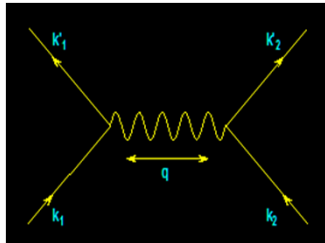
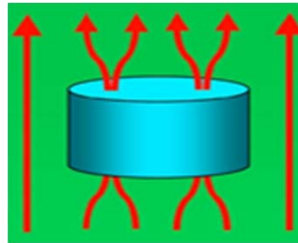


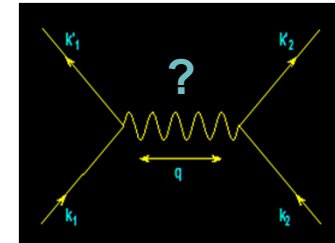
**From
Electrons
Paired**



**To
Electric
Power**



**...And...
Back
Again**



**-- A Personal Journey in Superconductivity --
-- IBM, EPRI, and Beyond --**

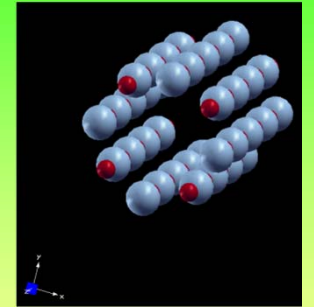
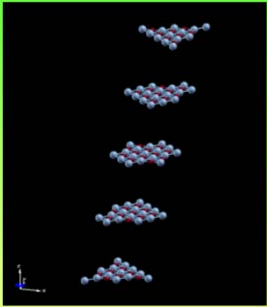
**Paul M. Grant
www.w2agz.com**

AGING IBM PENSIONER

IBM Almaden Research Center
650 Harry Road
San Jose, CA

ARC Auditorium
10:30AM – 11:30AM
Friday, 6 May 2011

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



**... And Now for
Something Completely
Different ...**

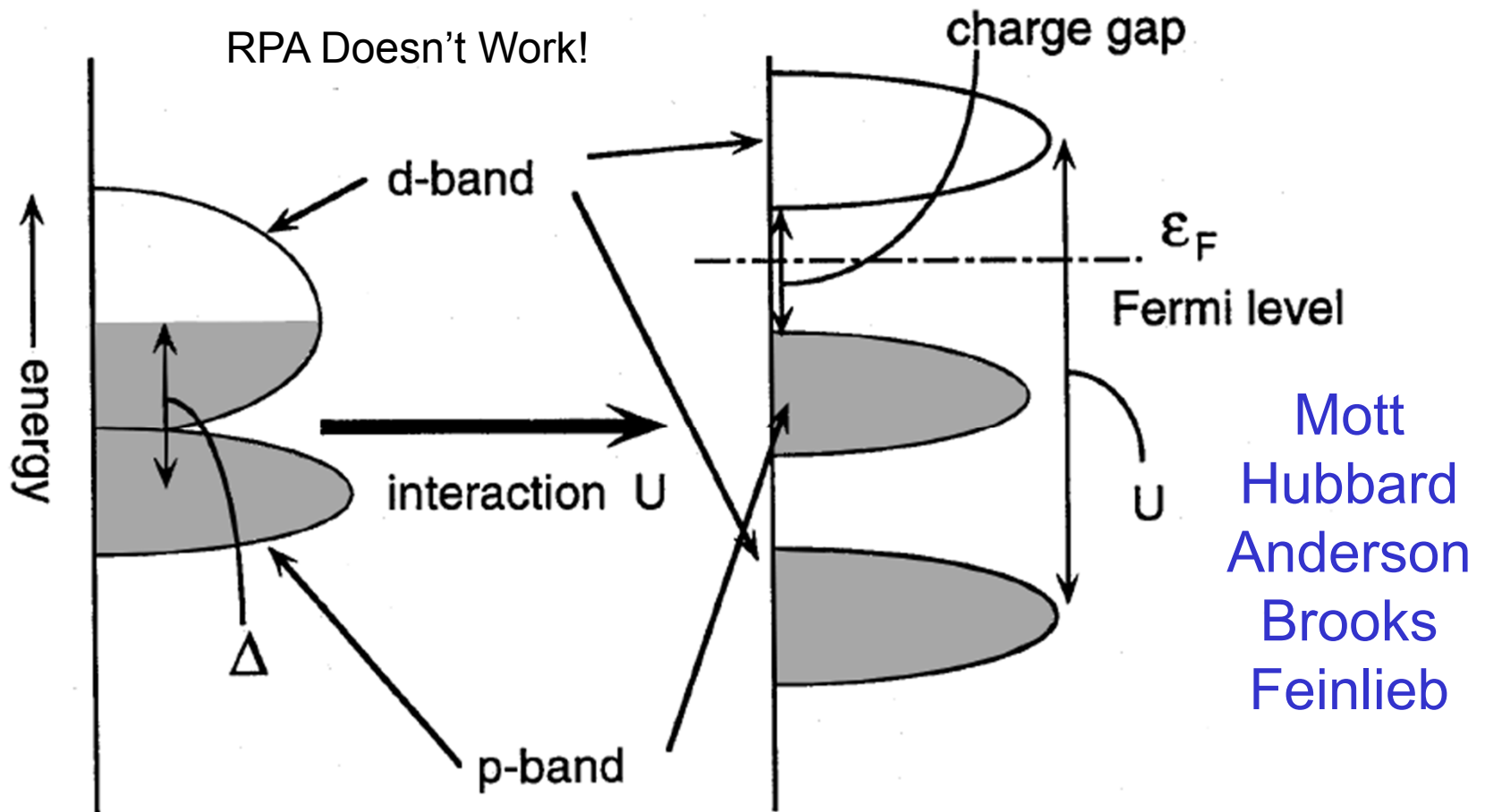
Back to the Future...

**My IBM SJRL Day Job of the 60s and 70s...
Electronic Structure Calculations**

Transition Metal Oxides

“Should be Metals, But Aren’t”

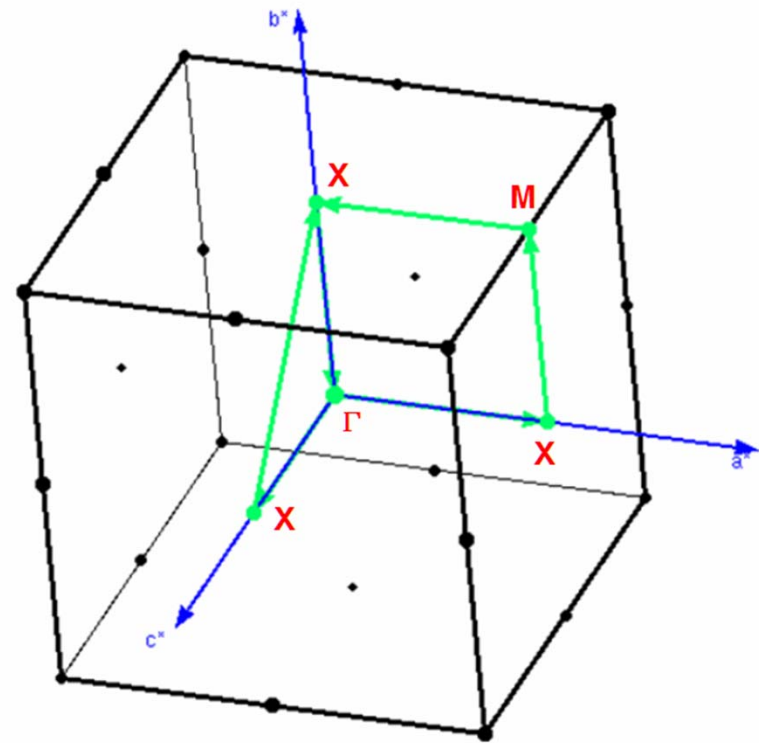
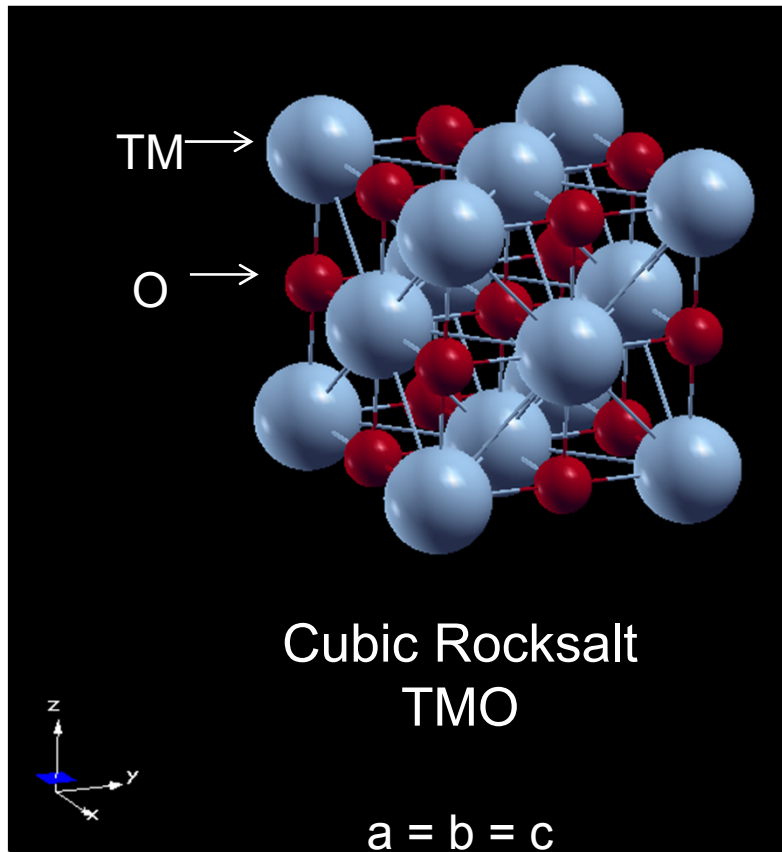
(Charge Transfer Insulators, Instead)



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

Cubic Rocksalt TMOs

Direct and Reciprocal Lattices



Cubic Rocksalt Divalent TMOs

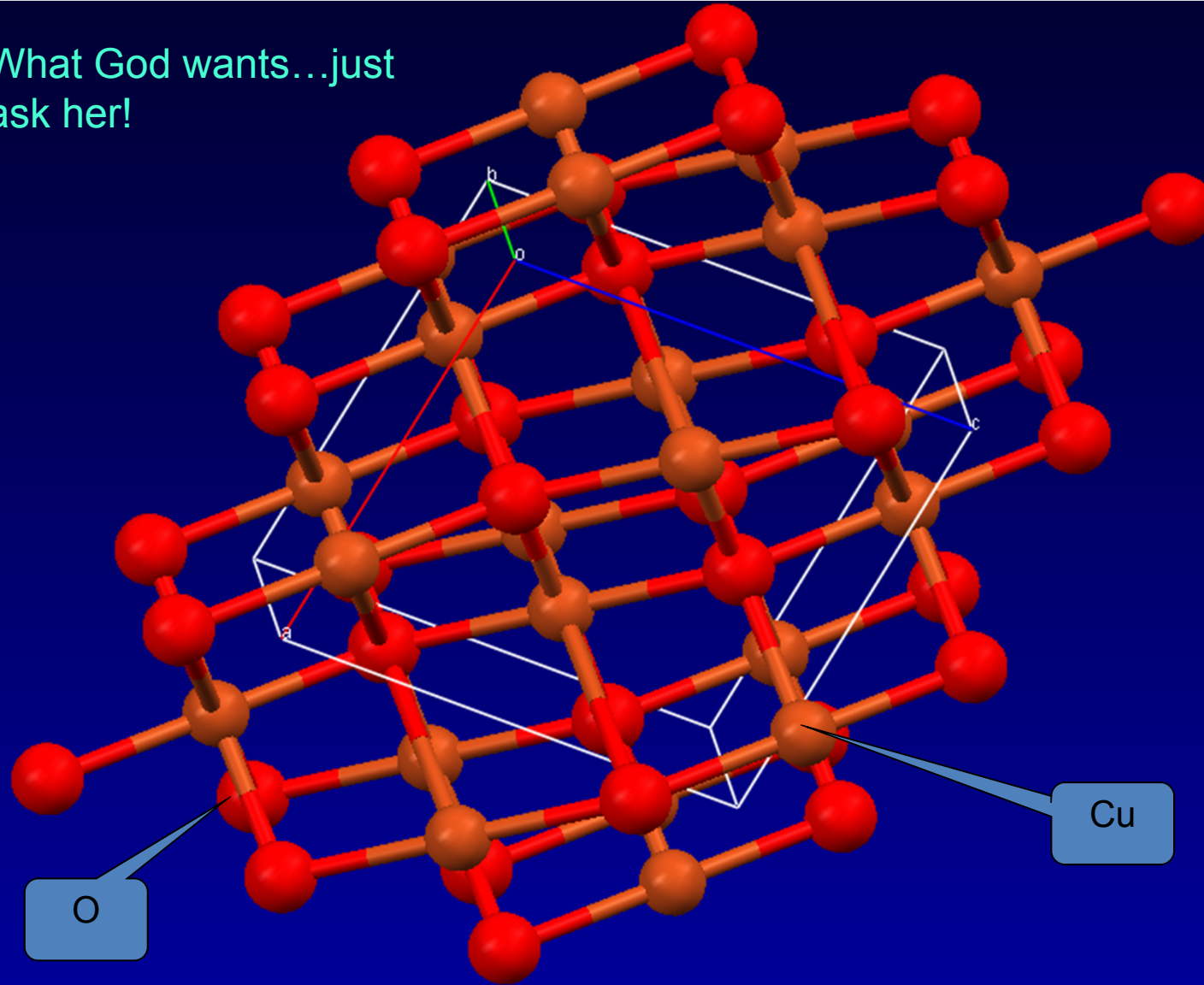
<u>TMO</u>	<u>3d Config</u>	<u>Properties</u>
MnO	5	MH-CTI (5.6)
FeO	6	MH-CTI (5.9)
CoO	7	MH-CTI (6.3)
NiO	8	MH-CTI (6.5)
CuO	9	<i>XX Doesn't Exist!</i>

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

Why Not?

Tenorite (Monoclinic CuO)

What God wants...just ask her!



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

...Let's see...

DFT & (LDA + U)

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

- Implemented in LMTO by Anisimov, et al, JPCM 2, 3973 (1990)
 - Applied to NiO, MnO, FeO, CoO and La₂CuO₄
- 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>

Proxy Structures

A New Materials Science Discipline

- You want to understand the basic physics of some given system...(e.g., HTSCs)
- So try to synthesize a simple proxy...(e.g., rocksalt CuO)
- But “Mother Nature” won’t “agree.” (She’s a woman!)
- However, you can build it in a computer and perform various “ab initio” experiments.
- And from such, numerically calculate “observables,” e.g., “response functions.”
- Try it out...it’s lots of fun! And perhaps you’ll discover something as well!

Tools

QUANTUM-ESPRESSO Suite of Codes

DFT (LDA+U) plus electron-phonon

Graphics by Tone Kolalj (XCrysDen)

www.quantum-espresso.org

“Dial-in” Parameters

$G^2 = 40 \text{ Ry}$ $\rho = 320 \text{ Ry}$

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

“Smearing” = Methfessel-Paxton

Pseudopotentials: Ultrasoft, XC = Perdew-Zunger

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



Viva Italia!

Hardware

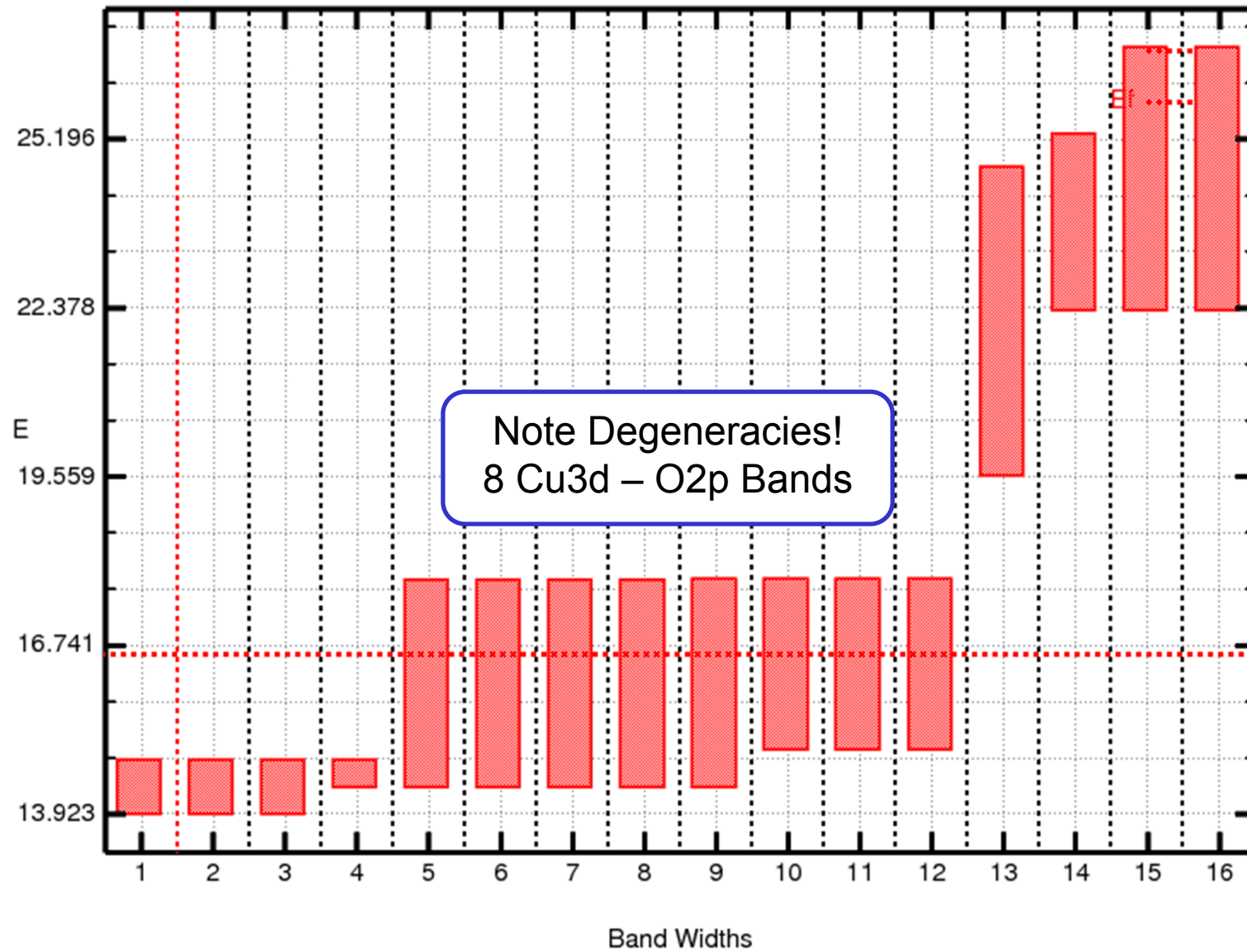
3.33 GHz Intel Core i7 – 12 GB+ (Gaming Box – Home Built)

Software

Linux Kubuntu

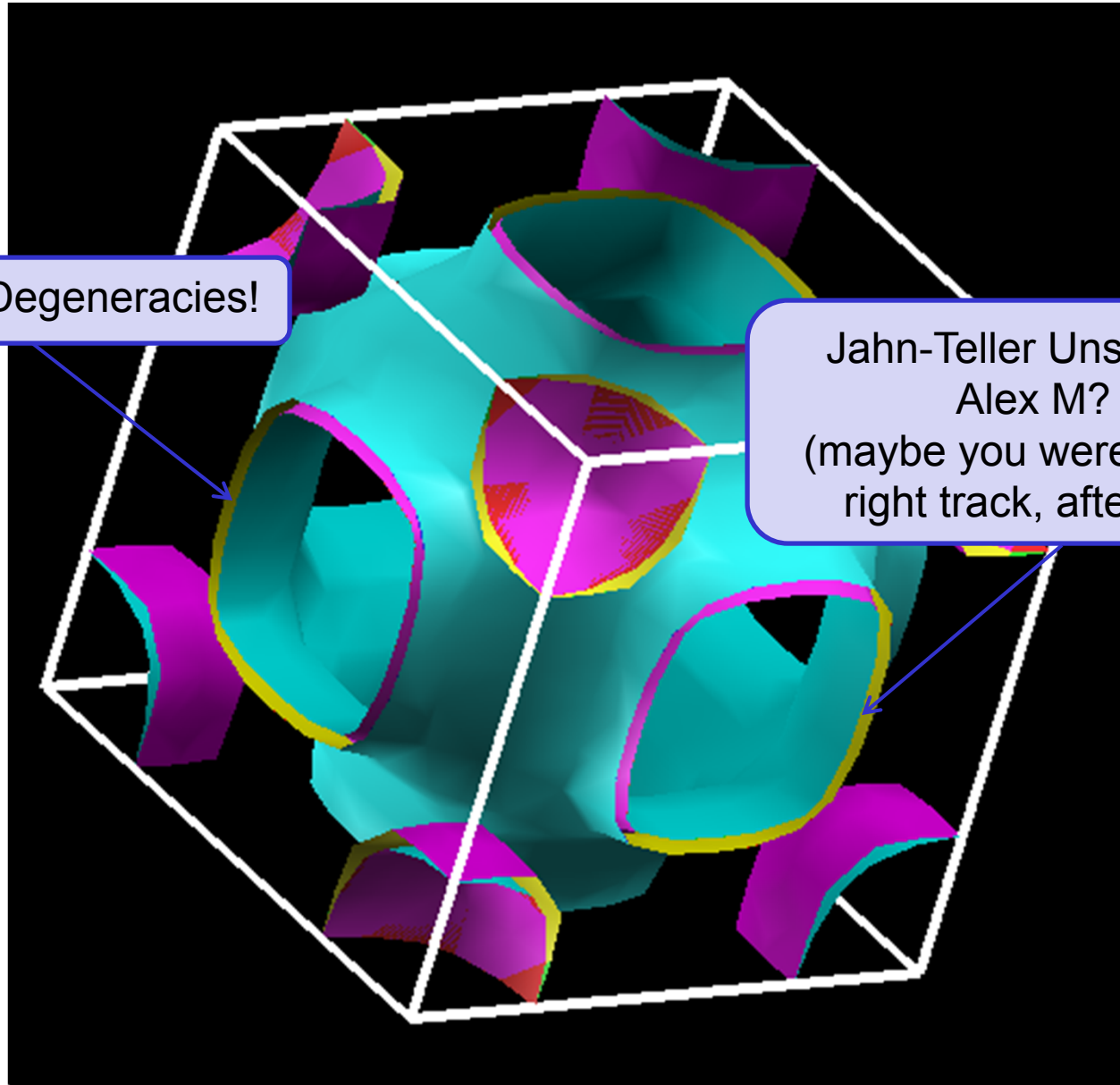
Rocksalt CuO Band Widths

$U = 0 \text{ eV}$



Rocksalt CuO Fermiology ($U = 0$ eV)

(8 Bands Combined)

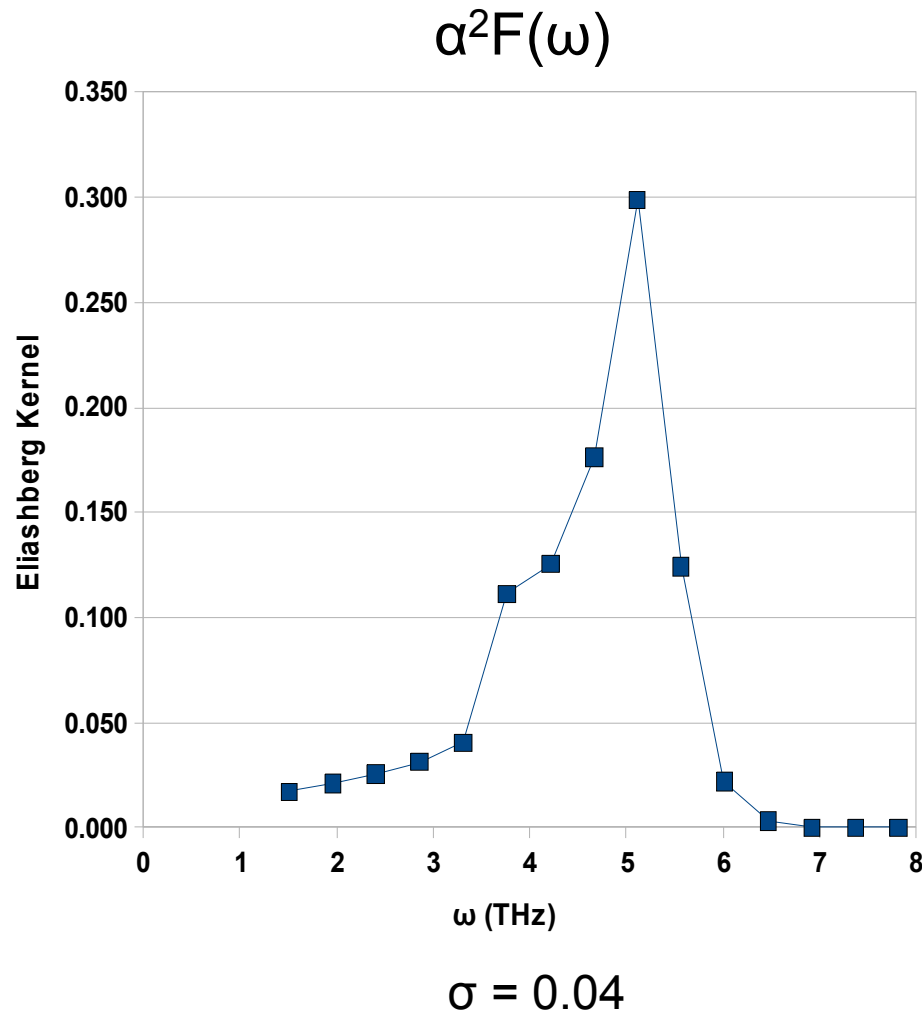


Note (Near) Degeneracies!

Jahn-Teller Unstable?
Alex M?
(maybe you were on the
right track, after all!)

Non-Magnetic ($U = 0$) Cubic Rocksalt CuO

-- Electron-Phonon Properties --



- $\lambda \sim 0.6 - 0.7$
- Consistent with other non-magnetic “HTSCs”

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

	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	-

Are There Phonons w/ High-Tc in YBCO?

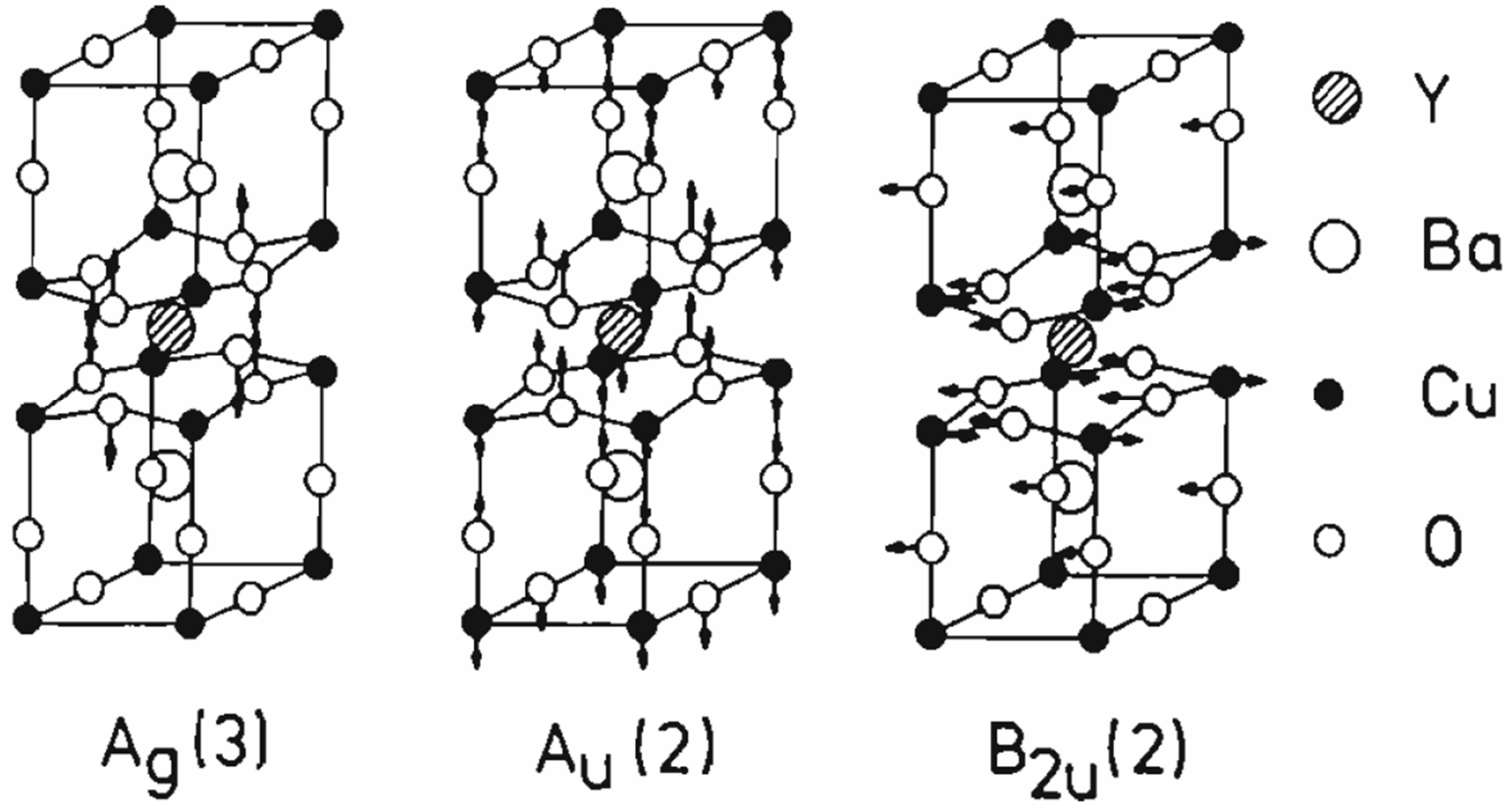
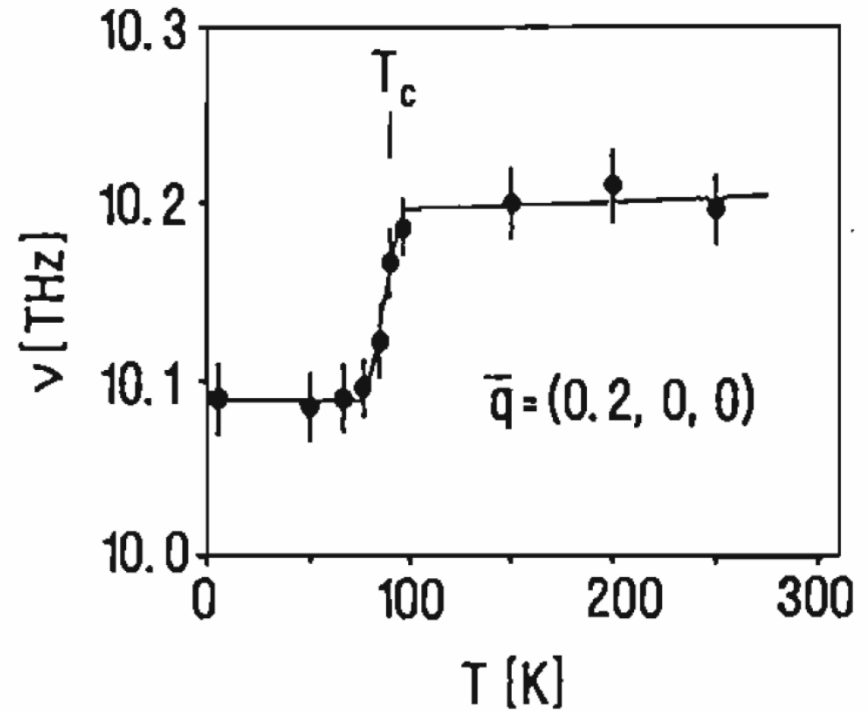
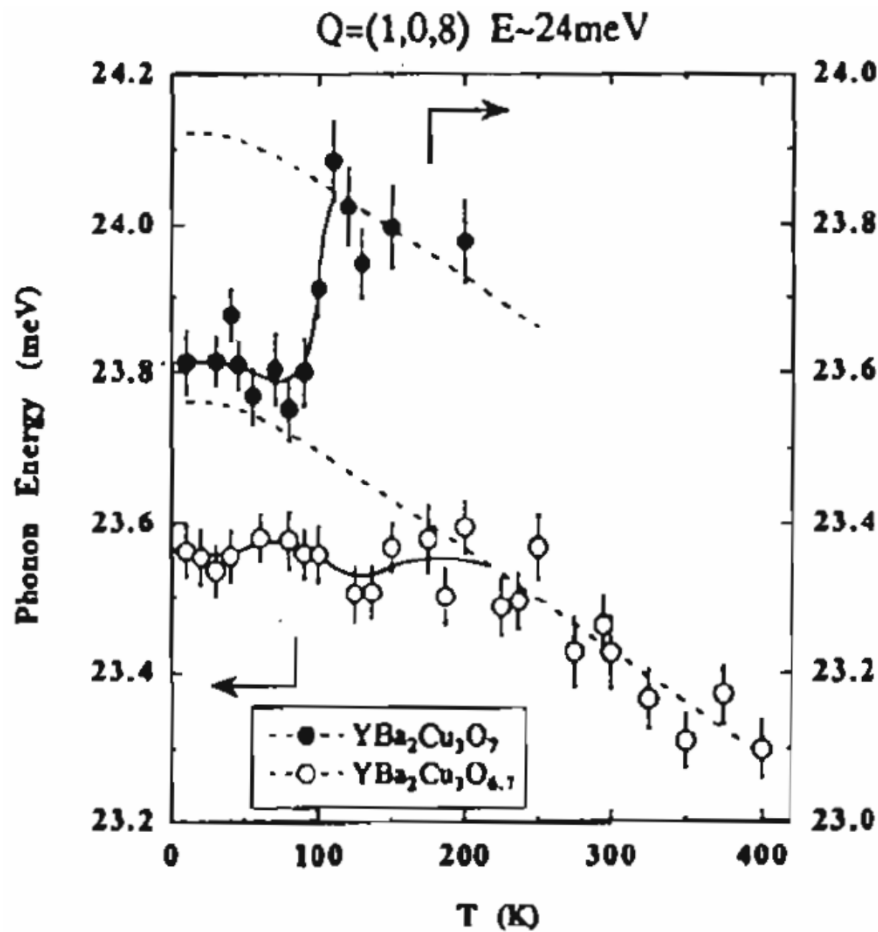


Fig. 38: Pintschovius and Reichardt, in Furrer, ISBN 0-7923-5226-2

Yes -- They're There!

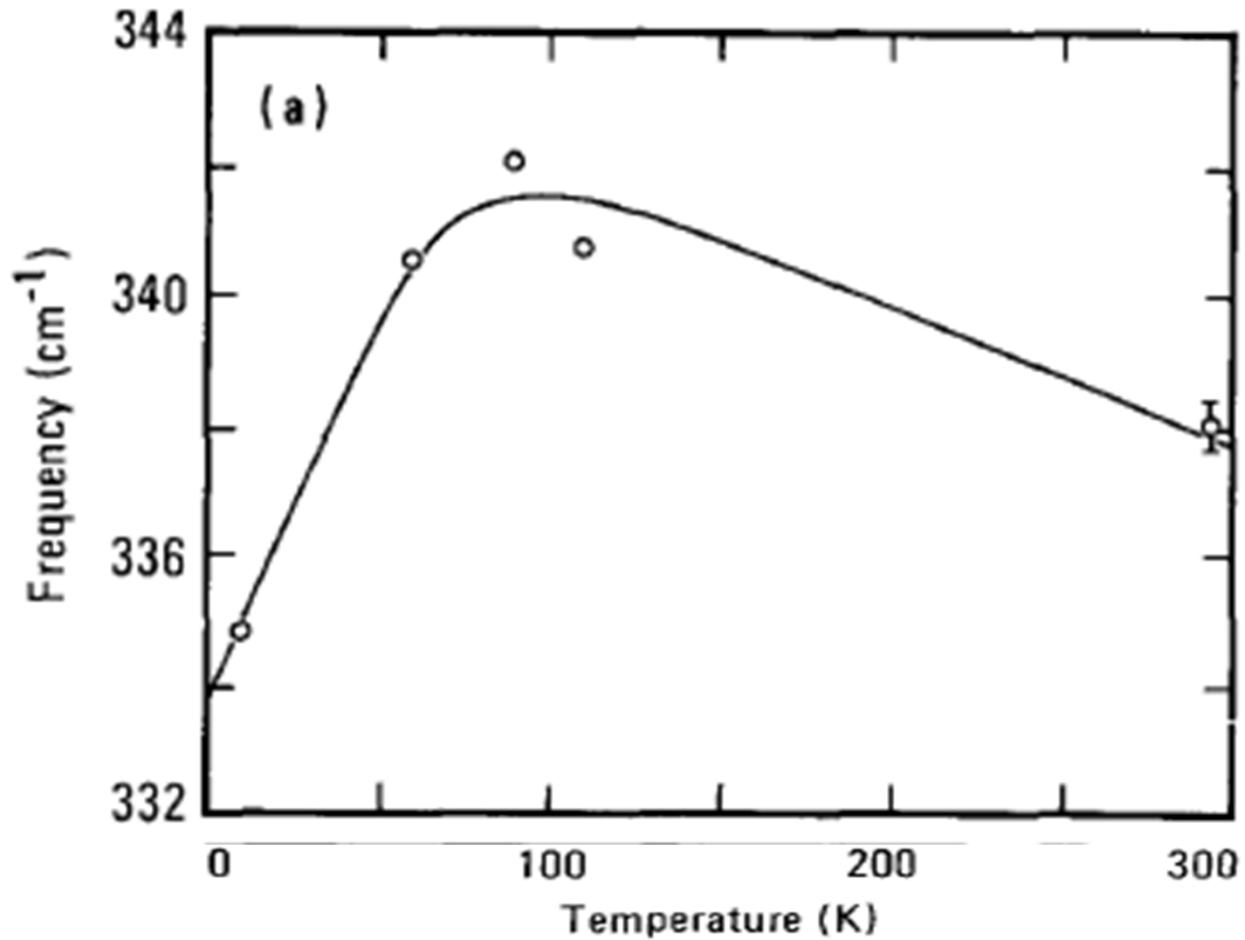


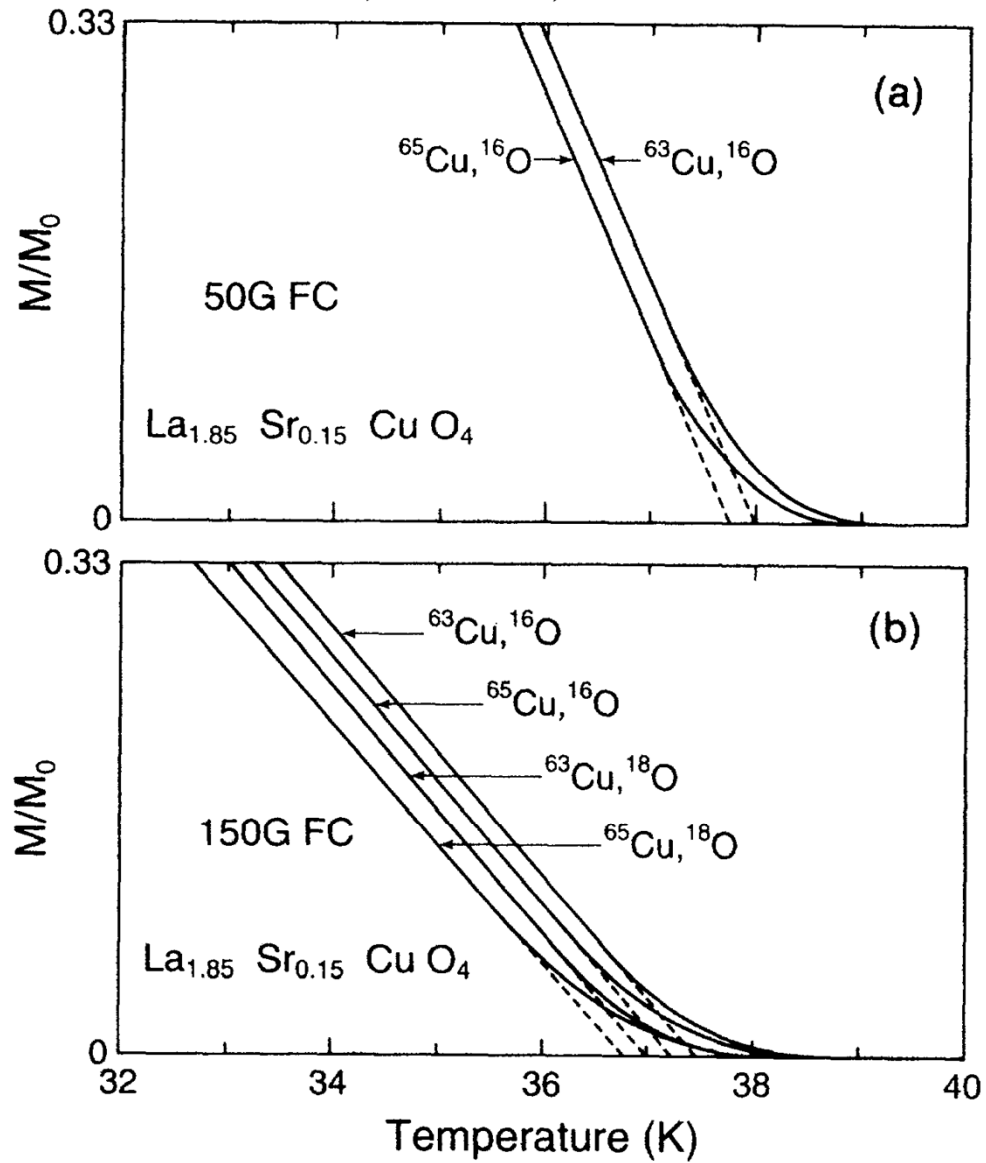
Pyka, et al., PRL 70, 1457, (1993)

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

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

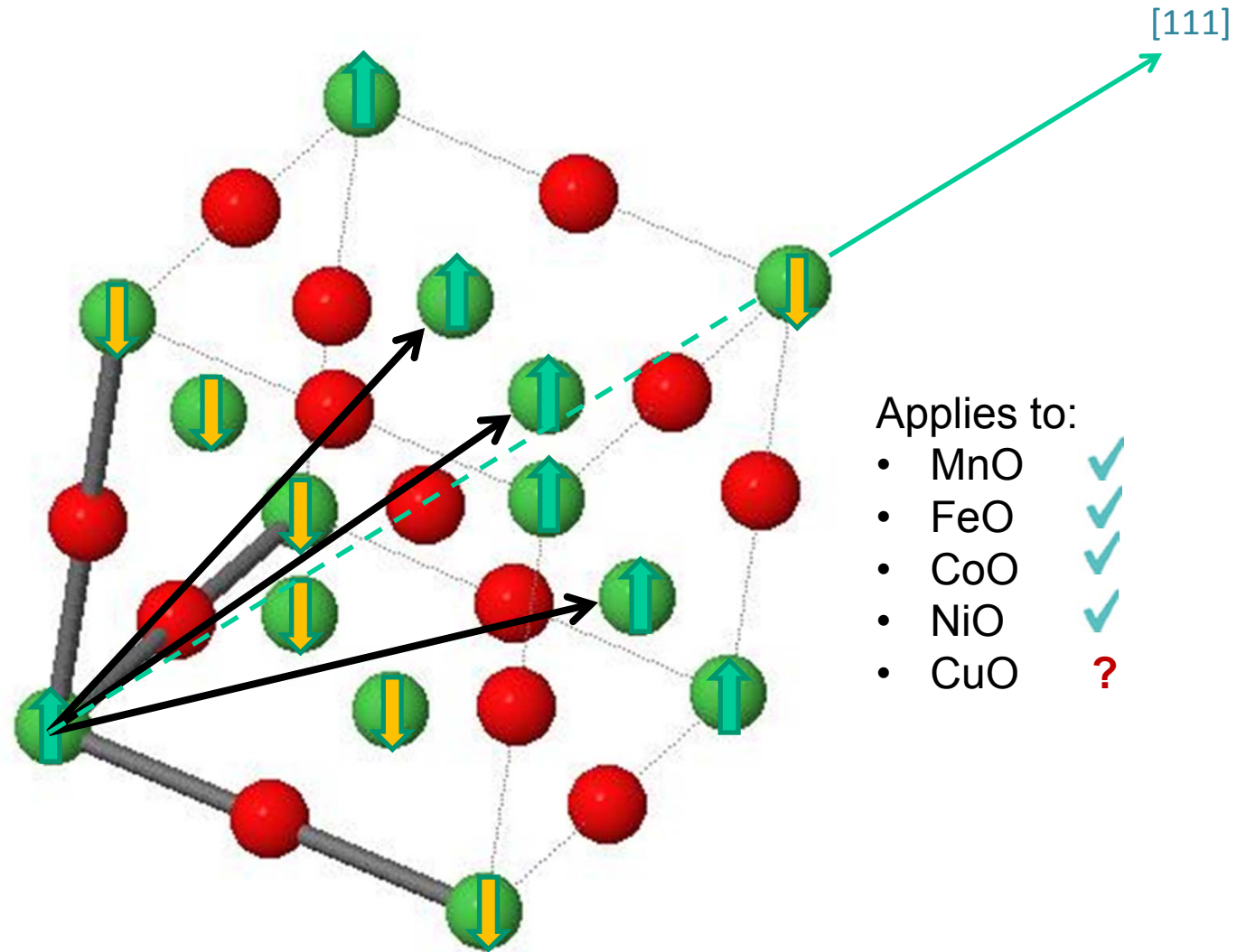
Raman Spectroscopy of YBCO



Copper and Oxygen Isotope Effects in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ J. P. Franck,¹ S. Harker,¹ and J. H. Brewer²

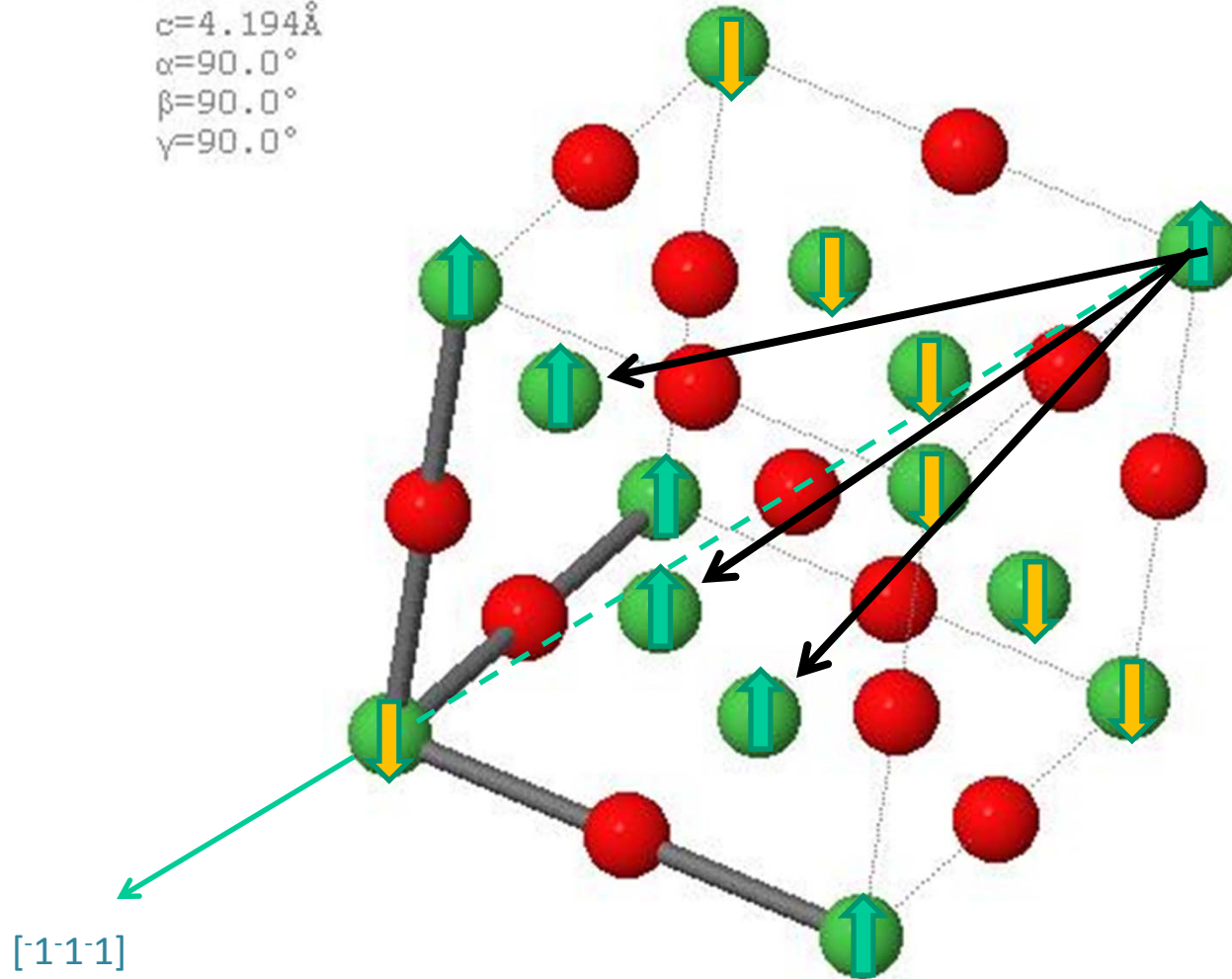
Proto-TMO AF-II Rocksalt Unit Cell

Fm-3m
a=4.194Å
b=4.194Å
c=4.194Å
α=90.0°
β=90.0°
γ=90.0°

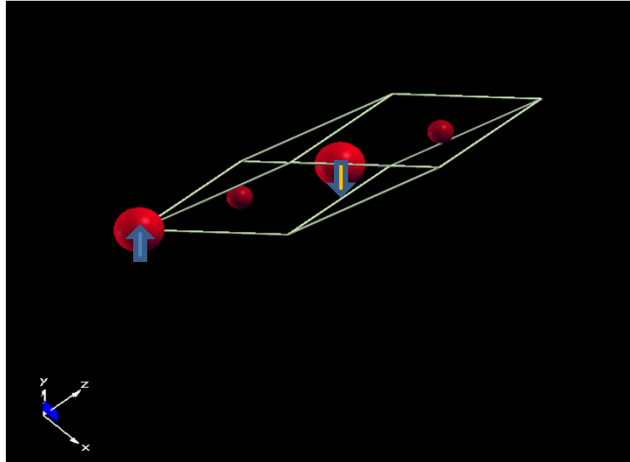


Proto-TMO AF-II Rocksalt

Fm-3m
a=4.194Å
b=4.194Å
c=4.194Å
 $\alpha=90.0^\circ$
 $\beta=90.0^\circ$
 $\gamma=90.0^\circ$



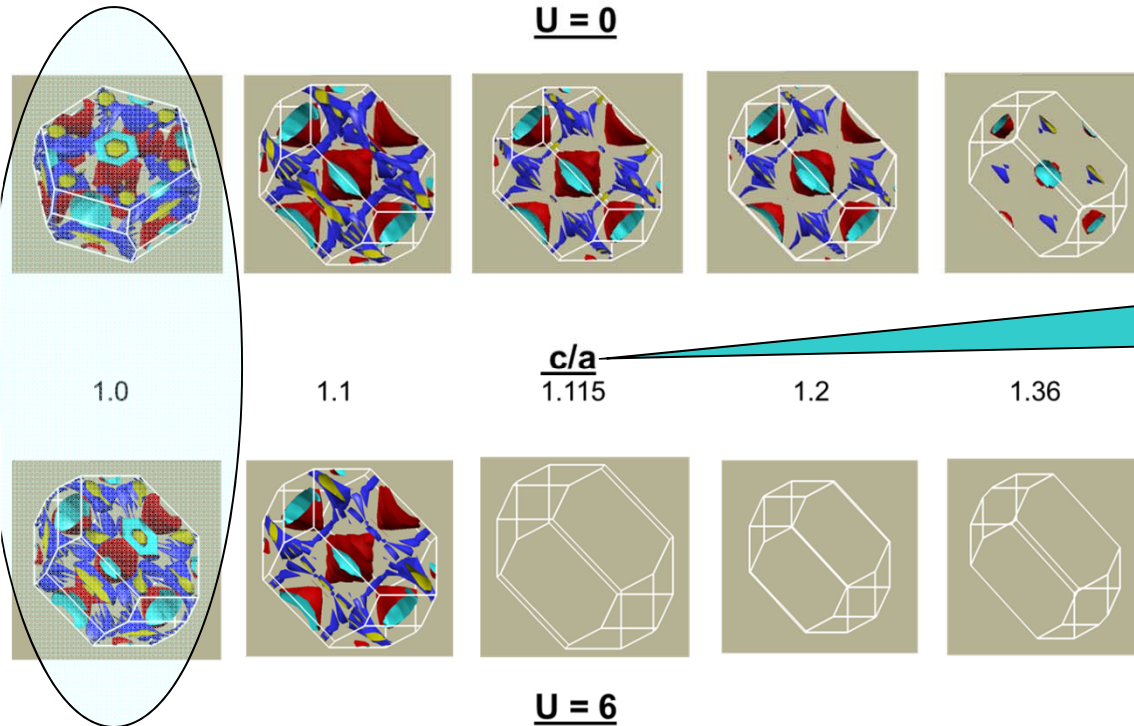
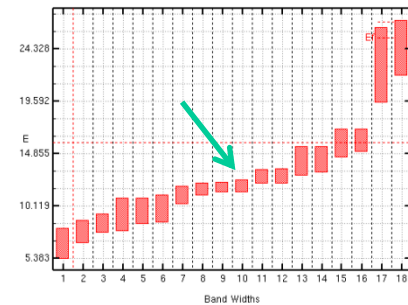
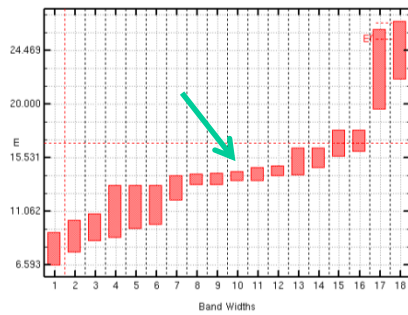
The Answer(s) !



TMO Asymmetric Type II
af-CuO Cell

LDA+U Calcs

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



U = 0

c/a
1.115

U = 6

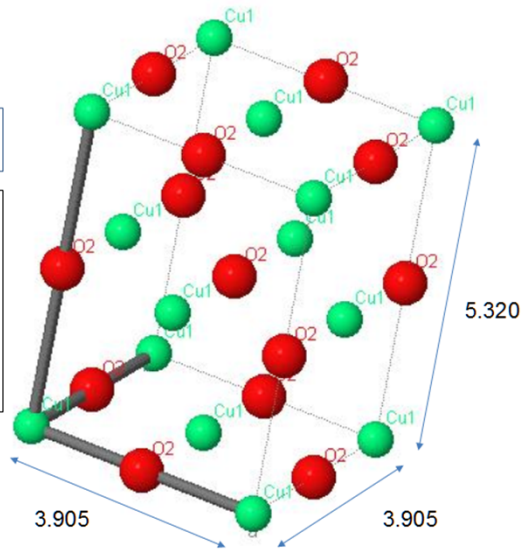
Tetragonal
Distortion

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

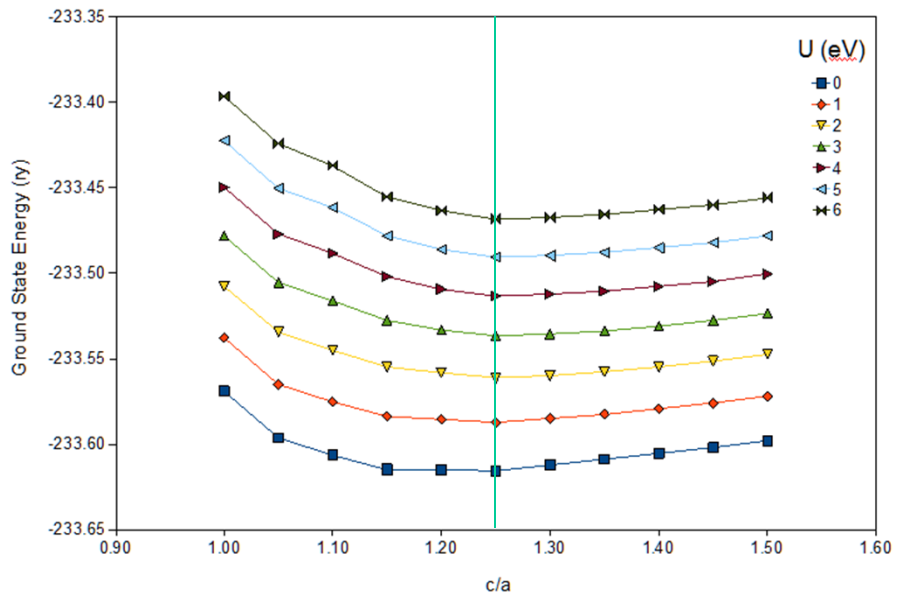
Tetragonal Rocksalt CuO

$Fm\bar{3}m$
 $a=3.905\text{\AA}$
 $b=3.905\text{\AA}$
 $c=5.320\text{\AA}$
 $\alpha=90.0^\circ$
 $\beta=90.0^\circ$
 $\gamma=90.0^\circ$
 $c/a = 1.36$

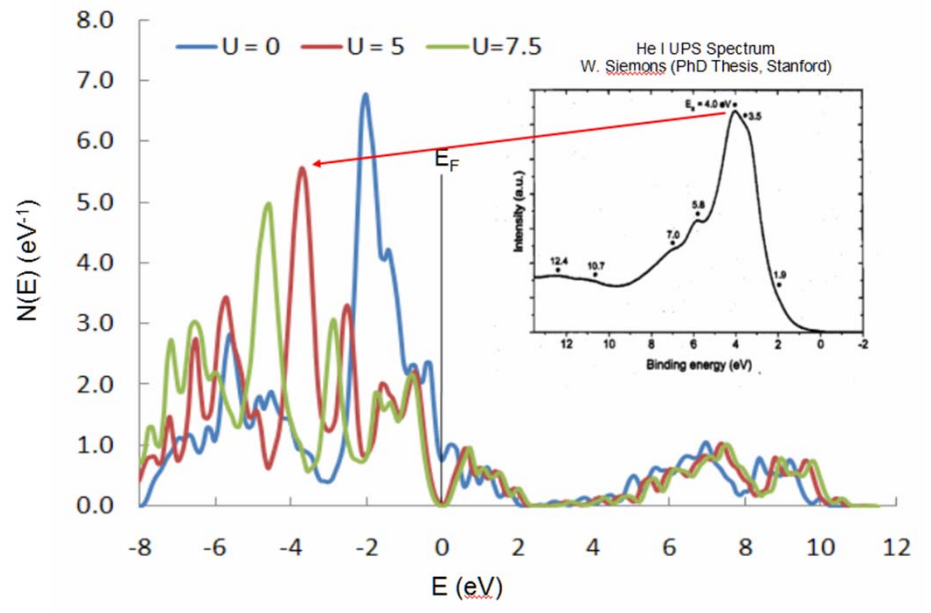
Measurements
 (Wolter Siemons)
 • 2-4 ML epi on STO
 • No Fermi Edge
 • No Exchange Bias on ferro-SRO ($T_c \sim 100-150\text{ K}$)



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)

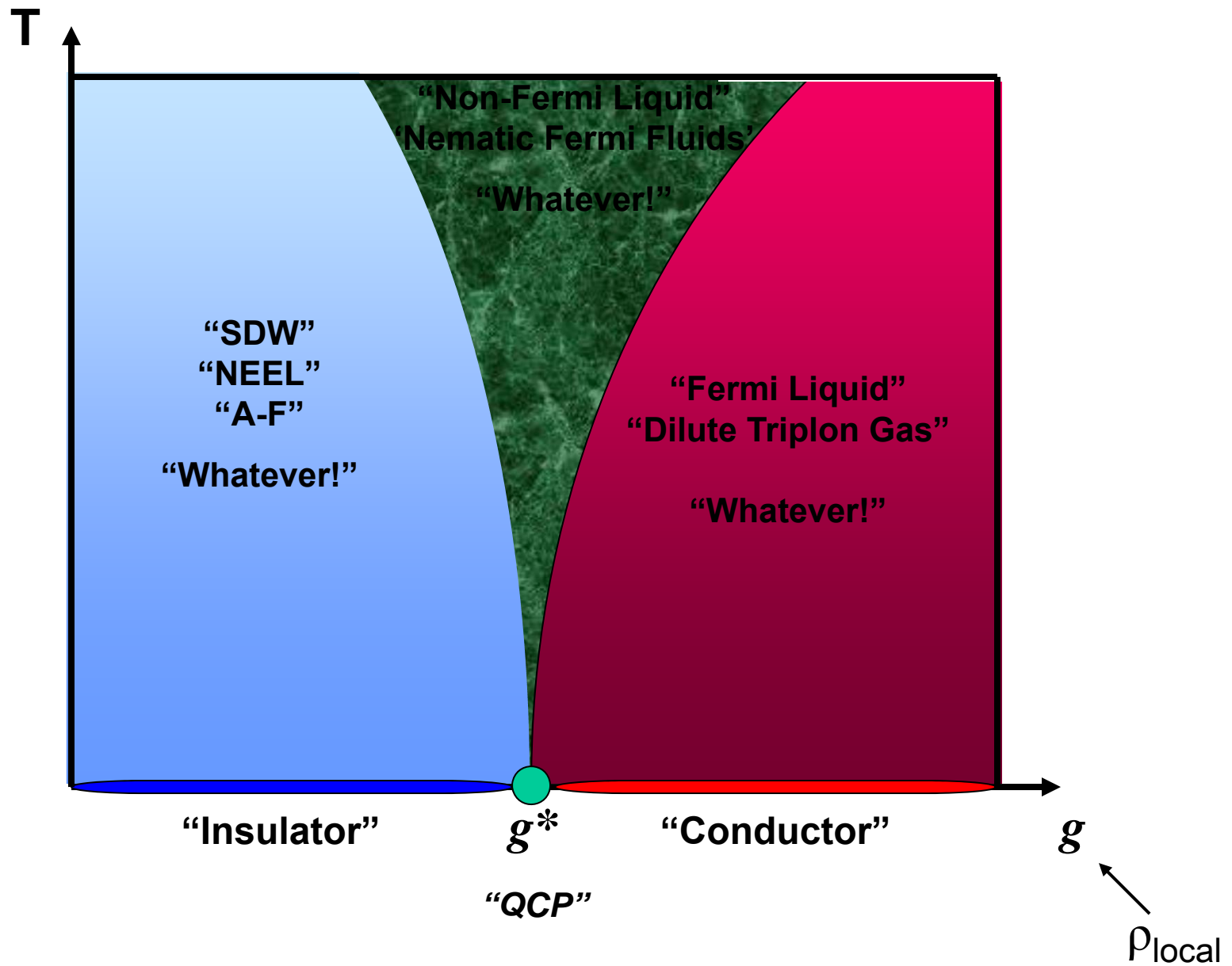
PHYSICAL REVIEW B **79**, 195122 (2009)



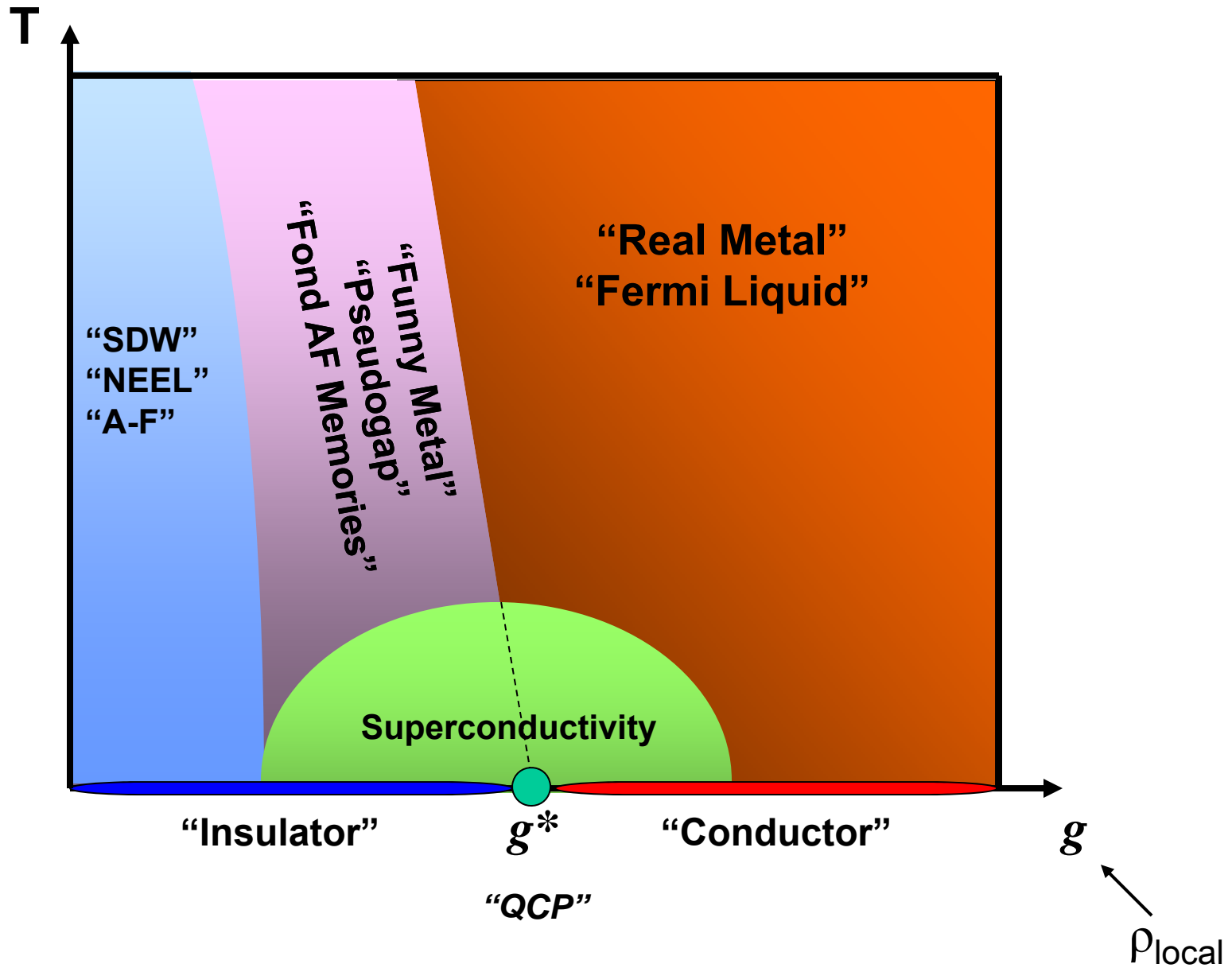
Tetragonal CuO: End member of the 3d transition metal monoxides

Wolter Siemons,^{1,2} Gertjan Koster,^{1,2,*} Dave H. A. Blank,¹ Robert H. Hammond,²
Theodore H. Geballe,² and Malcolm R. Beasley²

The Great Quantum Conundrum

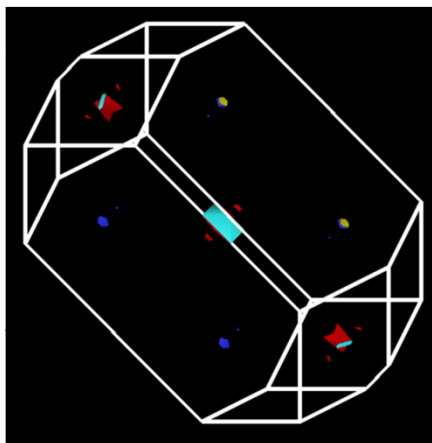
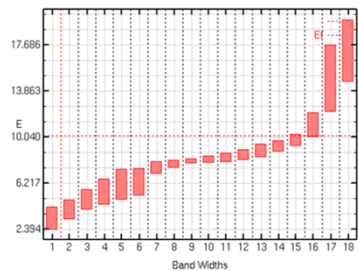


The Colossal Quantum Conundrum



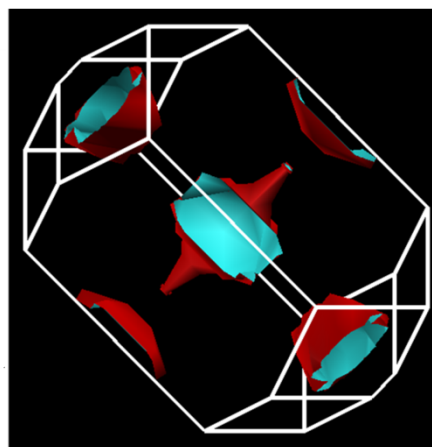
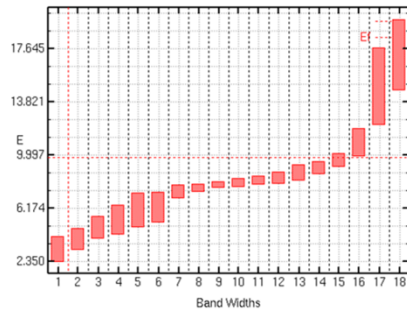
Hubbard (eV)

$U = 0$

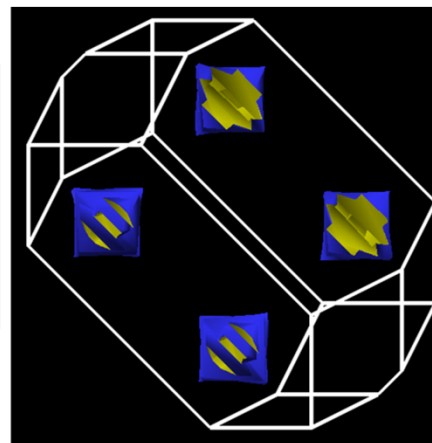
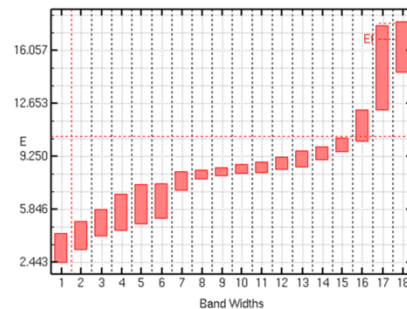


“Doping” (-e/CuO)

$n = 0.00$



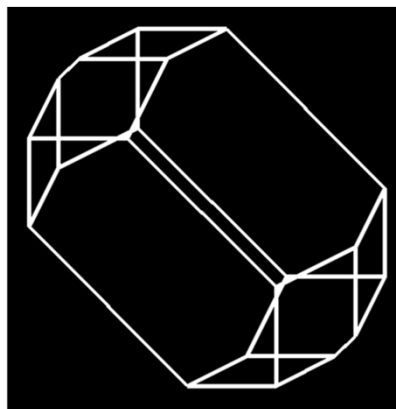
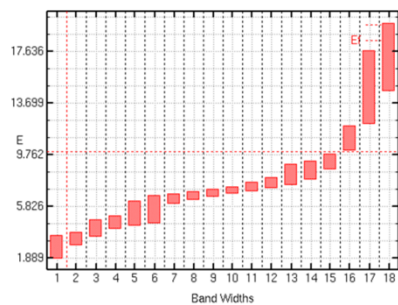
$n = +0.15$



$n = -0.15$

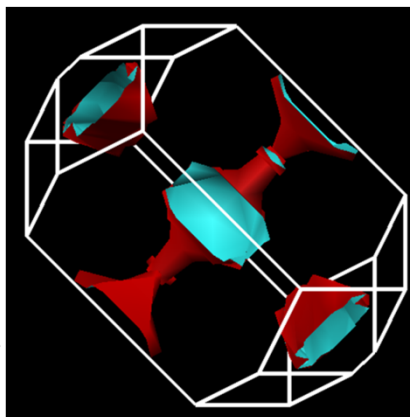
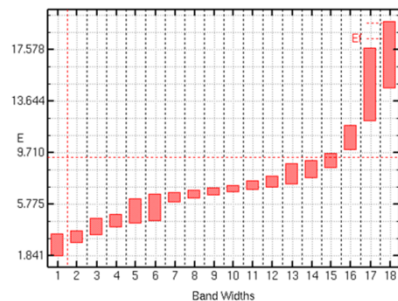
Hubbard (eV)

U = 3

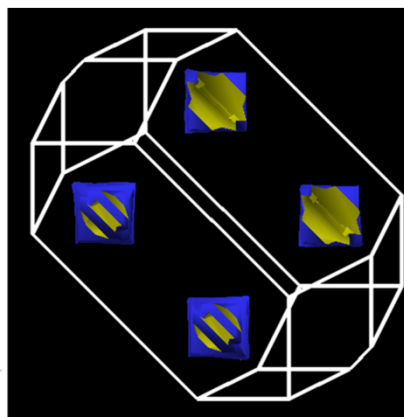
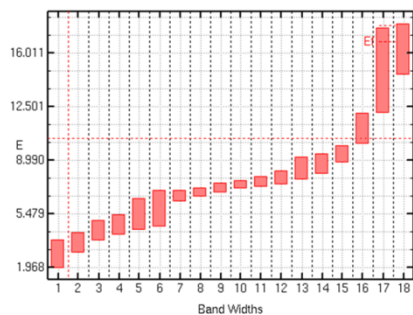


“Doping” (-e/CuO)

n = 0.00



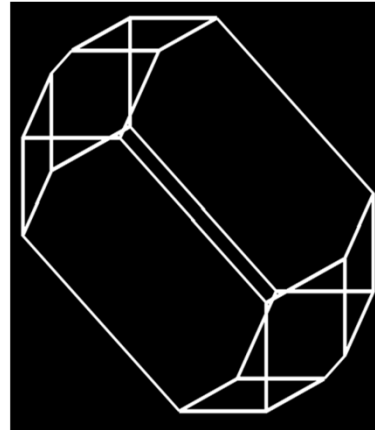
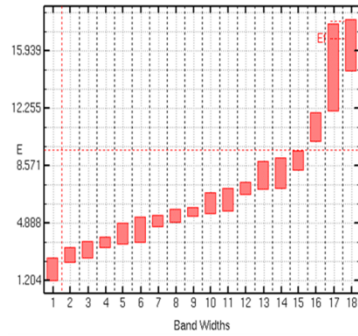
n = +0.15



n = -0.15

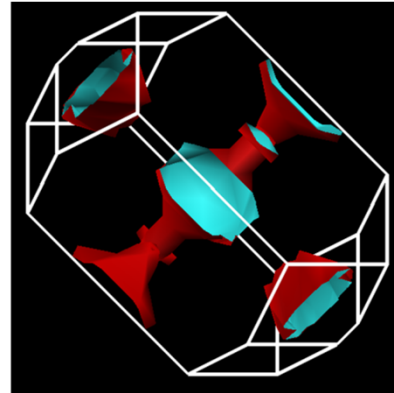
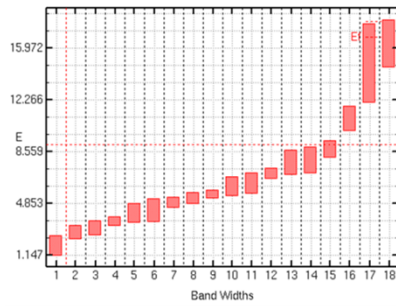
Hubbard (eV)

$U = 6$

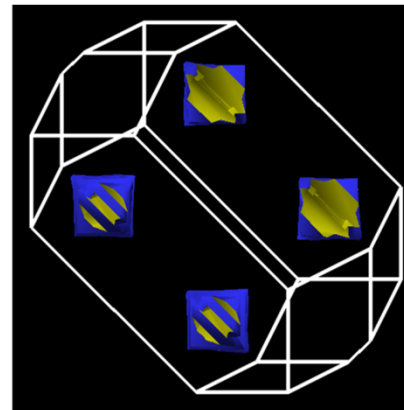
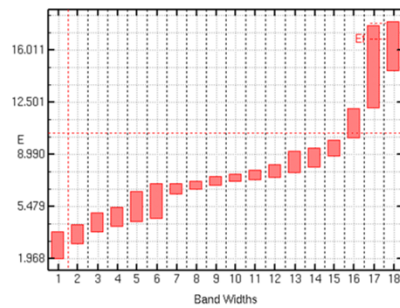


“Doping” (-e/CuO)

$n = 0.00$



$n = +0.15$



$n = -0.15$

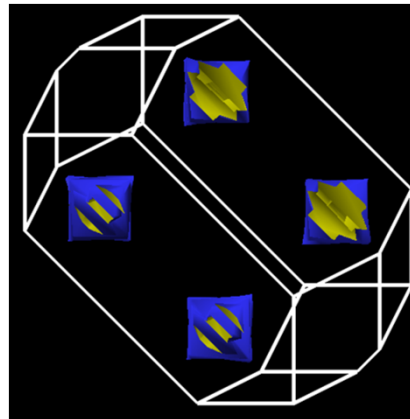
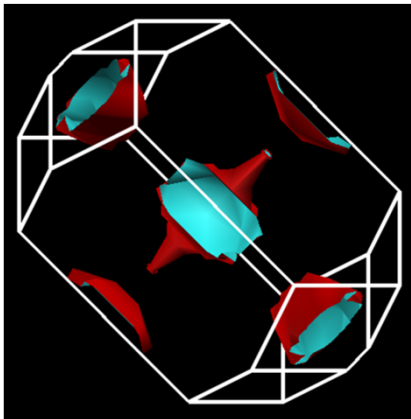
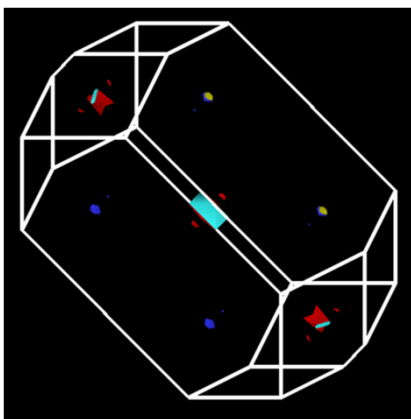
$\frac{U}{n}$

0.00

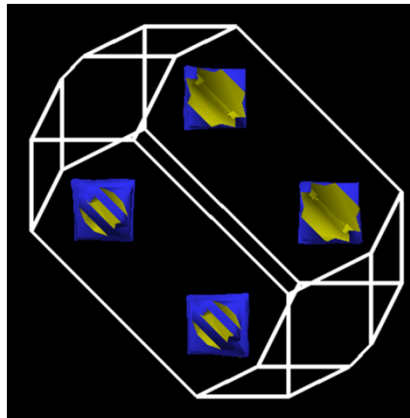
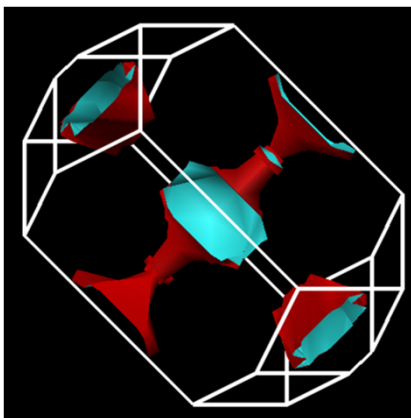
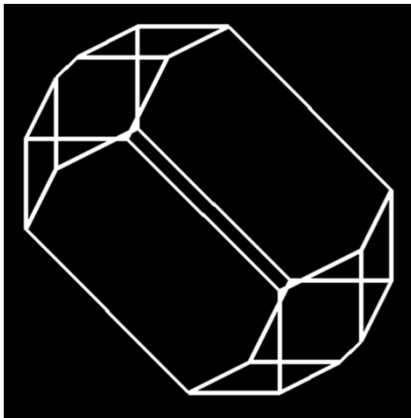
+0.15

-0.15

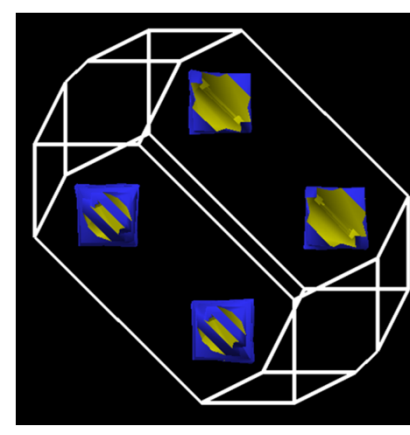
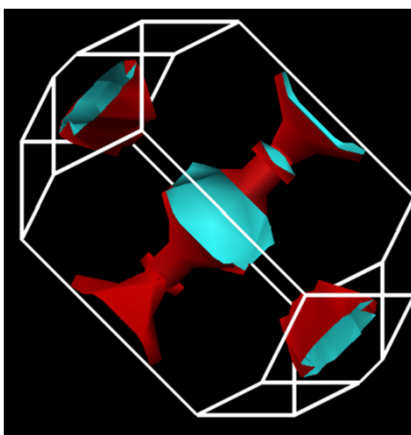
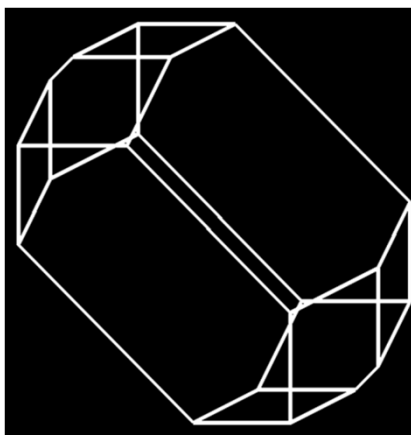
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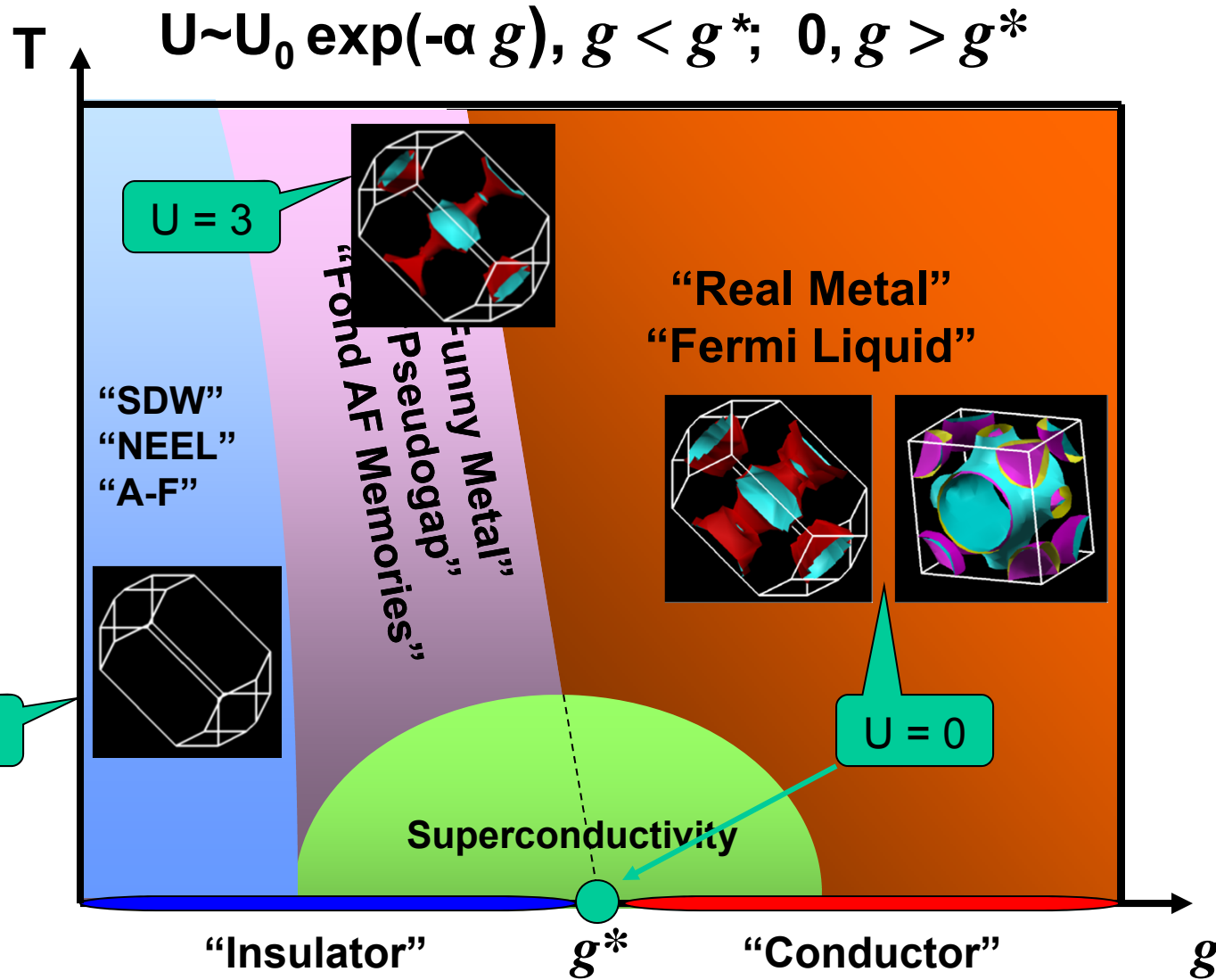
3



6



The Colossal Quantum Conundrum



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)

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

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

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

where the integral $\int d^2 p$ is taken over the Fermi surface and the electron-phonon matrix elements are given by¹⁴

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

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

$$g_{\nu}(pp') = \int \psi_p^*(\mathbf{r}_{p-p'\nu}) \nabla \mathcal{U} \psi_{p'} d\mathbf{r}. \quad (21)$$

What's the HTSC equivalent?

Generalized Linhard Function

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

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

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

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

$$\varepsilon_1(x, y) = 1 + \frac{q_{\text{TF}}^2}{8k_F^2 x^2} \left\{ 1 + \frac{1}{8x} \left[(1 + b^2 x^2 - v_+^2) \ln \left[\frac{(1 + v_+)^2 + b^2 x^2}{(1 - v_+)^2 + b^2 x^2} \right] + (1 + b^2 x^2 - v_-^2) \ln \left[\frac{(1 + v_-)^2 + b^2 x^2}{(1 - v_-)^2 + b^2 x^2} \right] \right] \right. \\ \left. - \frac{b}{2} \left\{ v_+ \left[\arctan \left[\frac{1 - v_+}{bx} \right] + \arctan \left[\frac{1 + v_+}{bx} \right] \right] + v_- \left[\arctan \left[\frac{1 - v_-}{bx} \right] + \arctan \left[\frac{1 + v_-}{bx} \right] \right] \right\} \right\}$$

where

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

“Fluctuations?”
“Empirical?”

HO (1989)

Dielectric Response Function

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

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

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

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

Bottom Line

Can studying CuO proxies with DFT

+ LDA+U

+ phonons

+ spins

provide insight into the origins of High- T_C ?

I say “Yes,” but...

Size Matters...

...and I need a...

BIGGER COMPUTER!

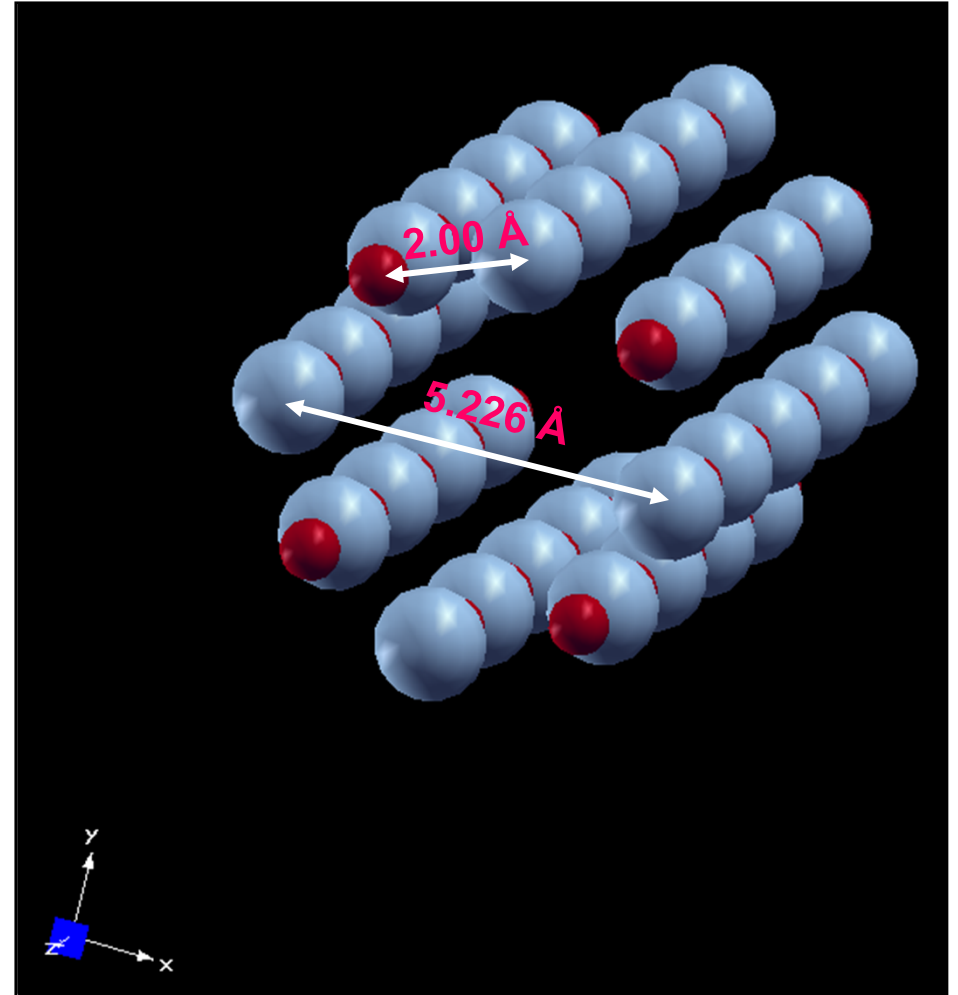
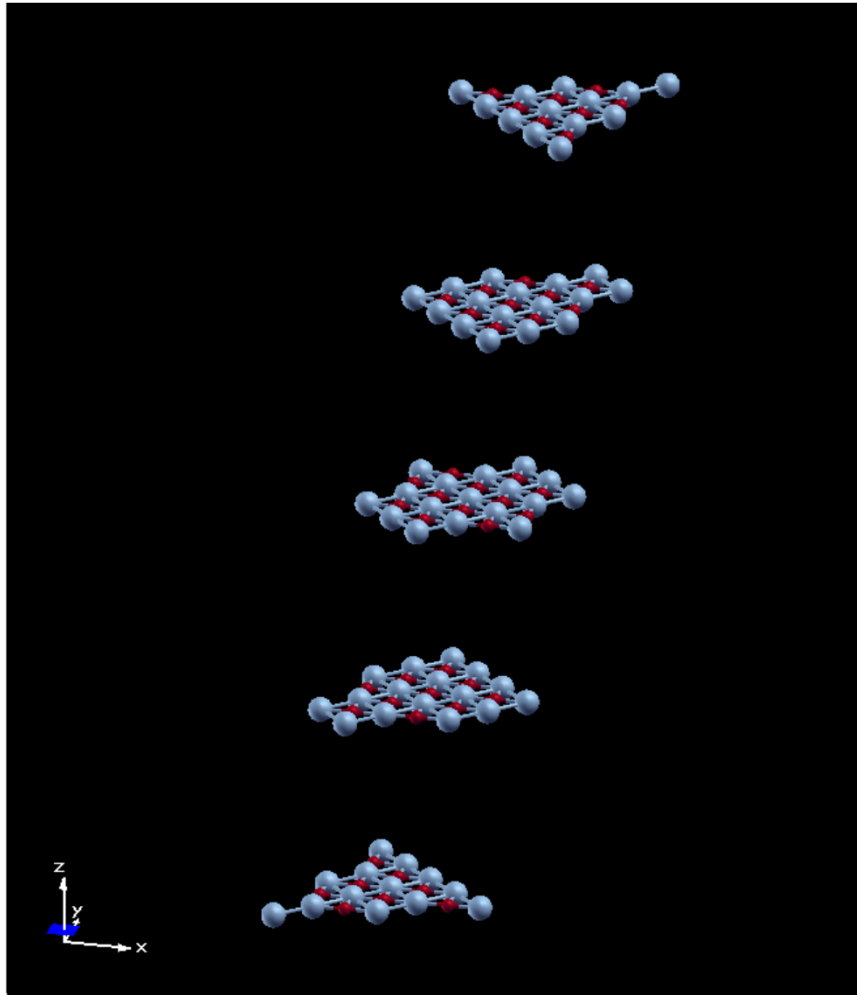
Other CuO Proxy Structures

- Studies in Progress -

Films

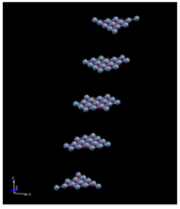
&

Tubes



$a = b = 3.905 \text{ \AA}$
 $c = 6 \times 3.905 = 23.43 \text{ \AA}$

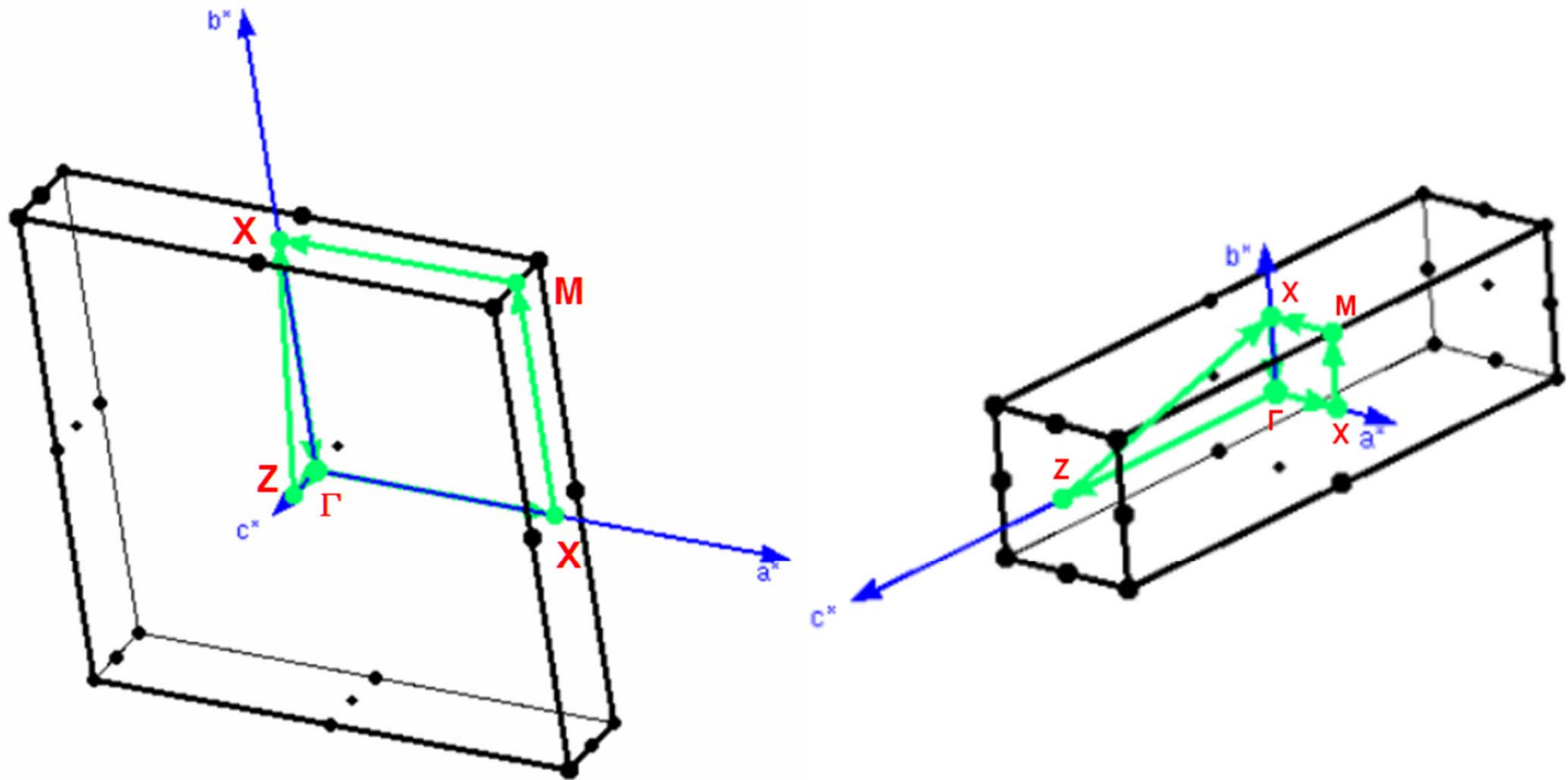
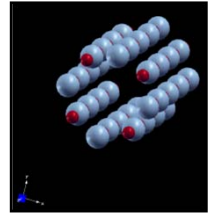
2 CuO segments per quadrant
16 \AA between tubes

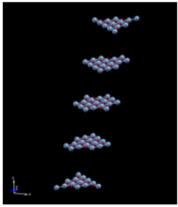


Films

&
Zones

Tubes

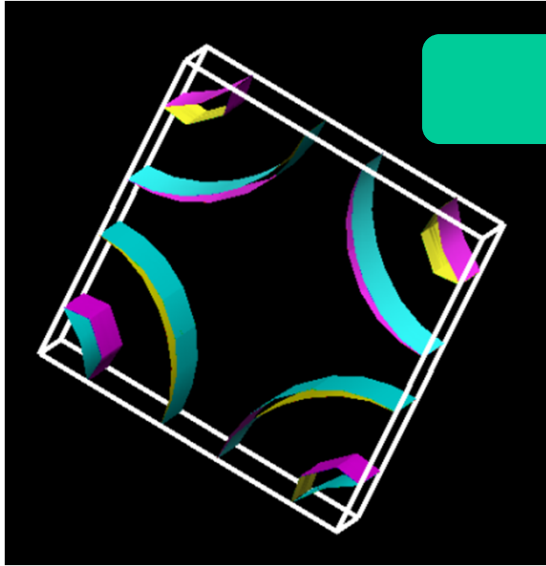
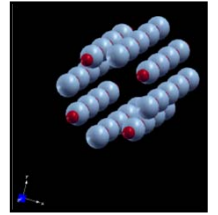




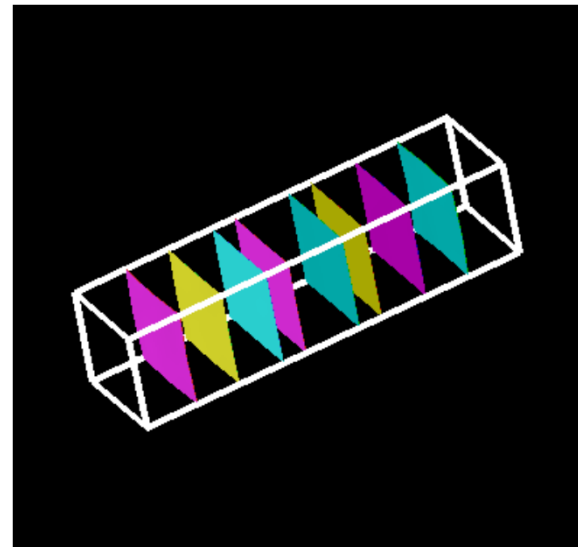
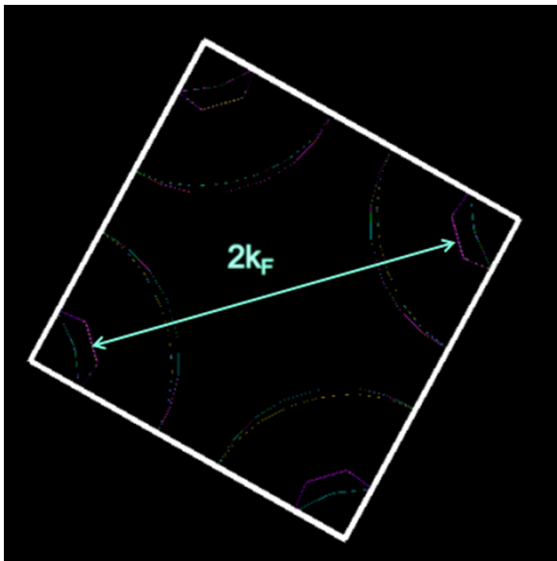
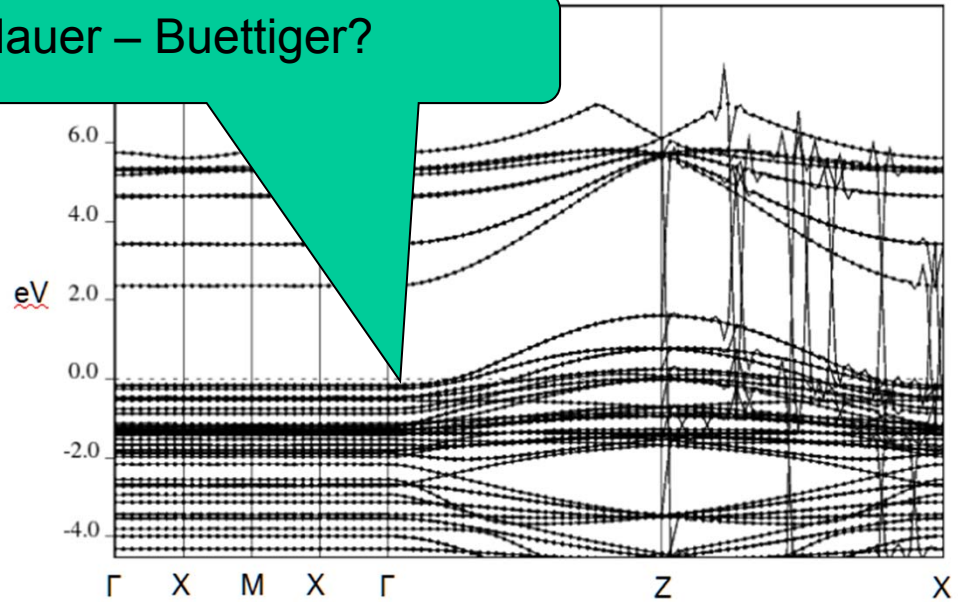
Films

&
States

Tubes



Landauer – Buettiger?



-- OK...Enough Already !

-- That's all for now !

-- But Stayed Tuned...