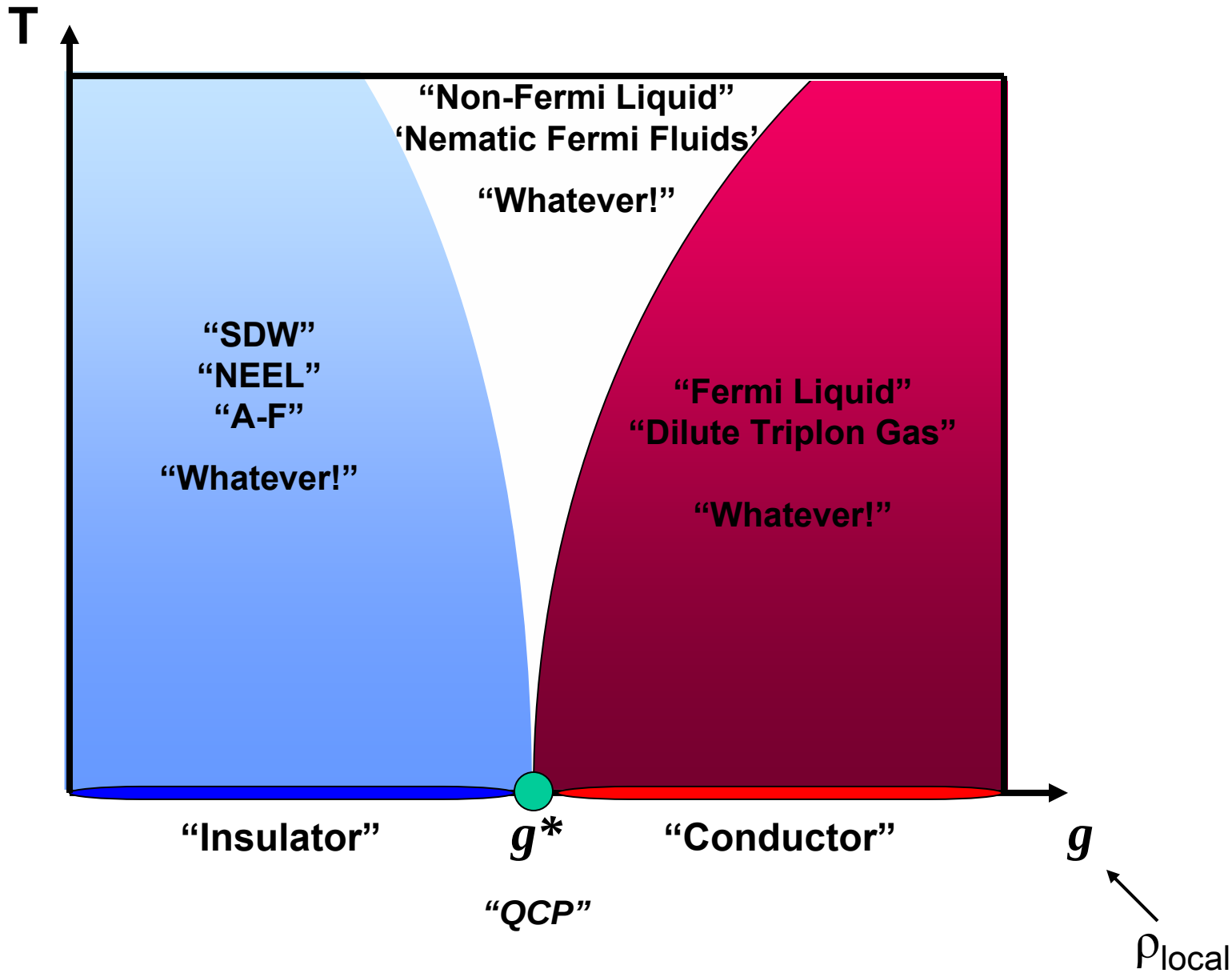
"**Electronic Properties of Rocksalt Copper Monoxide**,"
APS MAR09-2008-006217, P. M. Grant, Pittsburgh (2009)

PHYSICAL REVIEW B **79**, 195122 (2009)

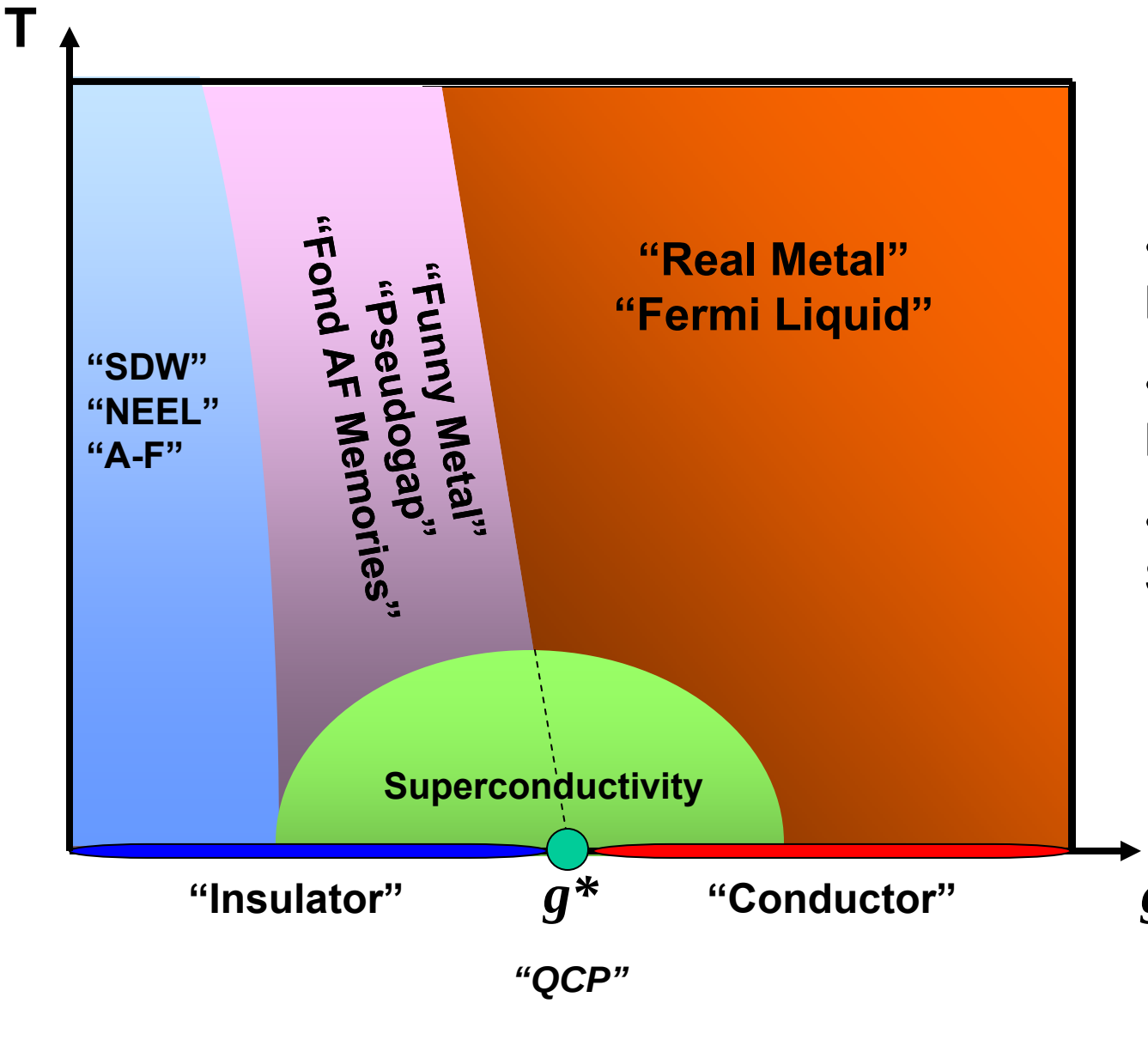
Tetragonal CuO: End member of the 3*d* transition metal monoxides

Wolter Siemons,[1,2] Gertjan Koster,[1,2,*] Dave H. A. Blank,[1] Robert H. Hammond,[2]
Theodore H. Geballe,[2] and Malcolm R. Beasley[2]

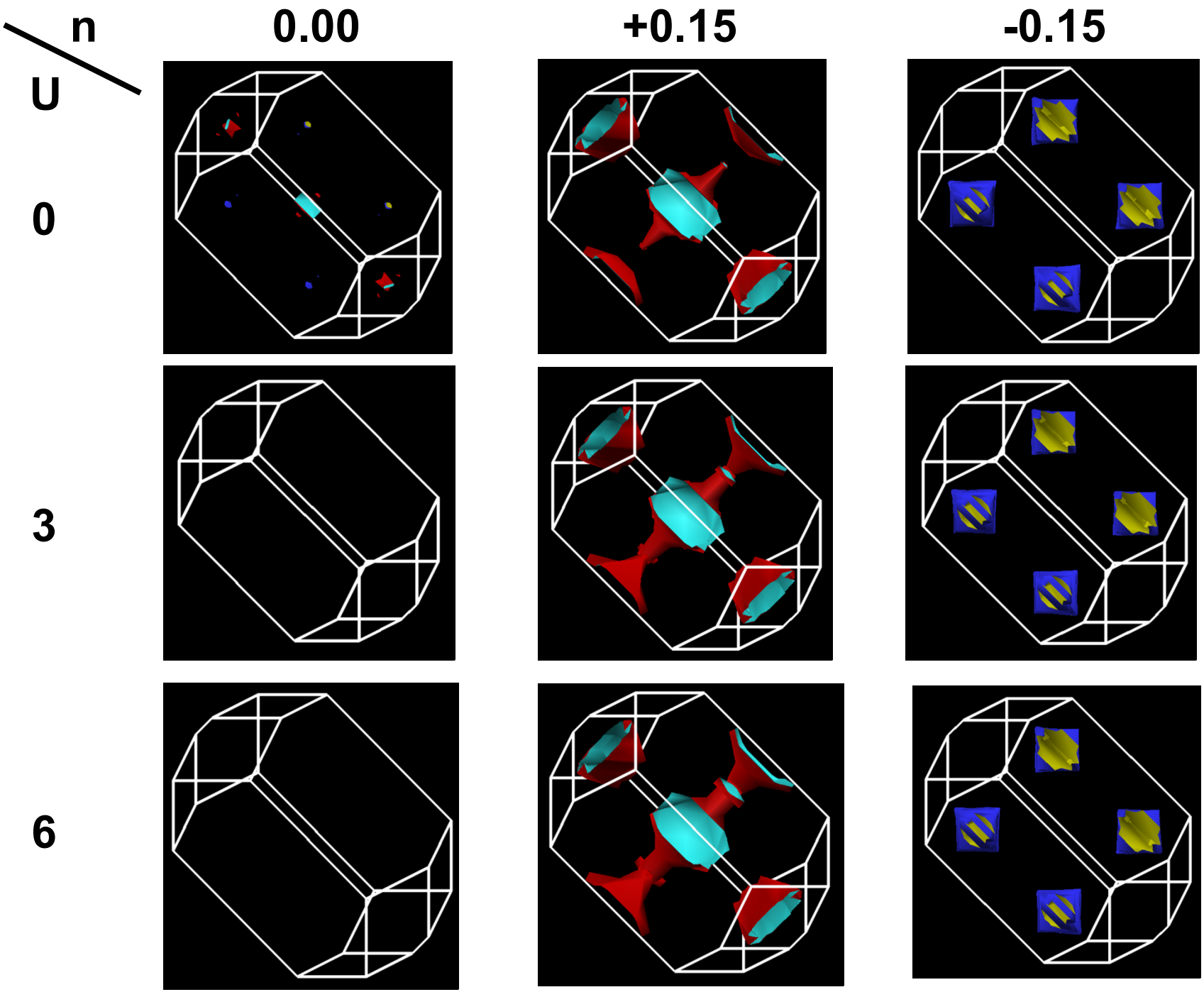
The Great Quantum Conundrum



The Colossal Quantum Conundrum

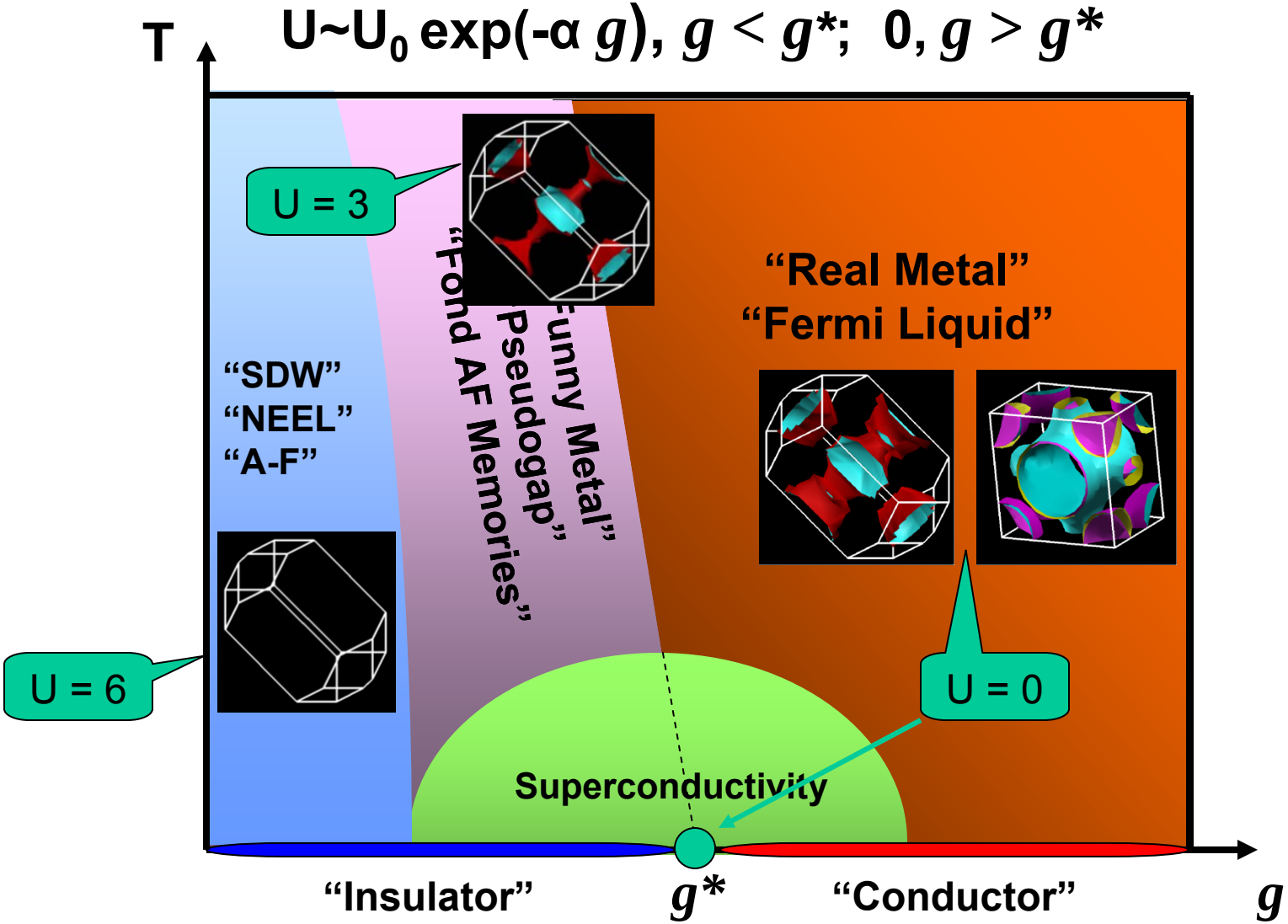


- CuO Perovskites
- Fe Pnictides
- Bechgaard Salts


n
U
0.00
+0.15
-0.15
0
3
6

The Colossal Quantum Conundrum

$U \sim U_0 \exp(-\alpha g)$, $g < g^*$; 0, $g > g^*$



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?)

- Generalized Linhard Response Function (RPA + fluctuations) *Hu and O'Connell (PRB 1989)*
- Dielectric Response Function *Kirznits, Maximov, Khomskii (JLTP 1972)*

Generalized Linhard Function

$$\chi^0(\mathbf{q},\omega)=\sum_{\mathbf{k},\sigma}\frac{f(\mathbf{k})-f(\mathbf{k}+\mathbf{q})}{\hbar\omega-(\varepsilon_{\mathbf{k}+\mathbf{q}}-\varepsilon_{\mathbf{k}})+iDq^2}$$

$$D=\lim_{t\to\infty}\frac{1}{2t}\overline{\delta\mathbf{R}^2(t)}$$

$$V(\mathbf{q})=4\pi e^2/q^2$$

$$\epsilon(\mathbf{q},\omega)=1-V(\mathbf{q})\chi^0(\mathbf{q},\omega)$$

$$\epsilon_1(x,y)=1+\frac{q_{\mathrm{TF}}^2}{8k_F^2x^2}\left[1+\frac{1}{8x}\left[(1+b^2x^2-\nu_+^2)\ln\left[\frac{(1+\nu_+)^2+b^2x^2}{(1-\nu_+)^2+b^2x^2}\right]+(1+b^2x^2-\nu_-^2)\ln\left[\frac{(1+\nu_-)^2+b^2x^2}{(1-\nu_-)^2+b^2x^2}\right]\right]\right.$$
$$\left.-\frac{b}{2}\left\{\nu_+\left[\arctan\left[\frac{1-\nu_+}{bx}\right]+\arctan\left[\frac{1+\nu_+}{bx}\right]\right]+\nu_-\left[\arctan\left[\frac{1-\nu_-}{bx}\right]+\arctan\left[\frac{1+\nu_-}{bx}\right]\right]\right\}\right]$$

(

where

$$x=\frac{q}{2k_F},\quad y=\frac{\hbar\omega}{4\varepsilon_F},\quad q_{\mathrm{TF}}^2=\frac{4me^2k_F}{\pi\hbar^2},\quad b=\frac{2mD}{\hbar},\quad \nu_\pm=x\pm y/x\ ,$$

(

HO (1989)

Dielectric Response Function

$$G(\mathbf{k}, i\omega_n) = 1/(i\omega_n - \xi_k)$$

$$F(\mathbf{p}, i\omega_n) = -G(\mathbf{p}, i\omega_n)G(-\mathbf{p}, -i\omega_n)T_c \sum_{\mathbf{m}} \int [d^3k/(2\pi)^3]$$

$$\times\ V(\mathbf{p} - \mathbf{k}, i\omega_n - i\omega_{\mathbf{m}})F(\mathbf{k}, i\omega_{\mathbf{m}})$$

$$V(\mathbf{q}, i\omega_n) = \frac{4\pi e^2}{q^2}\left[1 - \int_0^\infty \frac{dE^2\rho(\mathbf{q}, E)}{\omega_n^2 + E^2}\right]$$

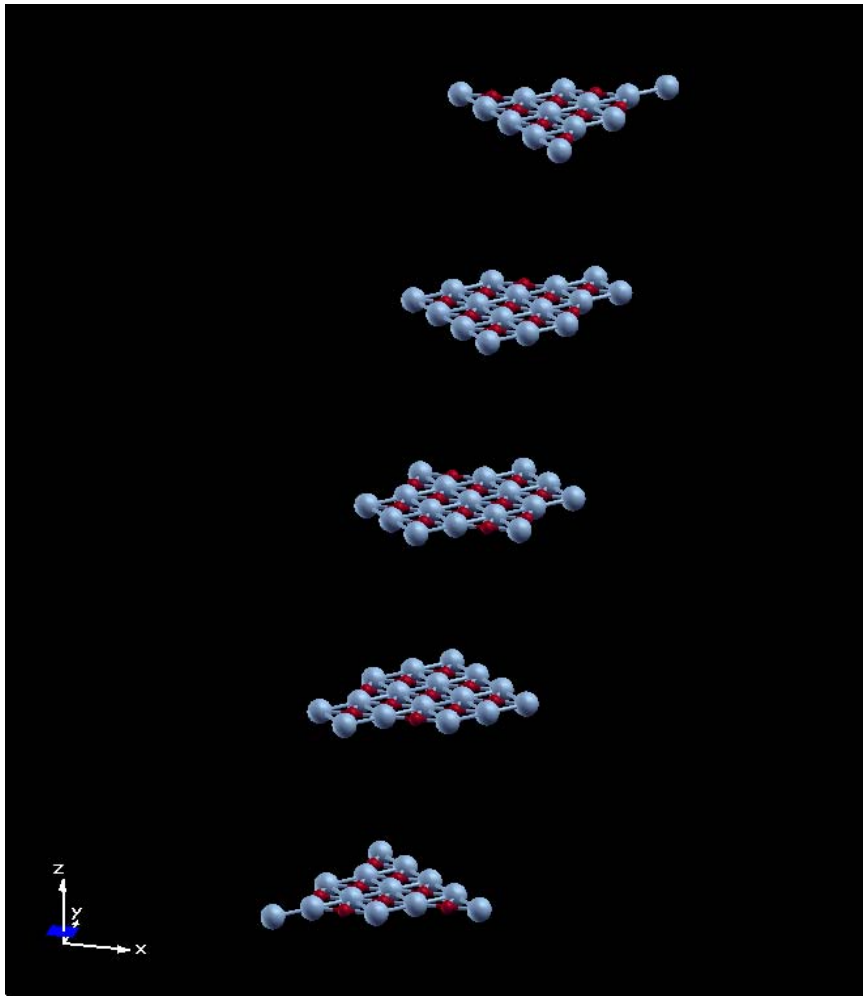
In principle, KMK can calculate the BCS gap for general “bosonic” fields, be they phonons, magnons, spin-ons, excitons, plasmons…or morons!

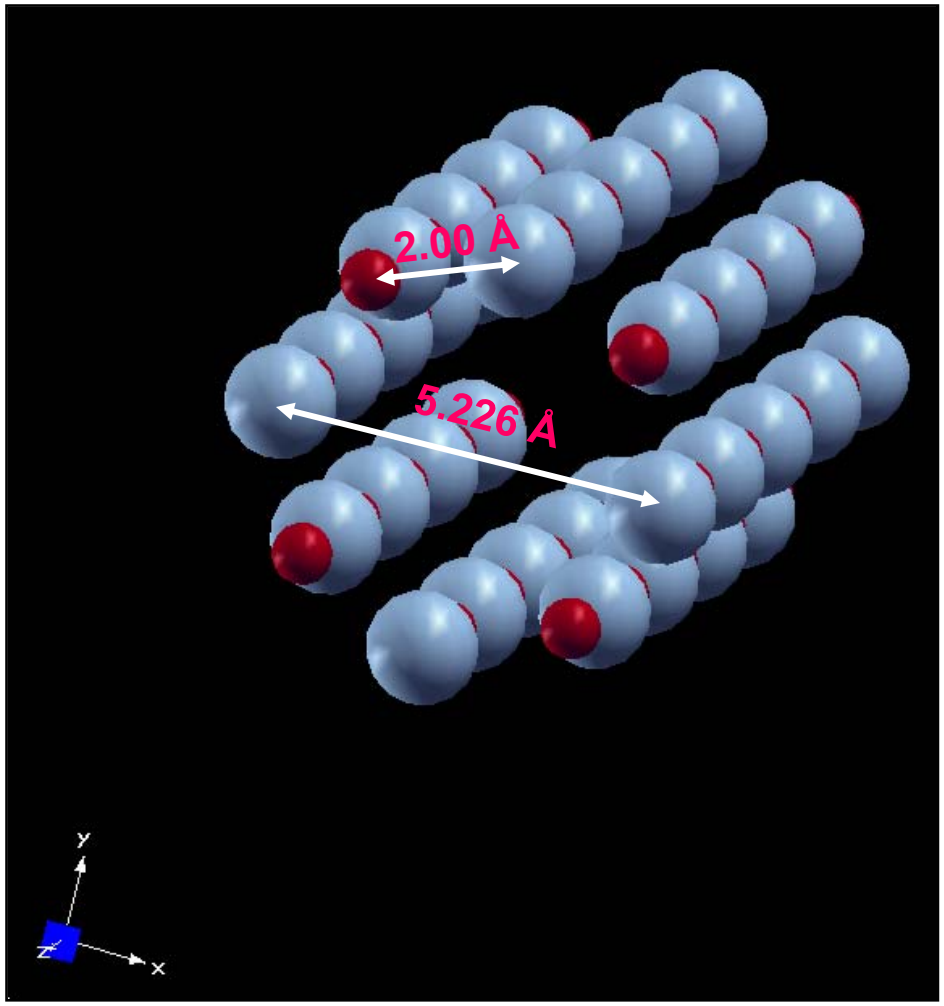
KMK (1972)

Other CuO Proxy Structures

- Studies in Progress -

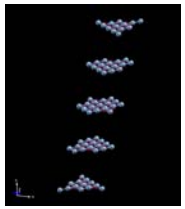
Films & Tubes





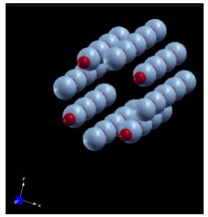
a = b = 3.905 Å
c = 6 x 3.905 = 23.43 Å

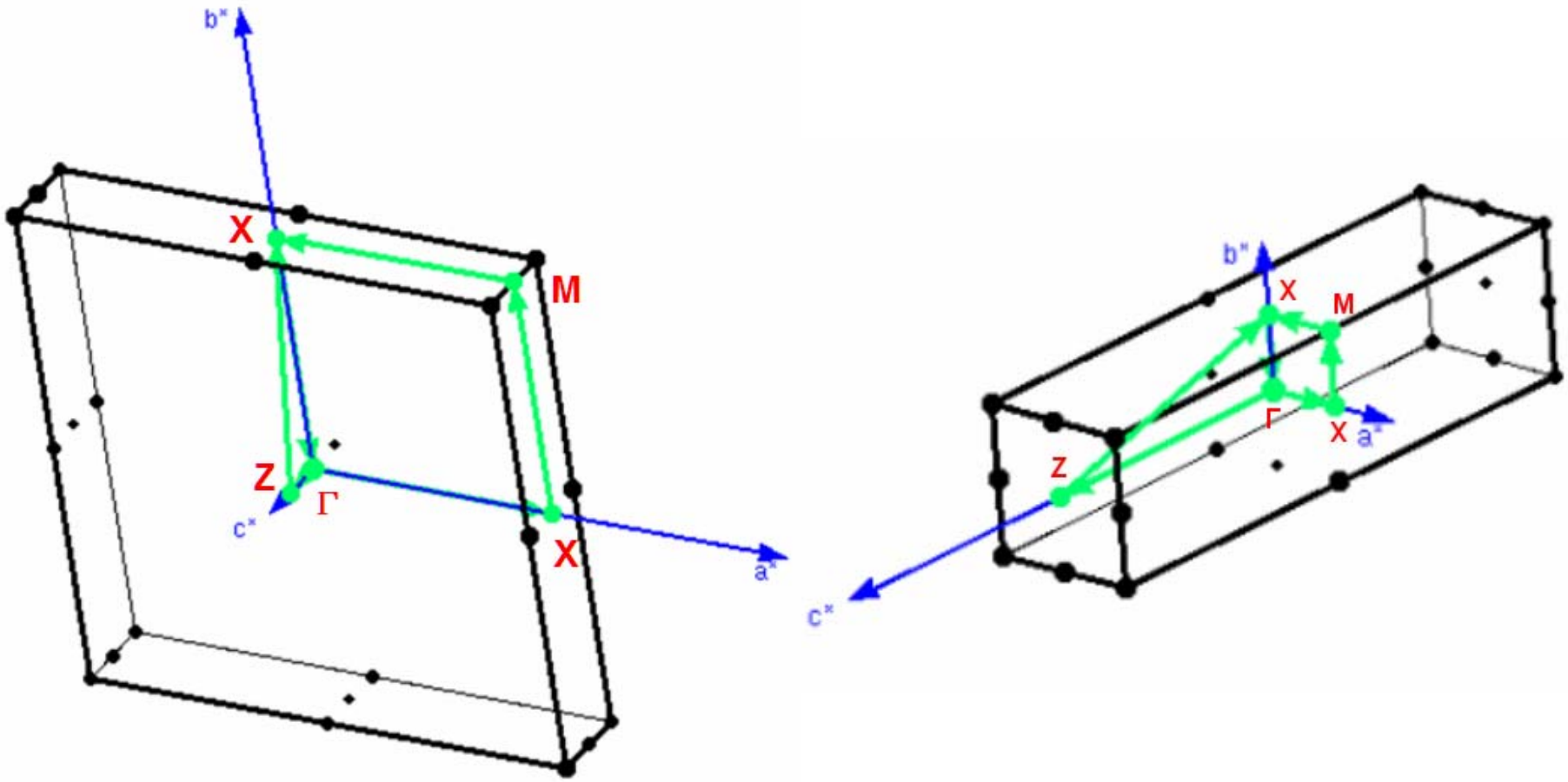
2 CuO segments per quadrant
16 Å between tubes

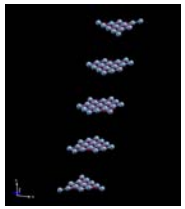


Films & Tubes

Zones







Films & Tubes

States