

Electronic Structure of Rocksalt Copper Monoxide: A Proxy for High Temperature Superconductivity

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Aging IBM Pensioner

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23 Years Ago...

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

...Still No Theory!

...at least not one everybody accepts

Agenda

- ...Still No Theory
- “Experimental Apparatus”
- Structural Issues
- Band Structure, DOS and Fermiology
- Superconductivity
- Conclusions/Homework

Theory of Everything

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

$$\mathcal{H} = - \sum_j \frac{\hbar^2}{2m_j} \nabla_j^2 - \sum_\alpha \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 - \sum_{j,\alpha} \frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \sum_{j,k} \frac{e^2}{|r_j - r_k|} + \sum_{\alpha,\beta} \frac{Z_\alpha Z_\beta e^2}{|R_\alpha - R_\beta|}$$

- | | | |
|--------------------|-----------------|------------------|
| • Hydrogen atom | • Proteins | • Flowers |
| • Methane molecule | • DNA | • Trees |
| • Water | • Viruses | • Cows |
| • Air | • Bacteria | • Cheese |
| • Rocks | • Yeast | • Sauce Bernaise |
| • Concrete | • Slime mold | • Computers |
| • Steel | • Butterflies | • Television |
| • Glass | • Sharks | • Cars |
| • Plastic | • Rats | • Jets |
| • Buildings | • Lawyers | • Lawnmowers |
| • Cities | • Ebola virus | • Sewage |
| • Continents | • Legislatures | • Spotted Oats |
| | • Civilizations | ... |

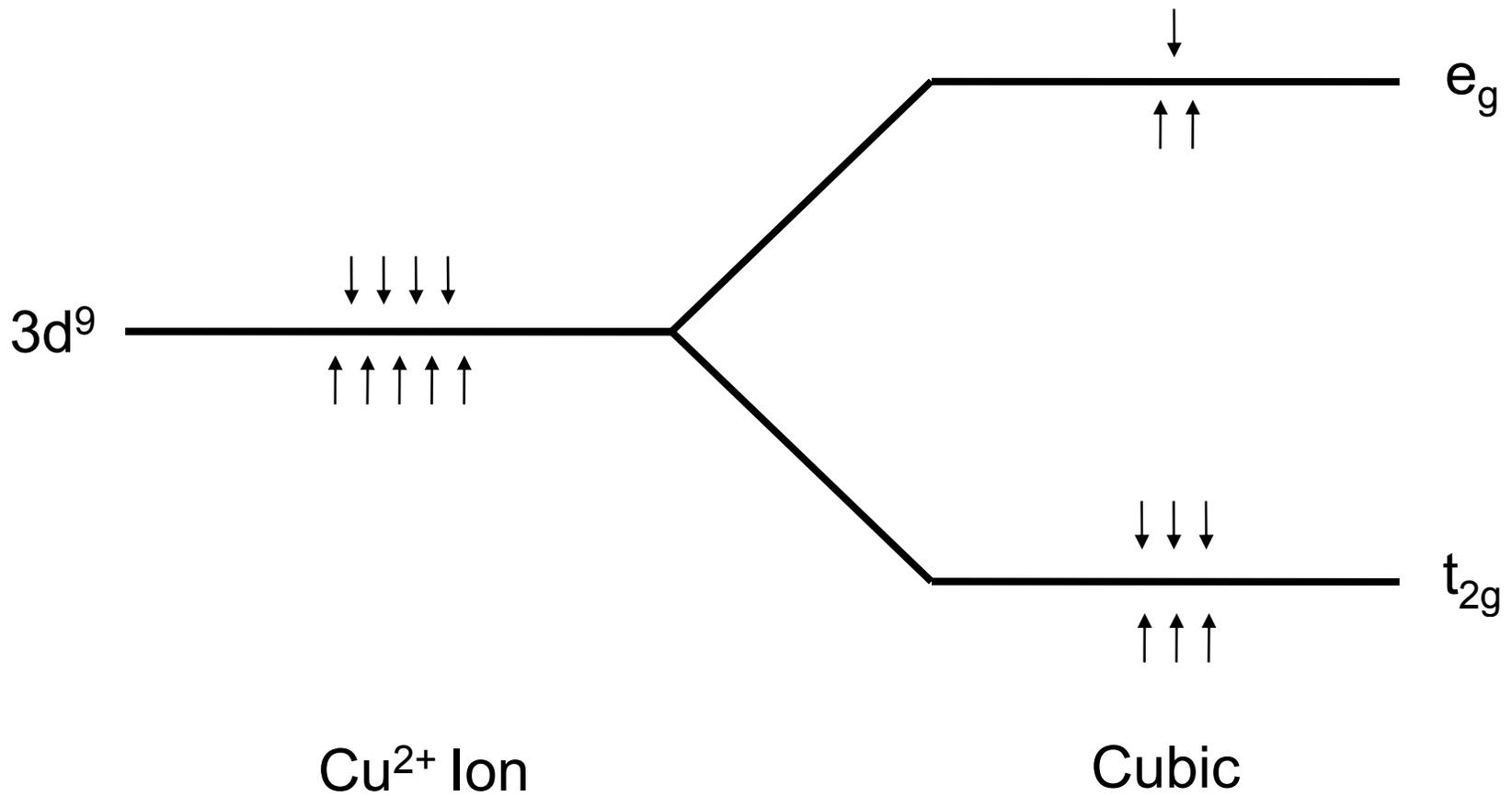
Should use the many body Dirac equation!

And Add Maxwell, Boltzman and Gibbs, and Newton

The crunch comes when \sum_i with $i \geq 3 \rightarrow$ "thermodynamic limit."

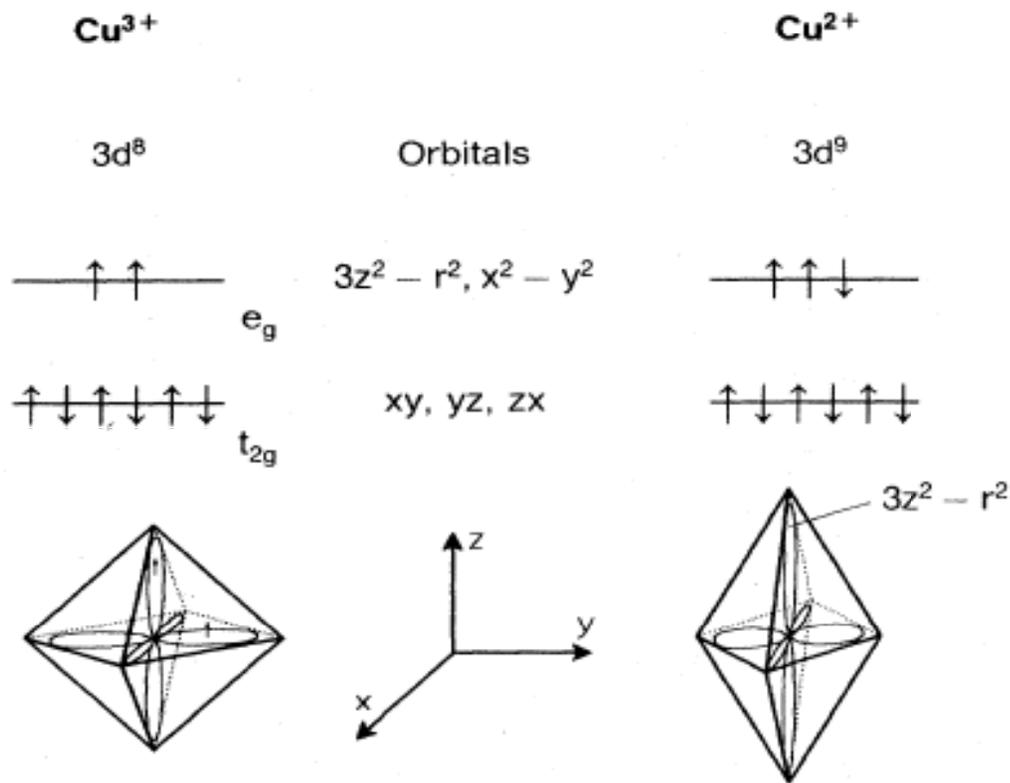
"Size Matters !"

Cu²⁺ 3d Multiplet Splitting (Cubic)

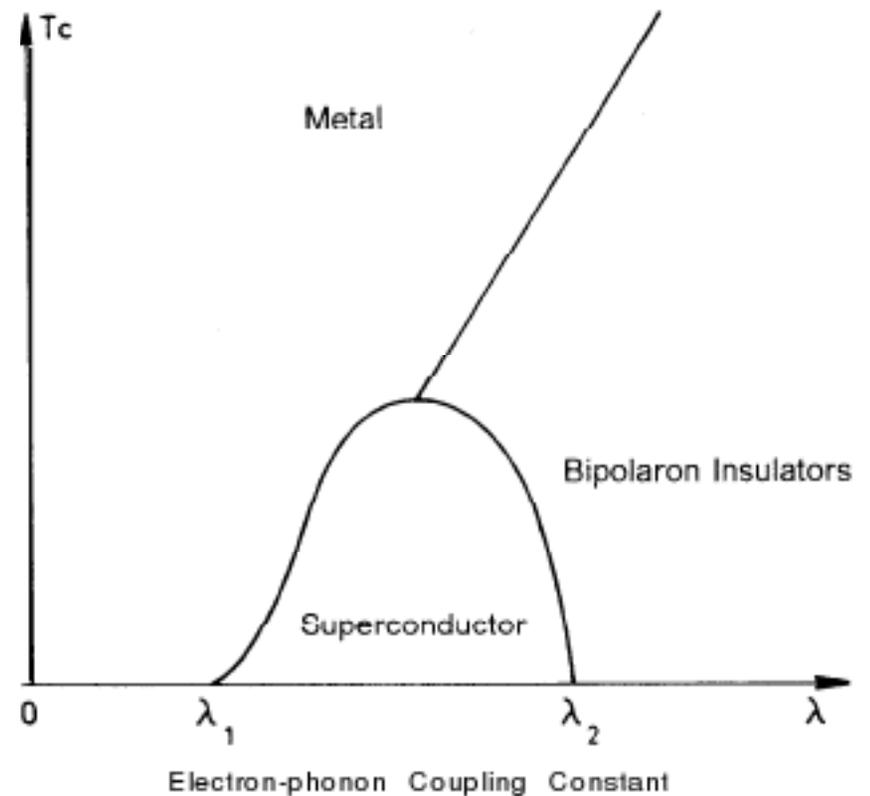


Bednorz-Mueller Nobel Lecture

Copper Ions in the Oxide Octahedron



*Jahn-Teller Effect:
Elongation of
the Octahedron*



After Chakravarty, (1979)!

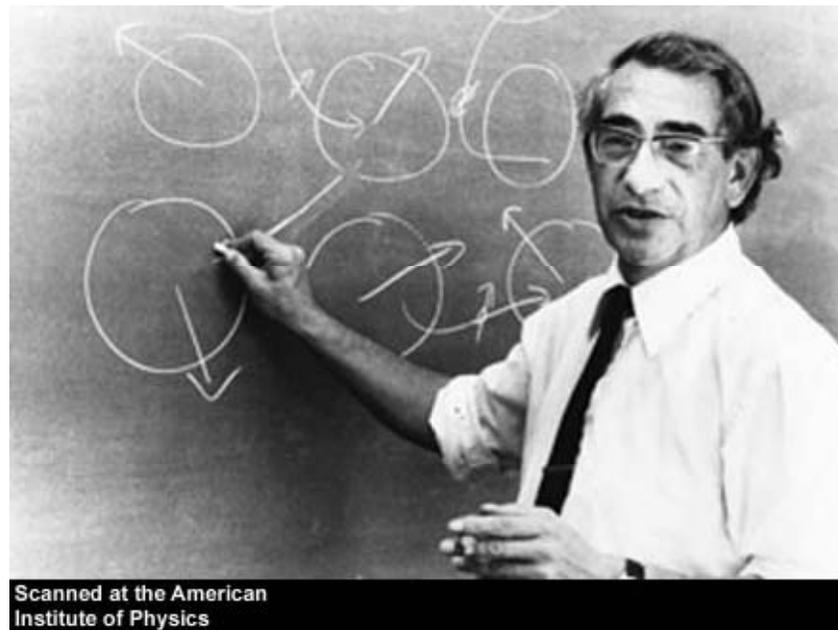
Hubbard Theory

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

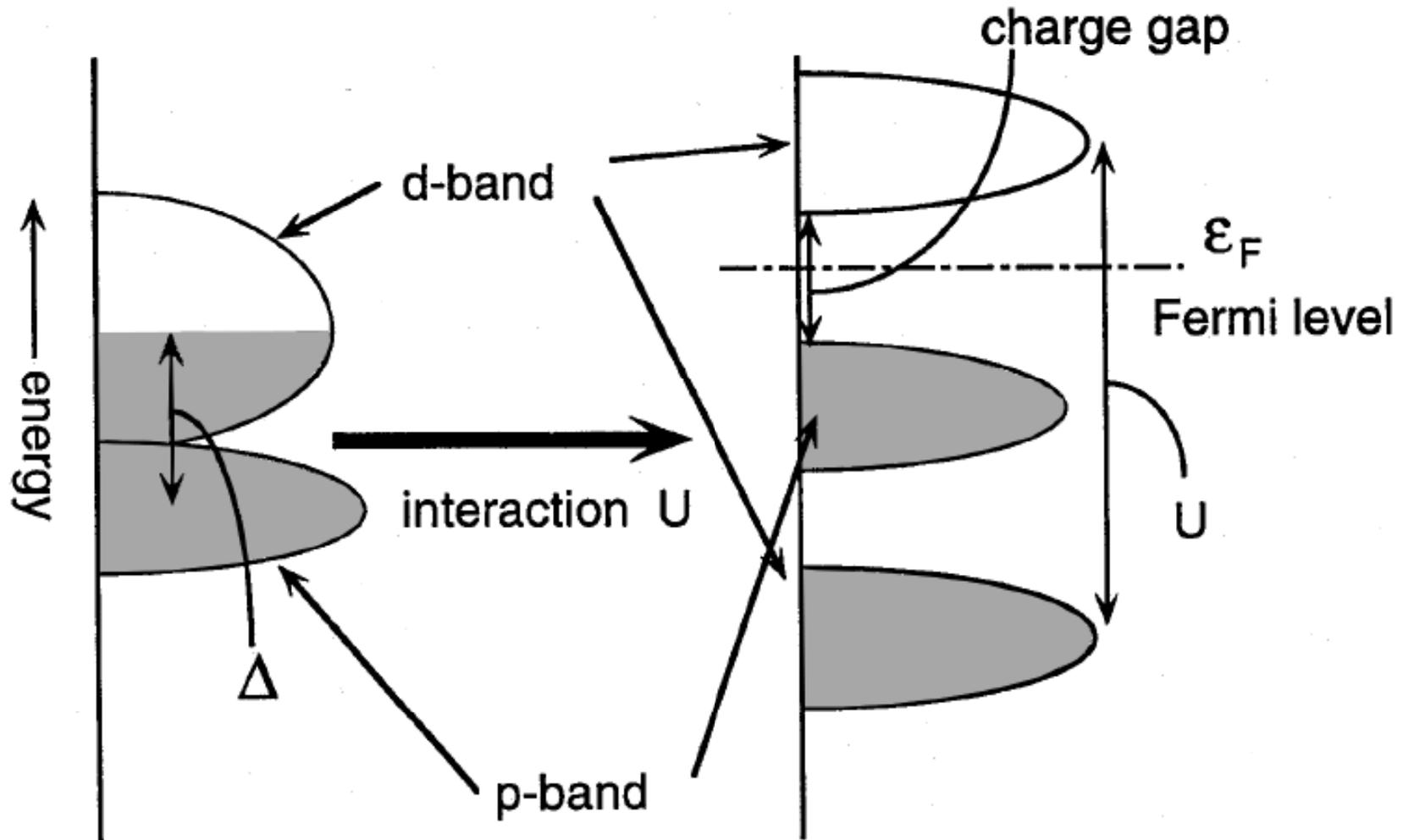
One-electron
"band" term

On-site "Hubbard"
double occupation
coulomb repulsion

Off-site
repulsion



Charge Transfer Insulator



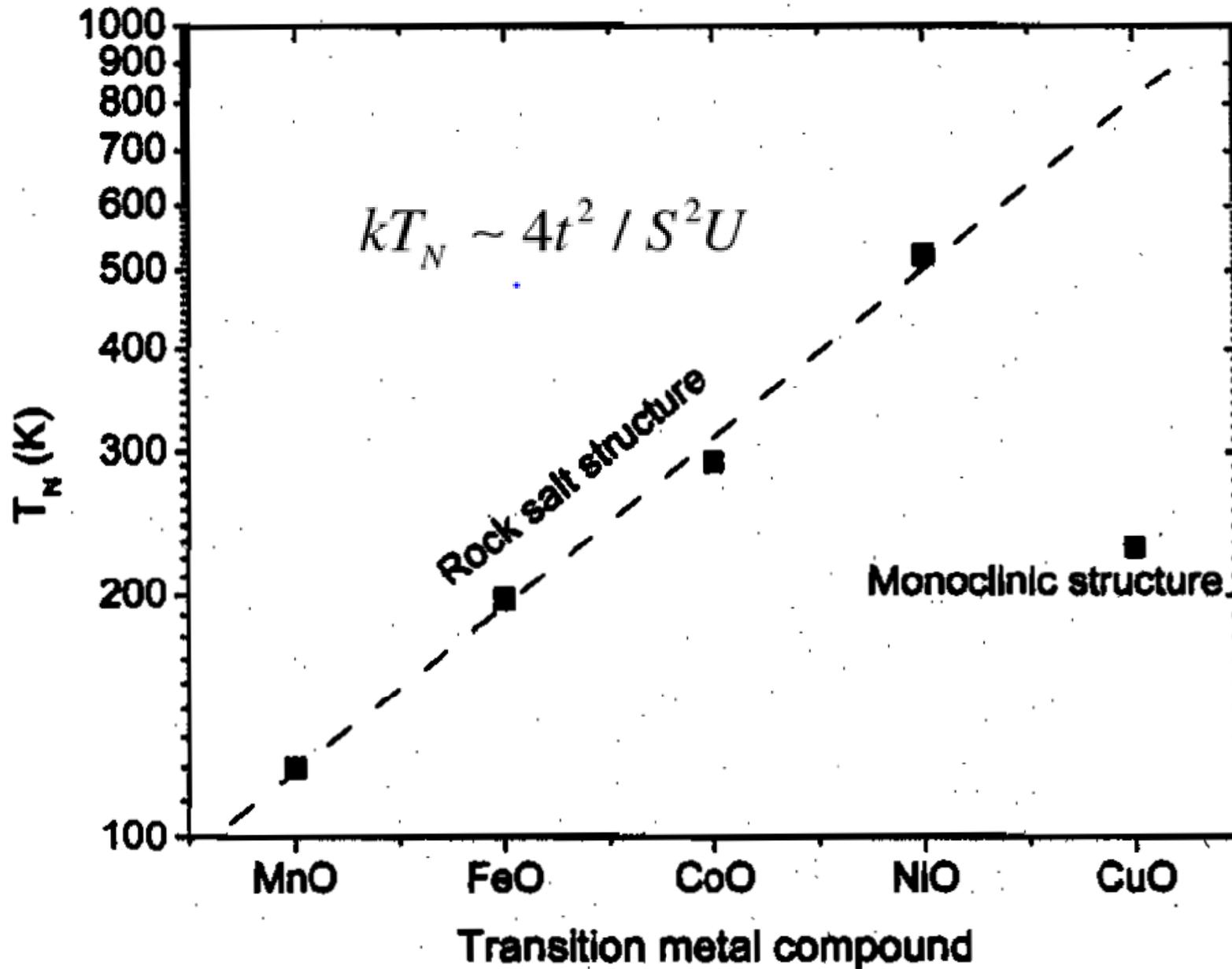
After Imada, et al, RMP 70, 1039 (1998)

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)!

Néel Temperature vs. TMO Atomic Number



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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>

Experimental Equipment (Software)

- QUANTUM-ESPRESSO Suit of Codes
 - DFT (LDA+U) plus electron-phonon
 - Graphics by Tone Kolalij (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: $2s^2 2p^4$

Experimental Equipment (Hardware)

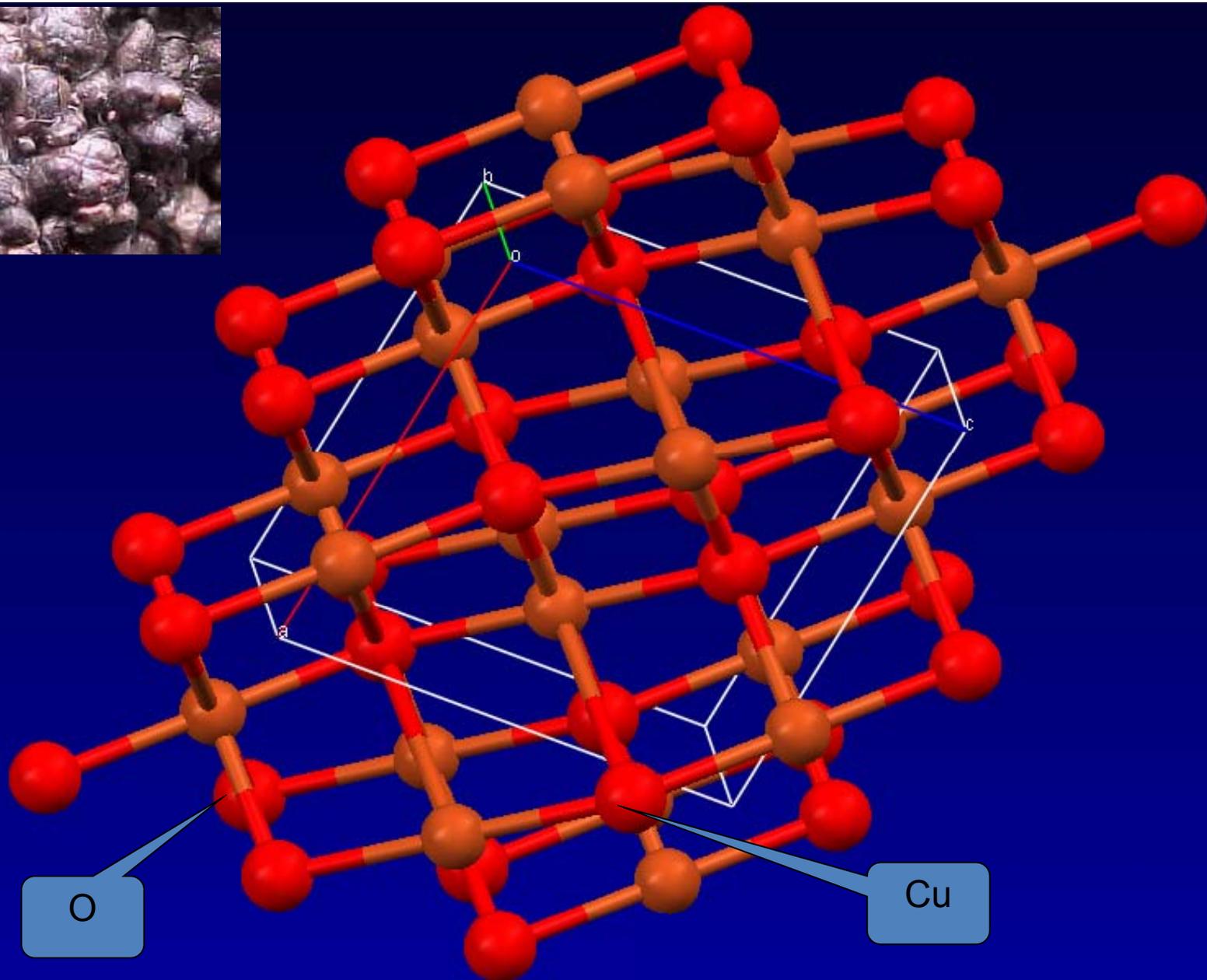
3-Cluster Home Network: AMD64 dual 3.5 GHz, 12 GB +
IBM-X41 +...



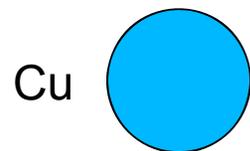
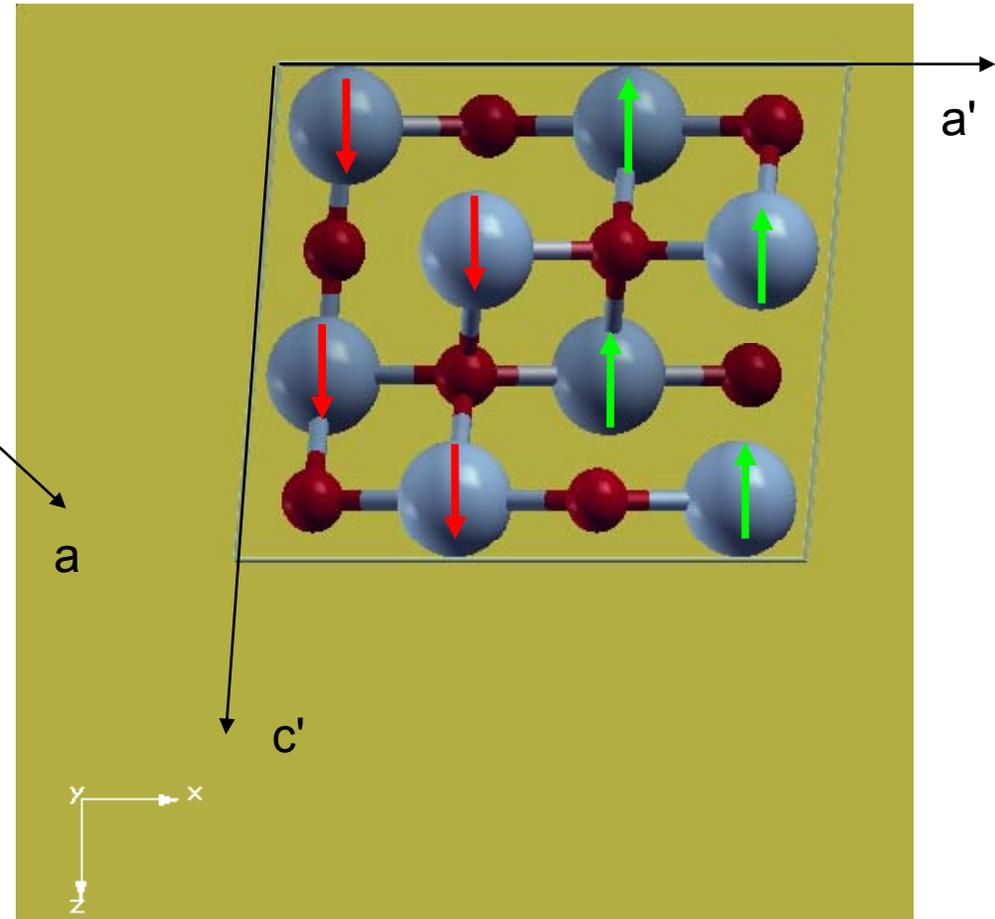
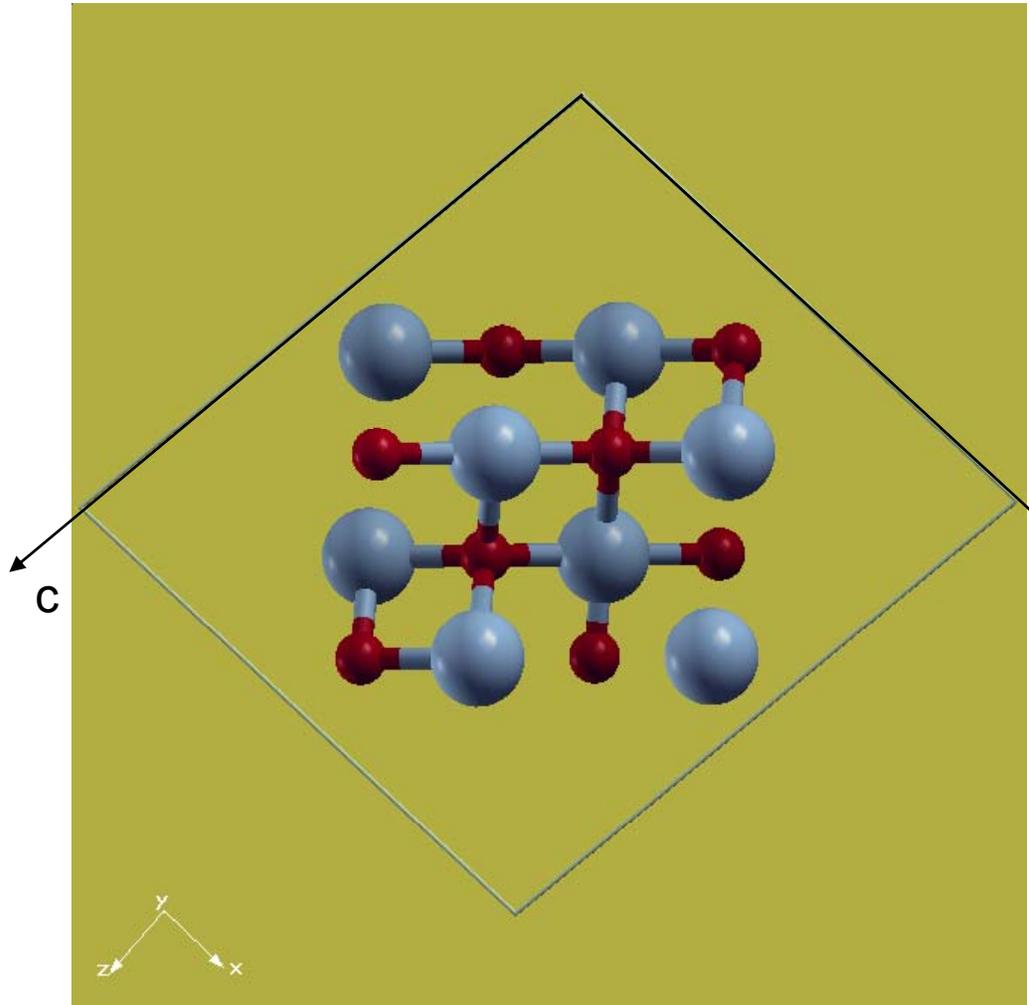
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Tenorite (Monoclinic CuO)!

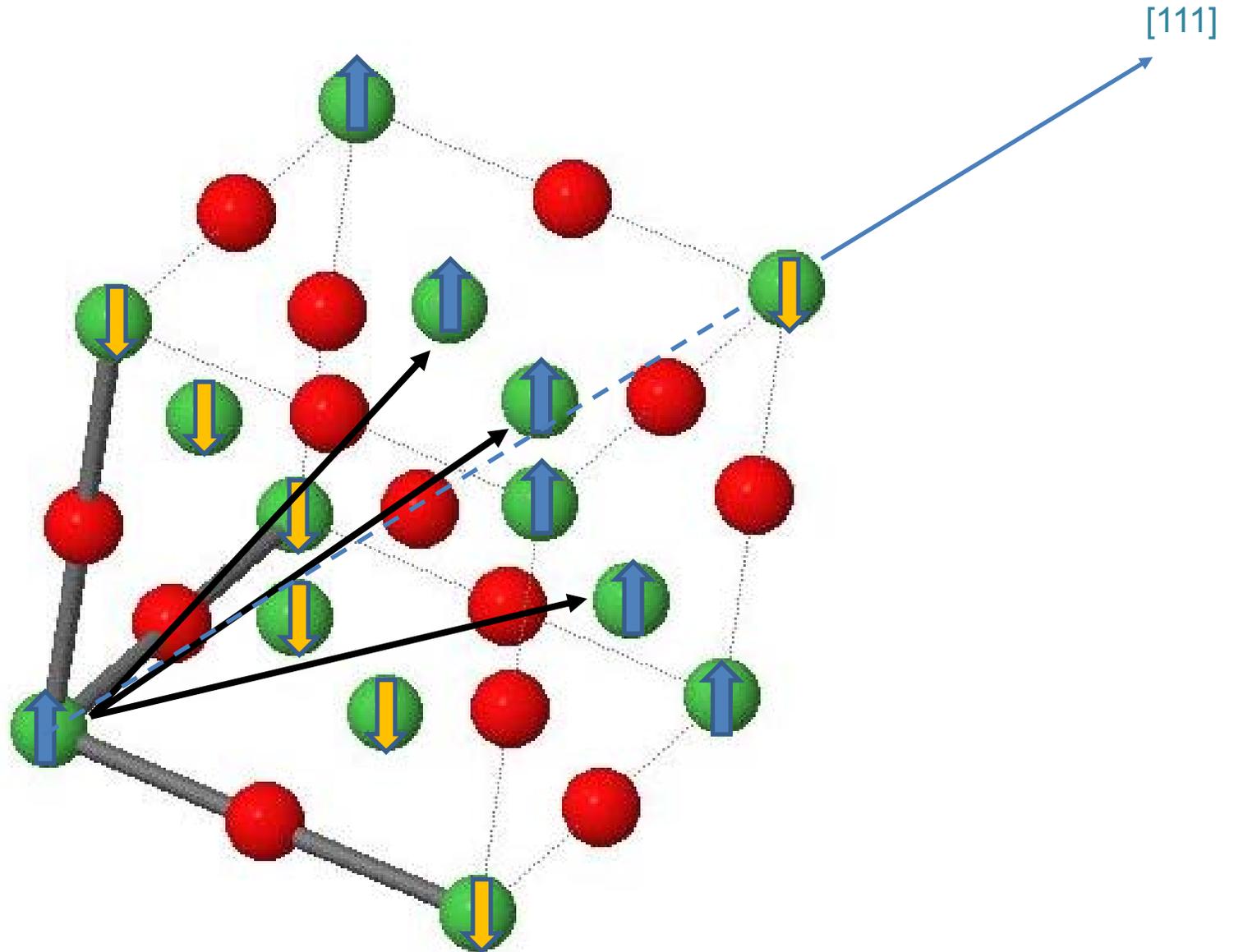
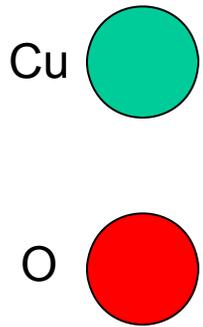


nm & af Unit Cells



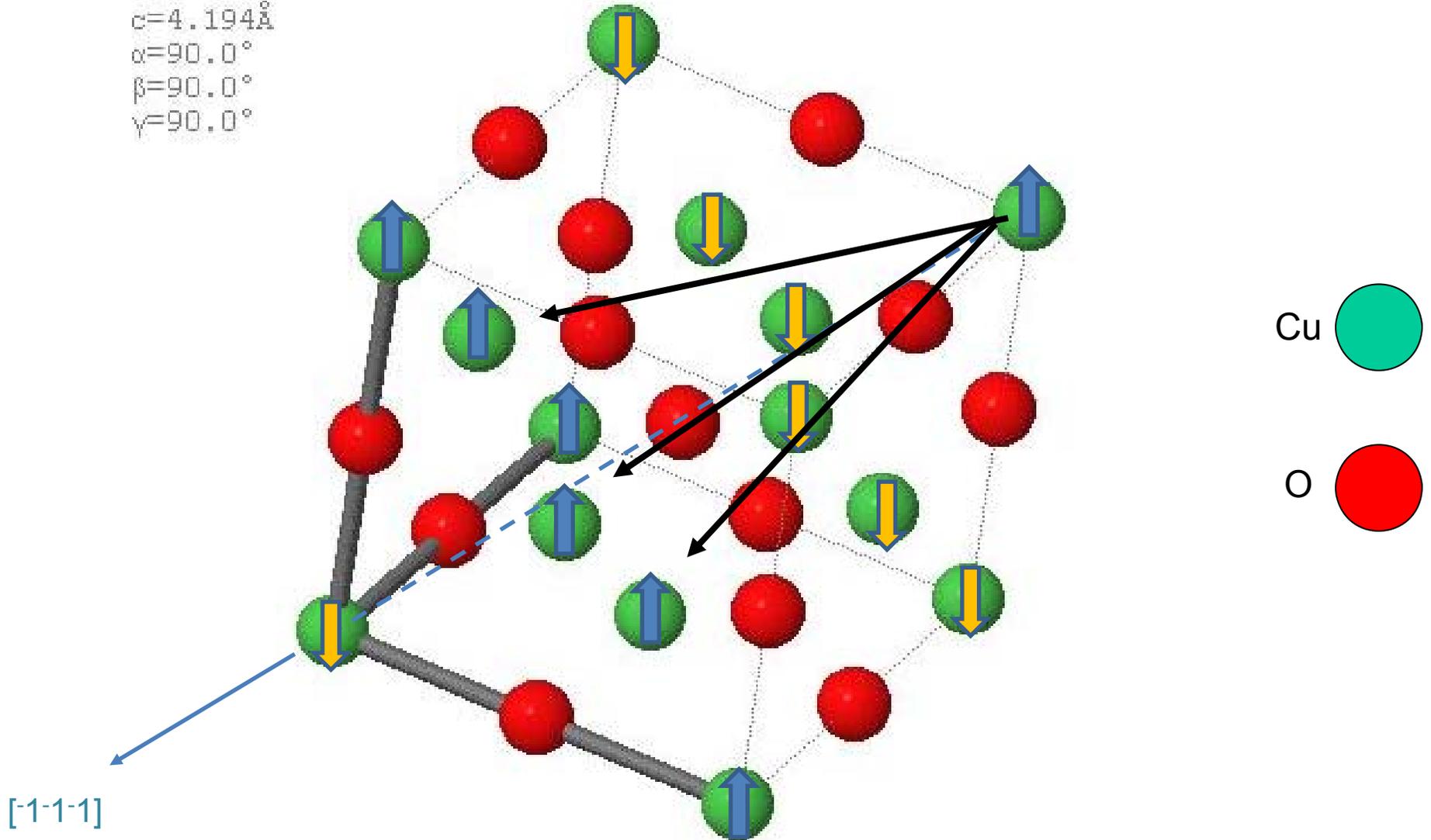
Proto-TMO AF Rock Salt

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

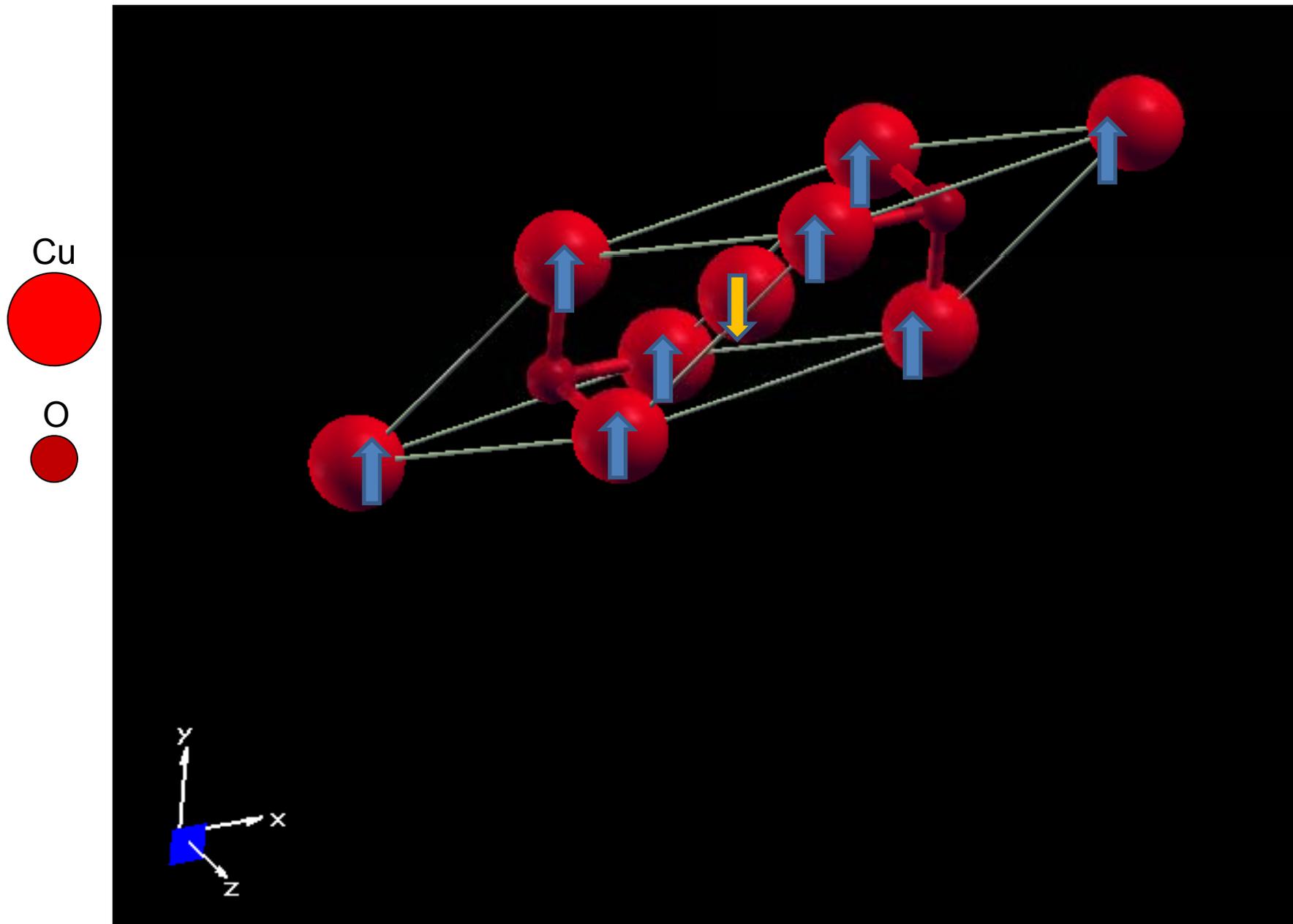


Proto-TMO AF Rock Salt

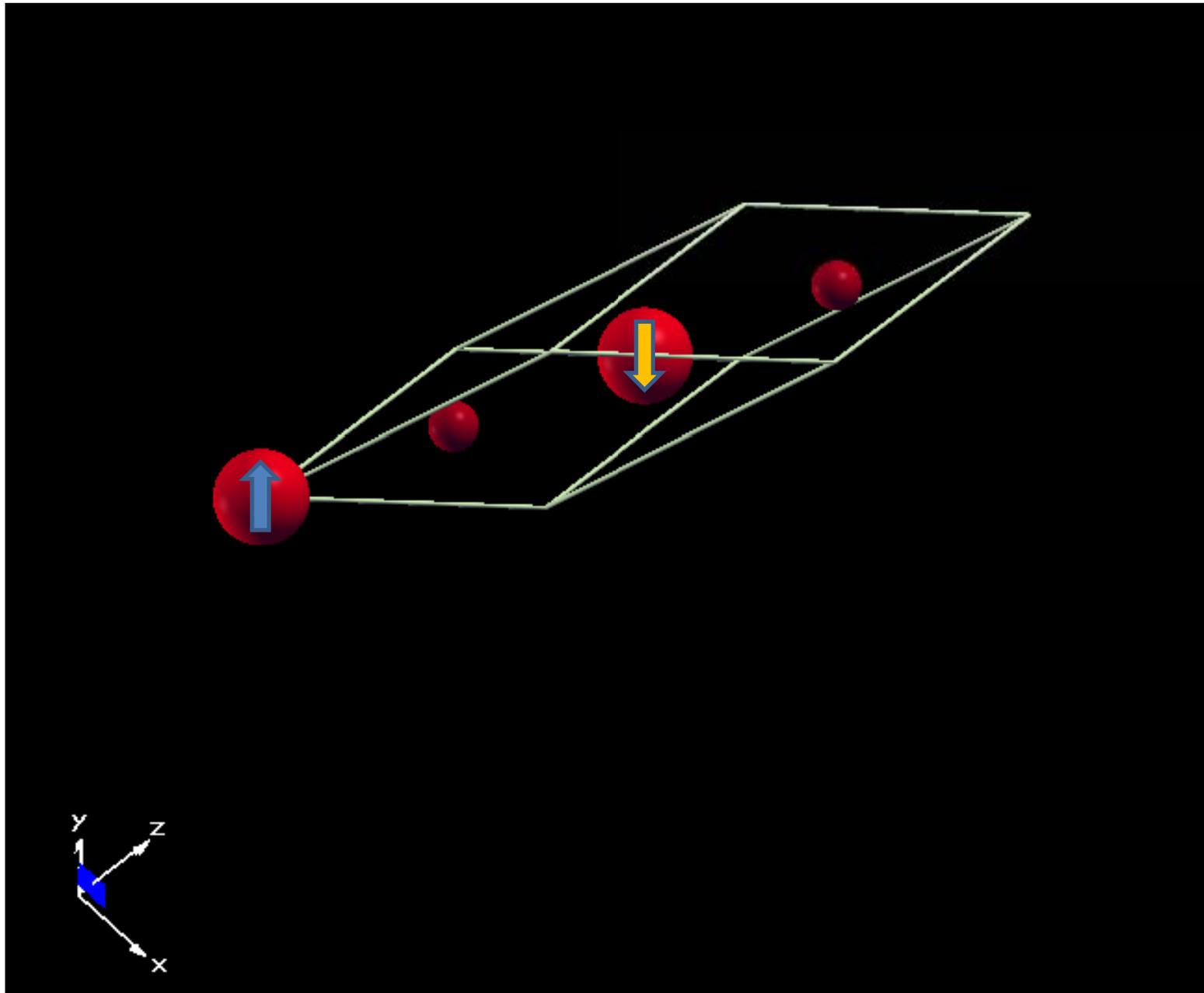
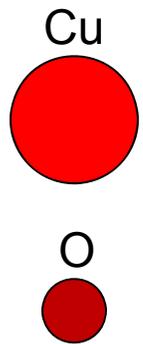
Fm-3m
a=4.194Å
b=4.194Å
c=4.194Å
 $\alpha=90.0^\circ$
 $\beta=90.0^\circ$
 $\gamma=90.0^\circ$



AF Type II Primitive Cell



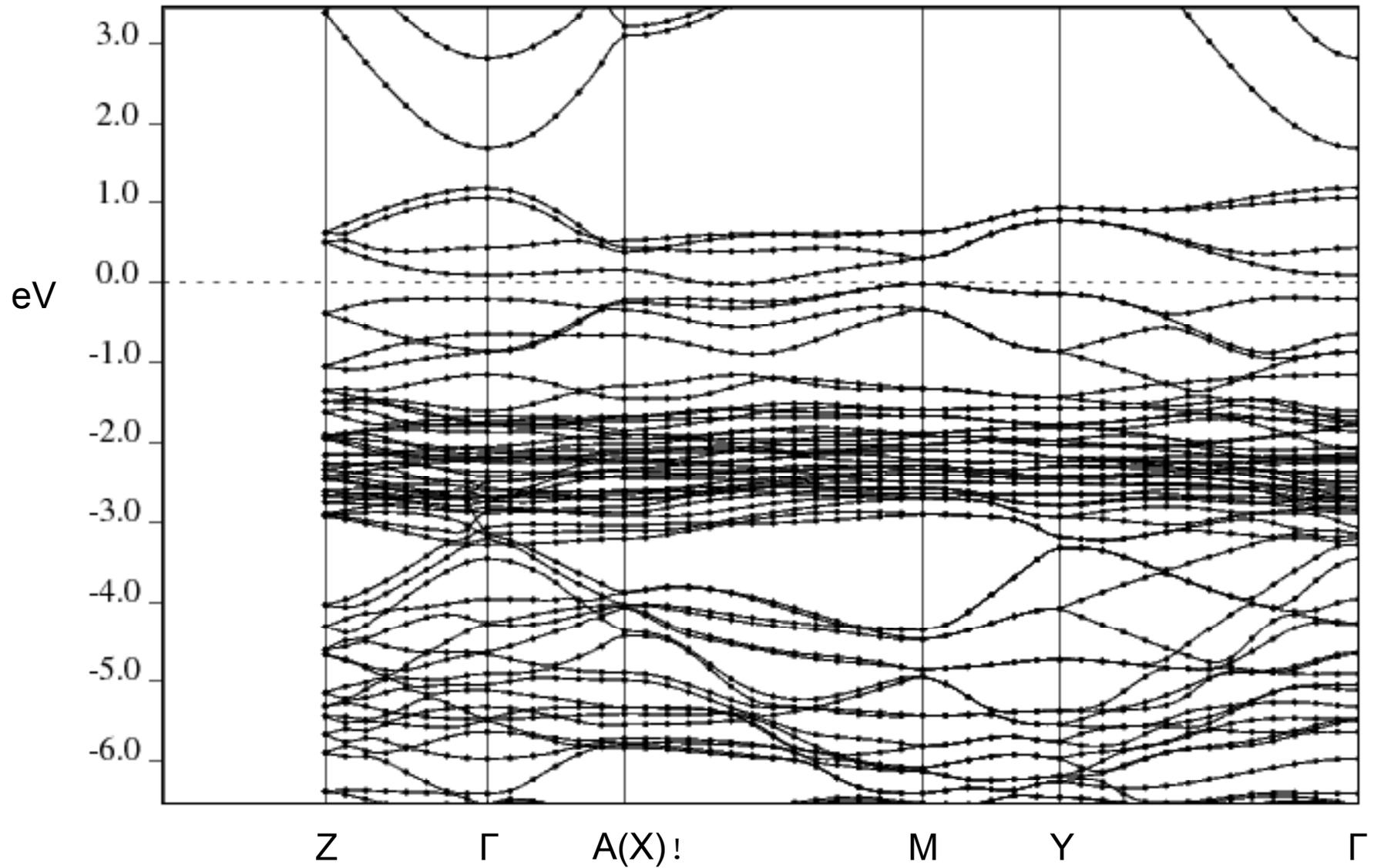
Basic Asymmetric AF Cell



Agenda

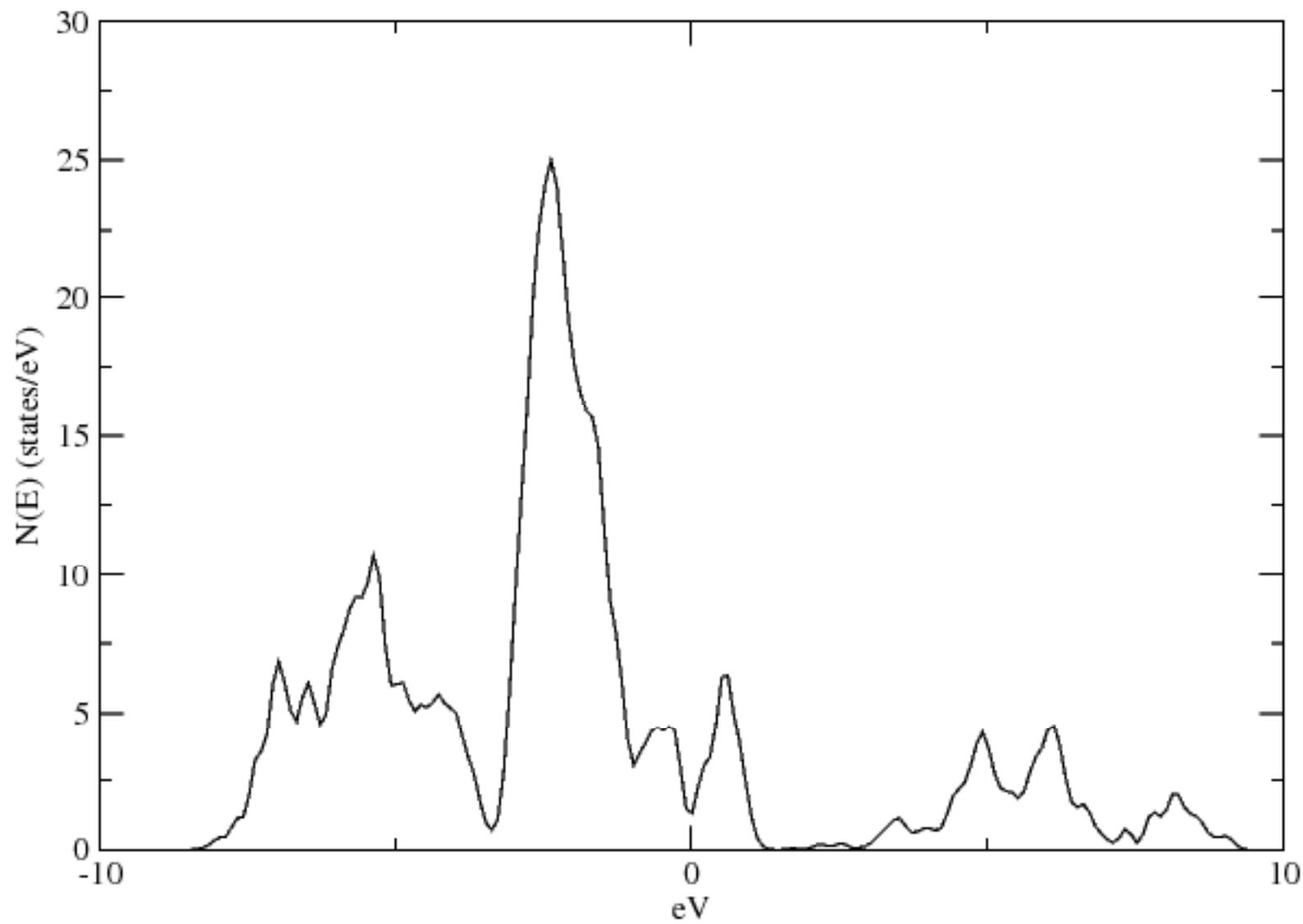
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Tenorite ($U = 0$)

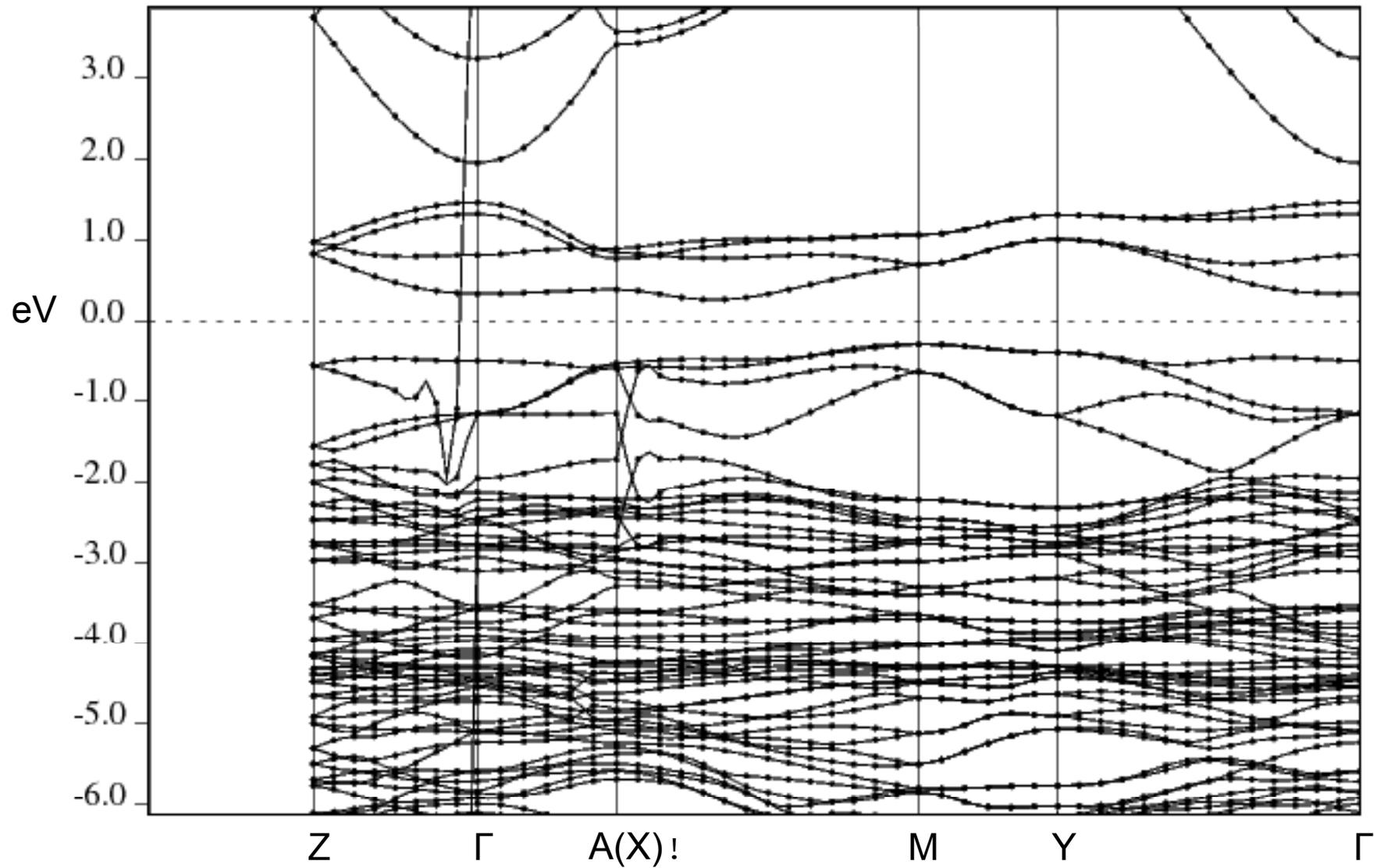


af-Tenorite DOS Plot

$U = 1.d-7$ $E_f = 10.5211$

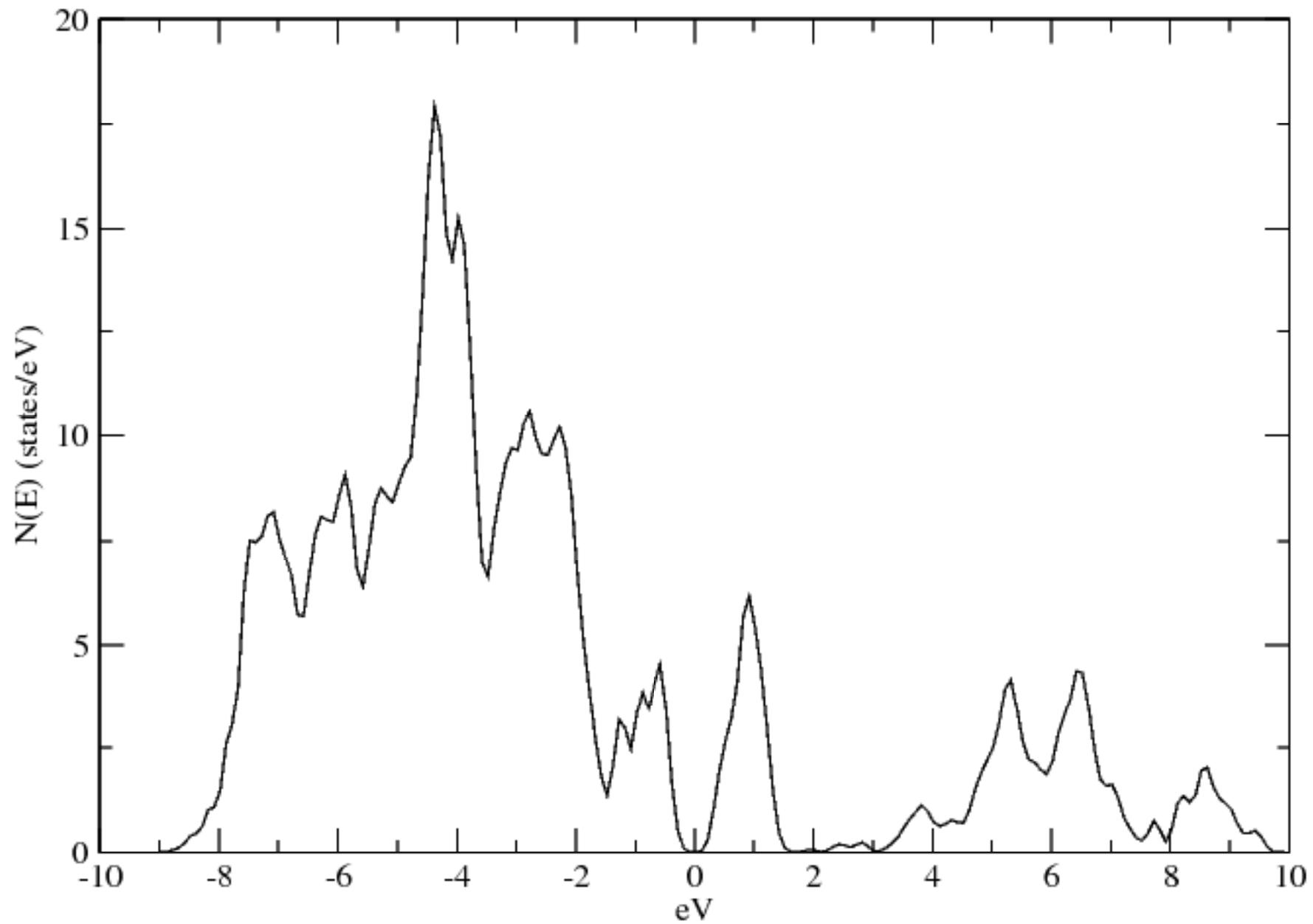


Tenorite ($U = 5$)



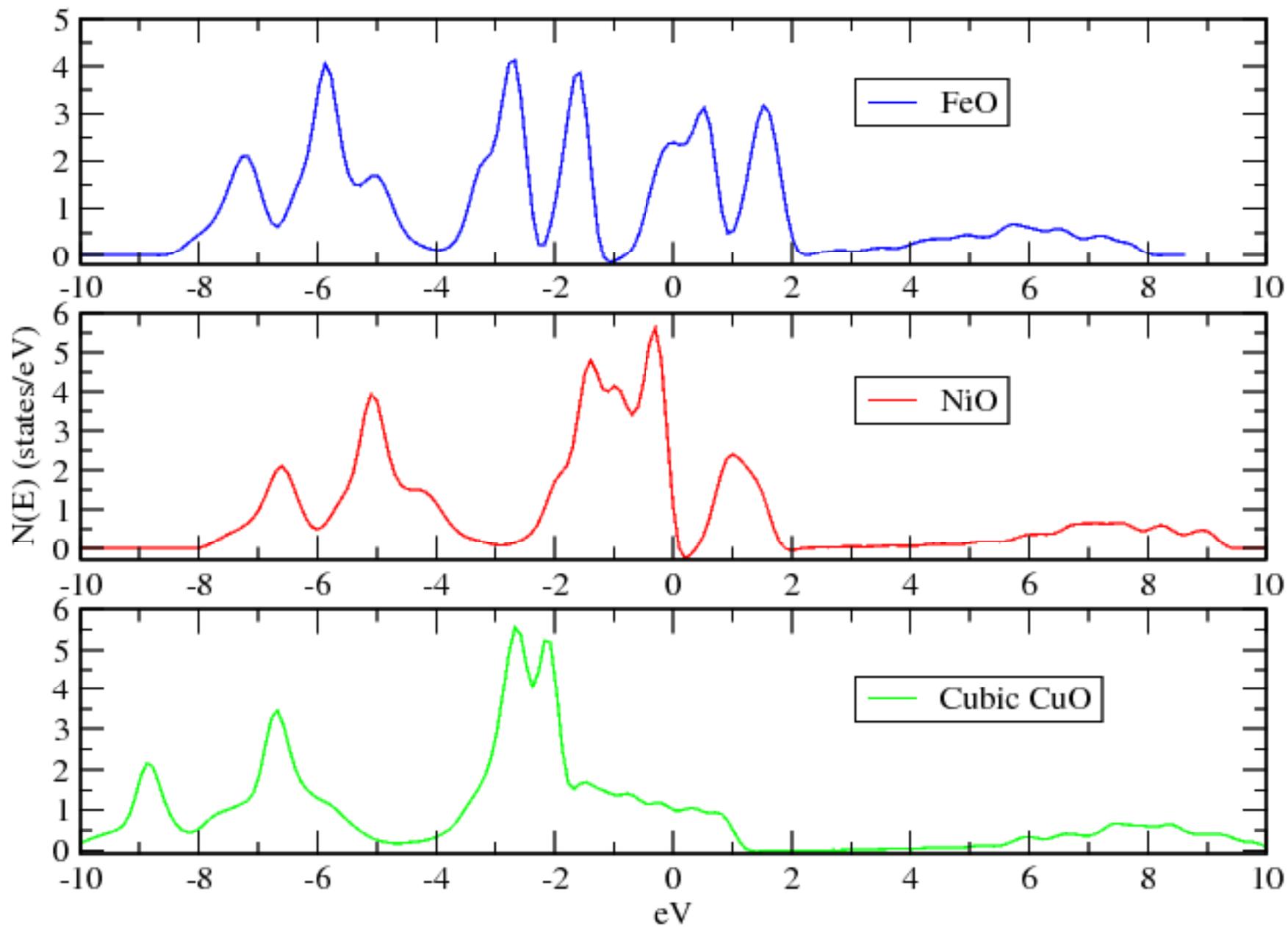
af-Tenorite DOS Plot

$U = 5$ $E_f = 10.1435$



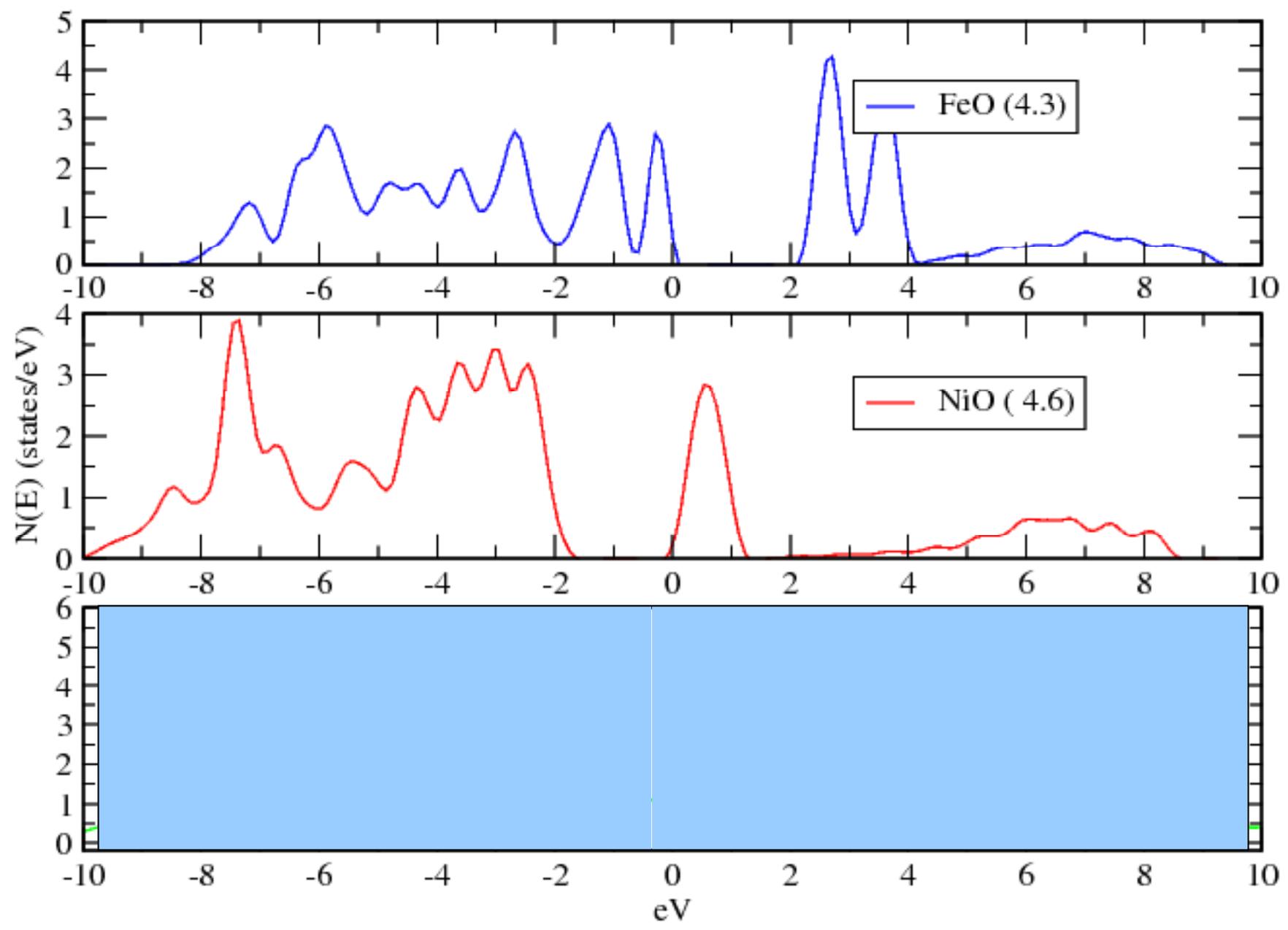
TMO_dos Plot

$U = 0$

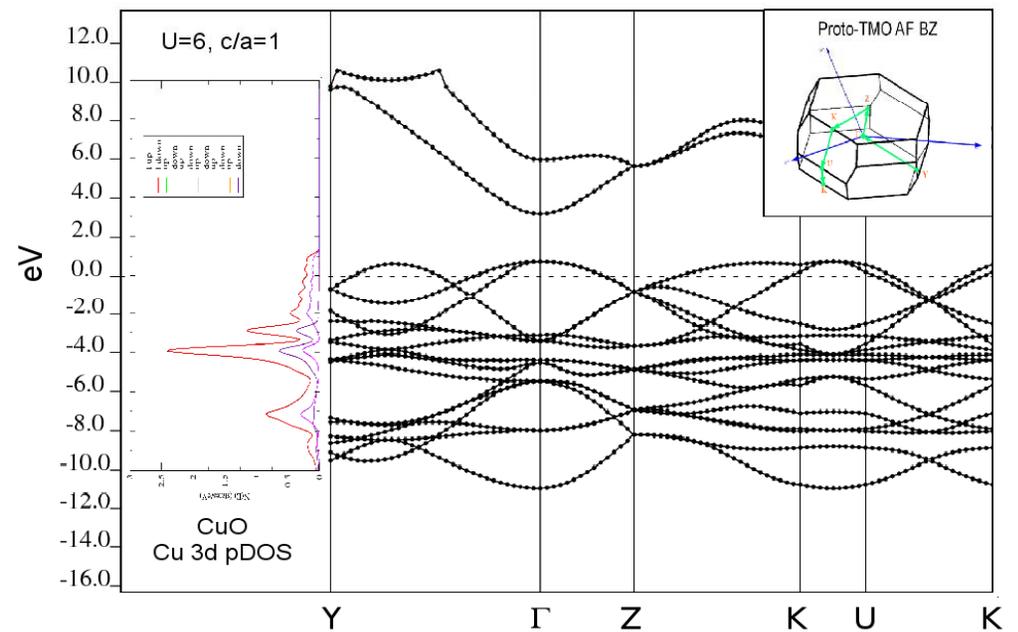
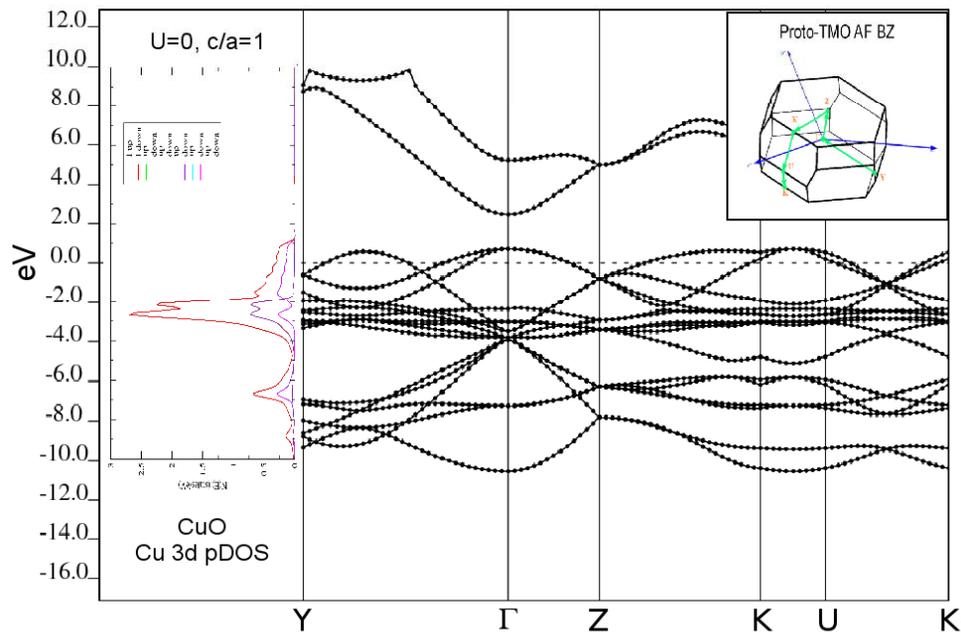
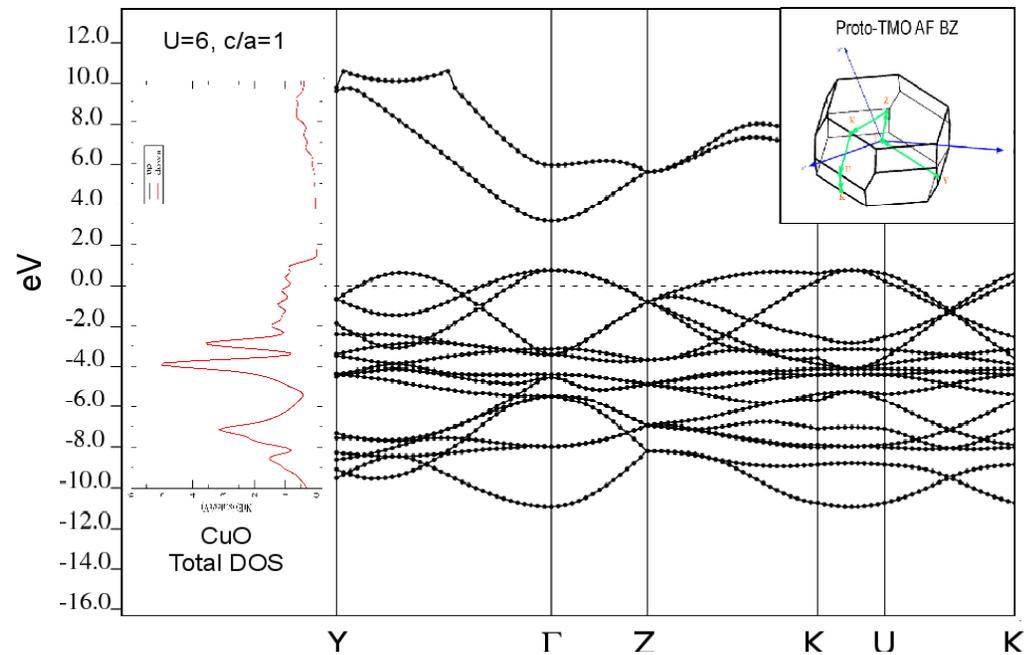
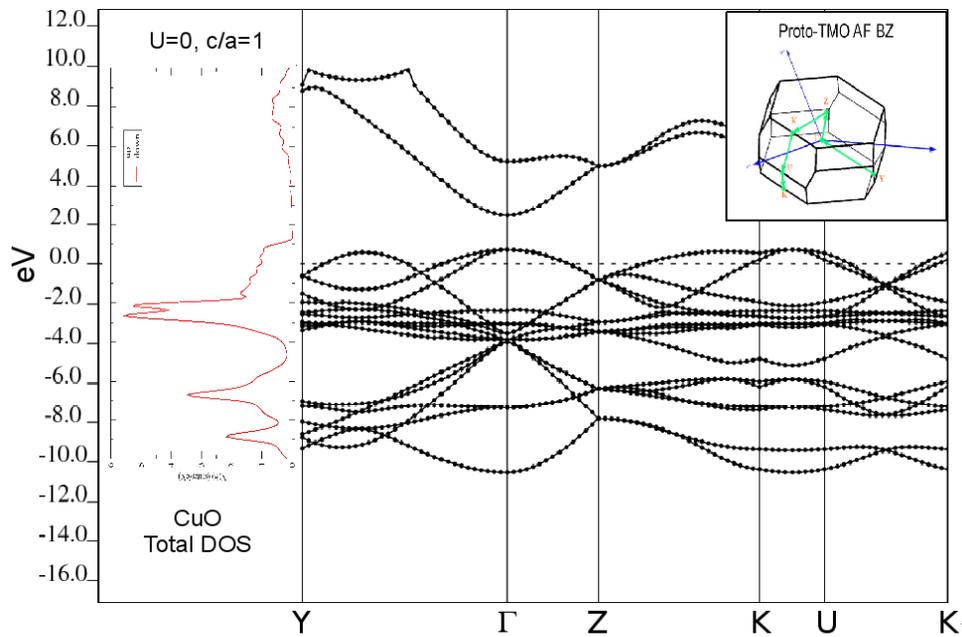


TMO_dos Plot

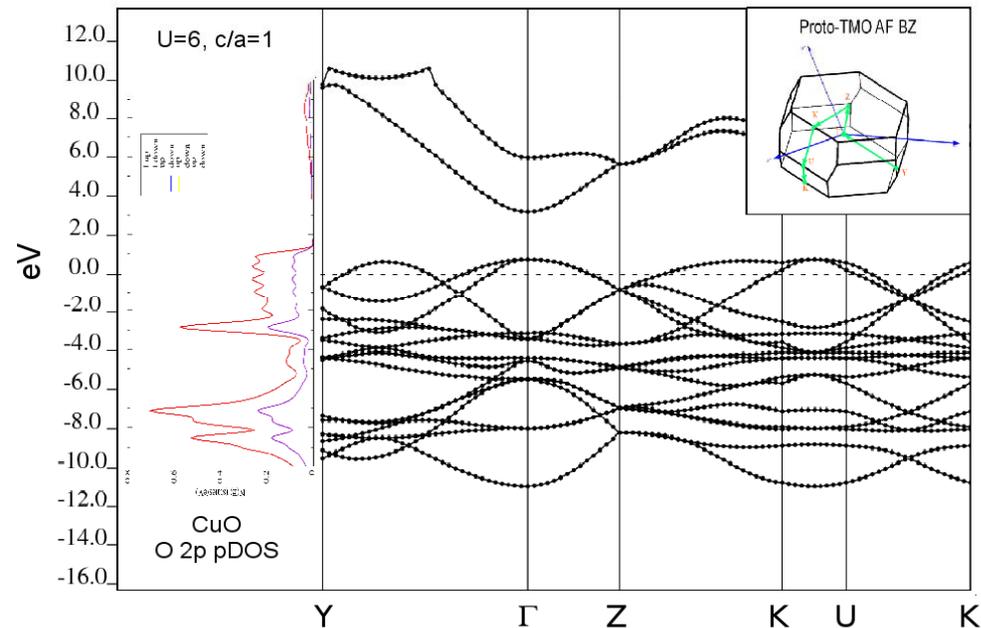
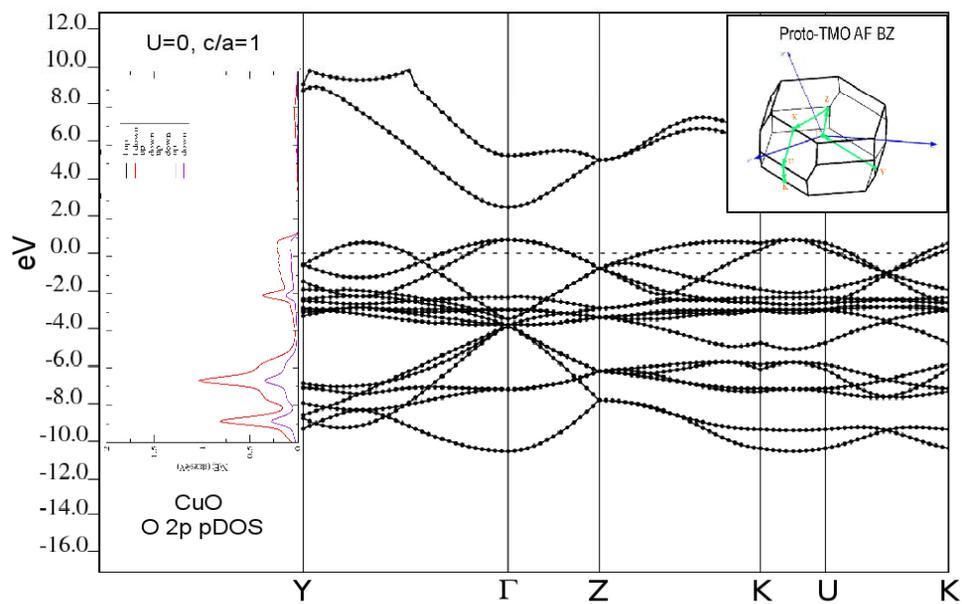
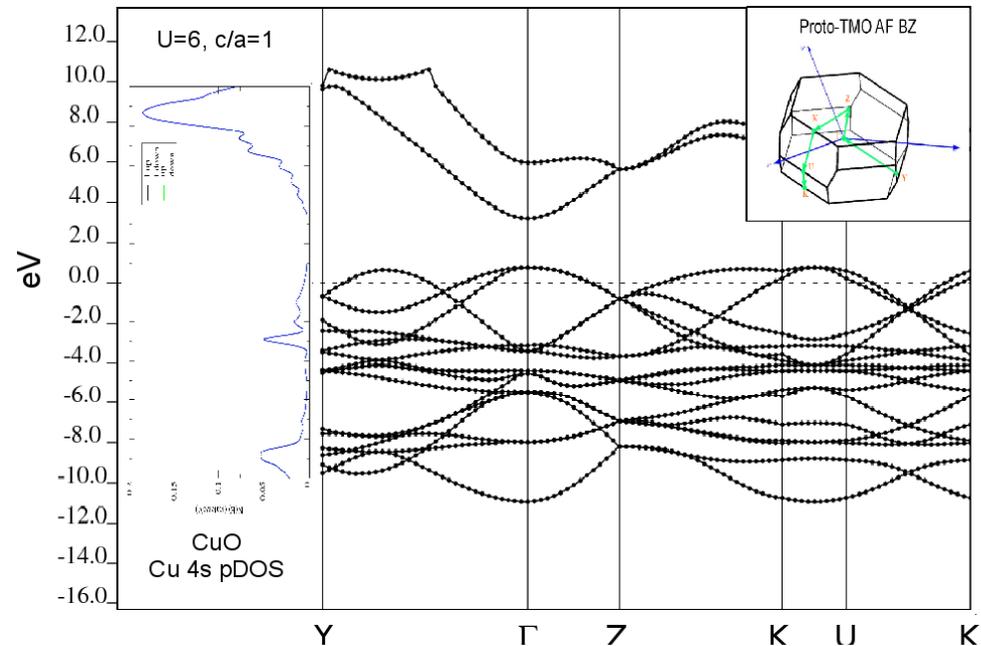
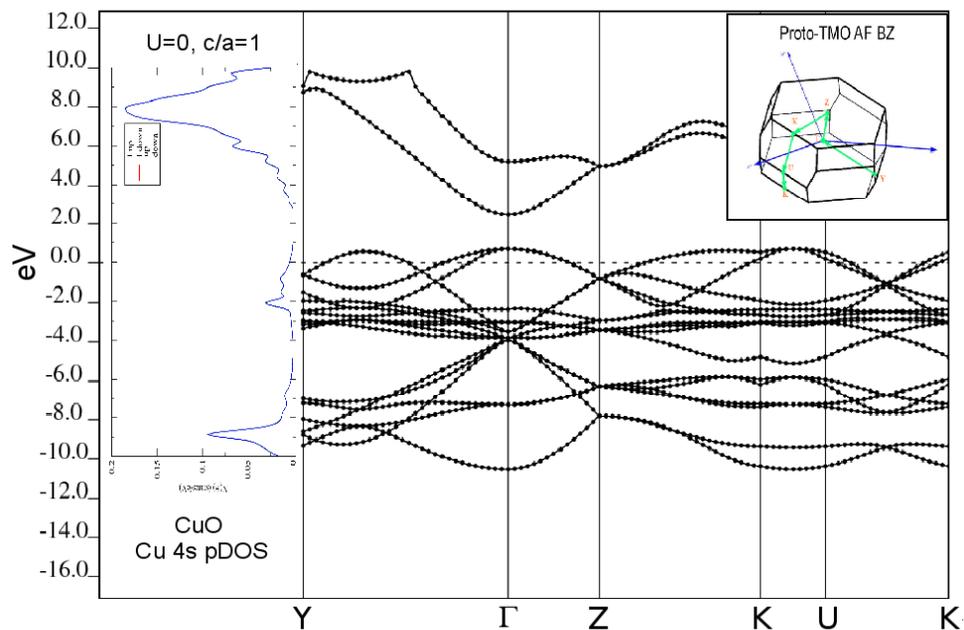
$U > 0$



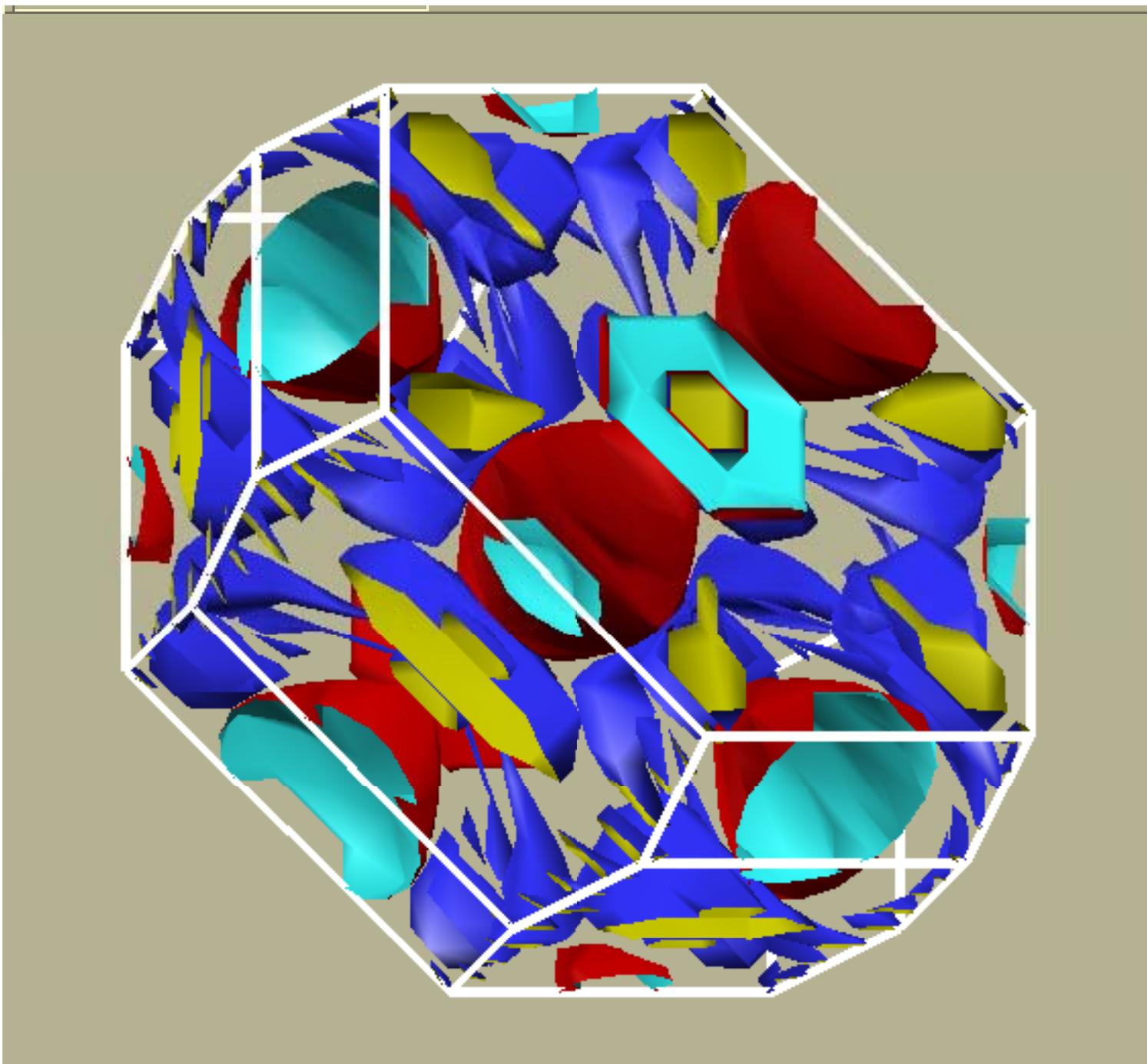
Cubic Rocksalt CuO



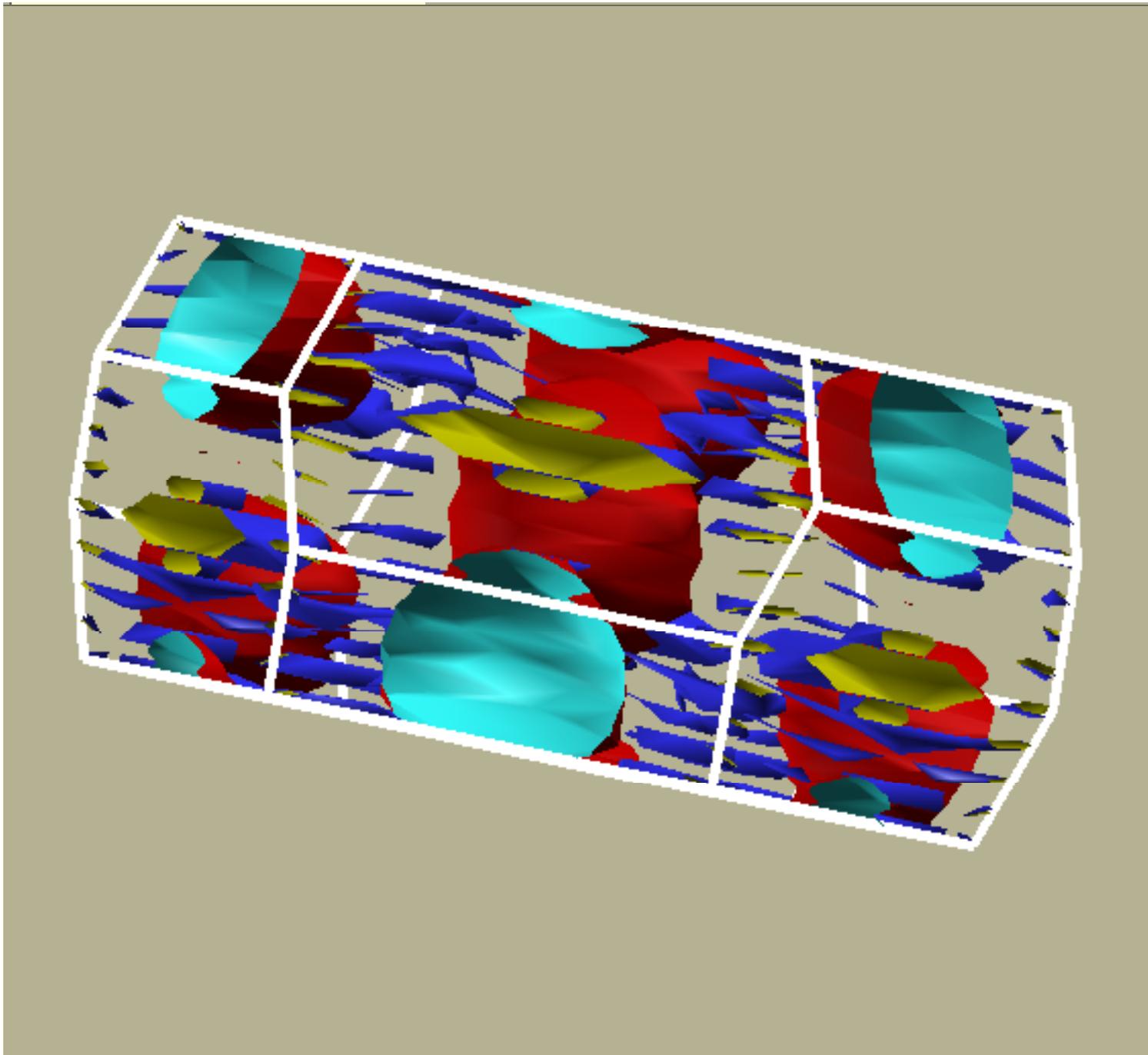
Cubic Rocksalt CuO (Cu 4s & O2p)!



Fermi Surface of $U=0$ c-rs-CuO in the AF II Primitive Brillouin Zone...



...Oriented to Display Nesting Features.



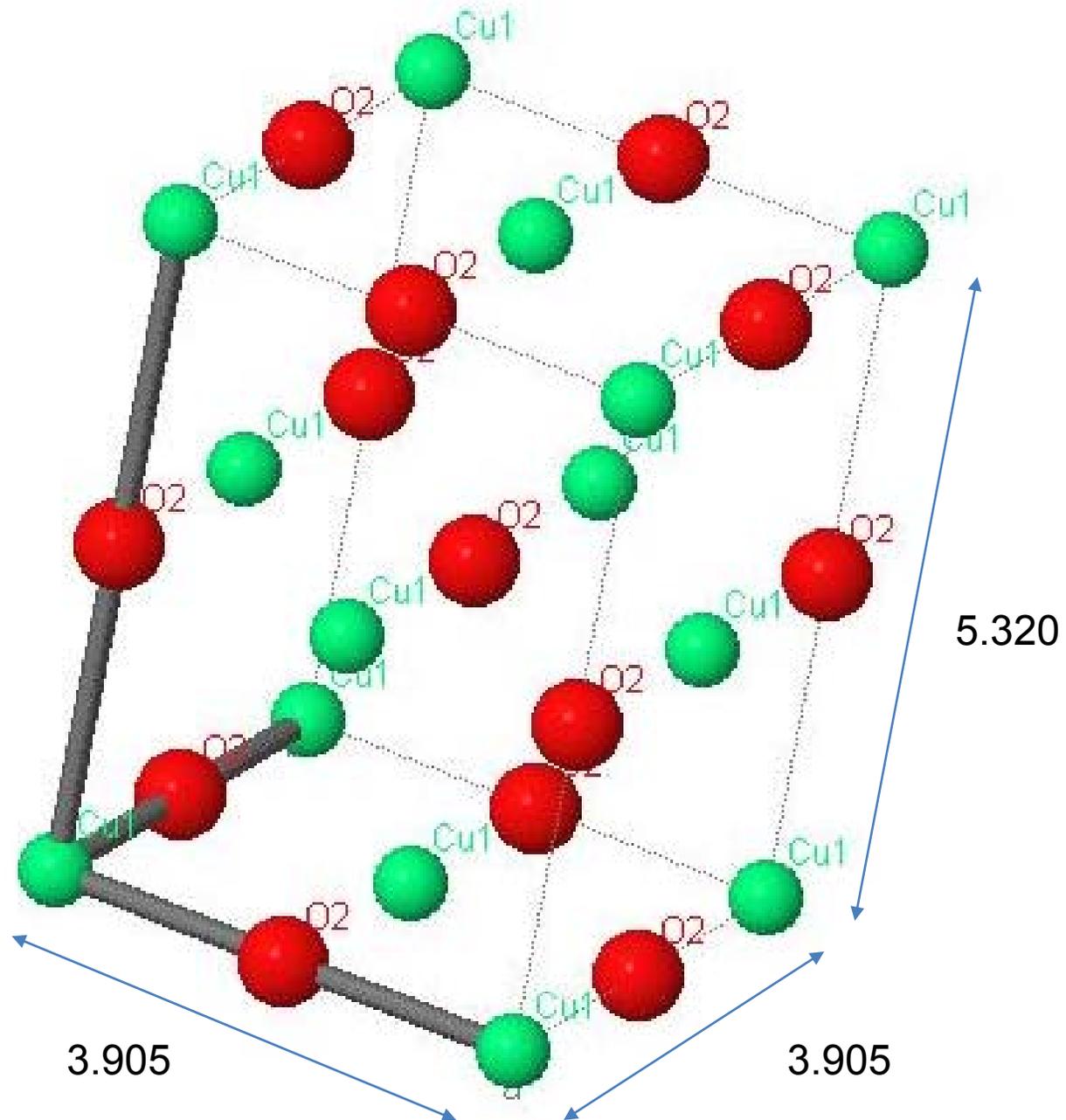
Tetragonal CuO

Fm-3m
a=3.905Å
b=3.905Å
c=5.320Å
 $\alpha=90.0^\circ$
 $\beta=90.0^\circ$
 $\gamma=90.0^\circ$

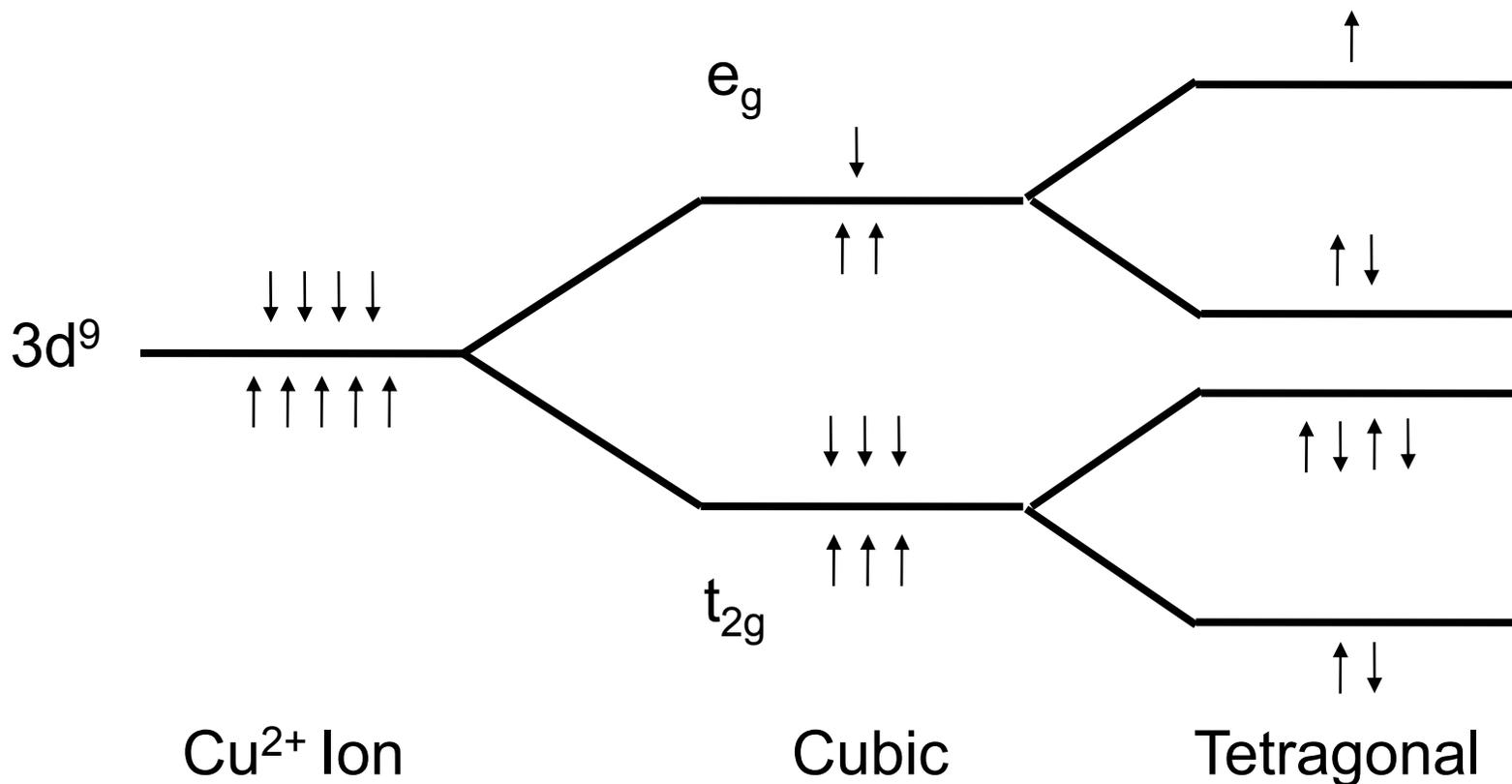
$$c/a = 1.36$$

Measurements (Wolter Siemons)

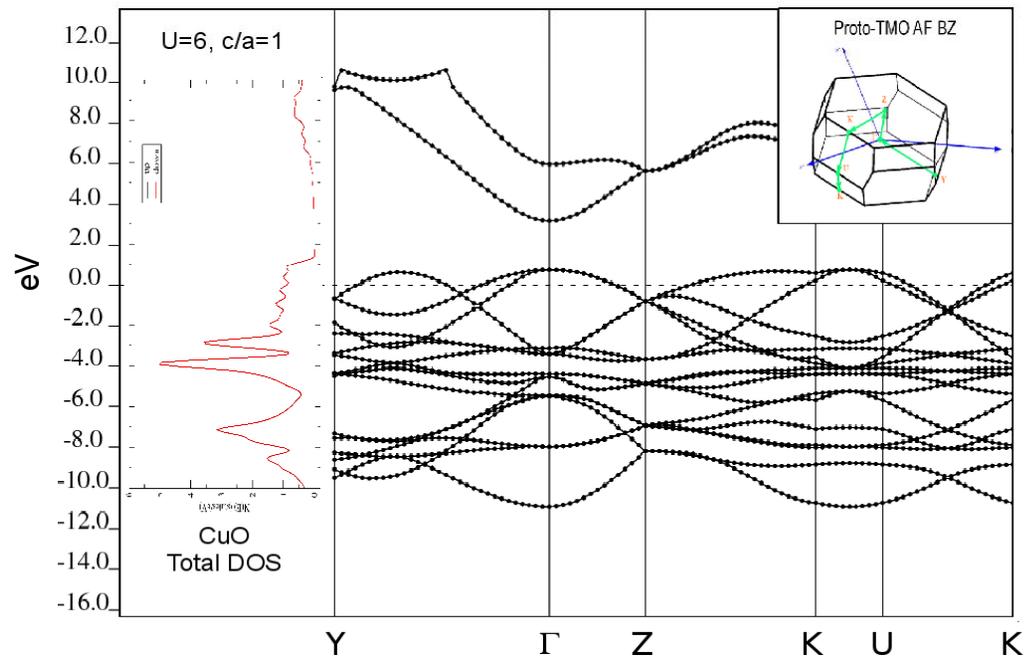
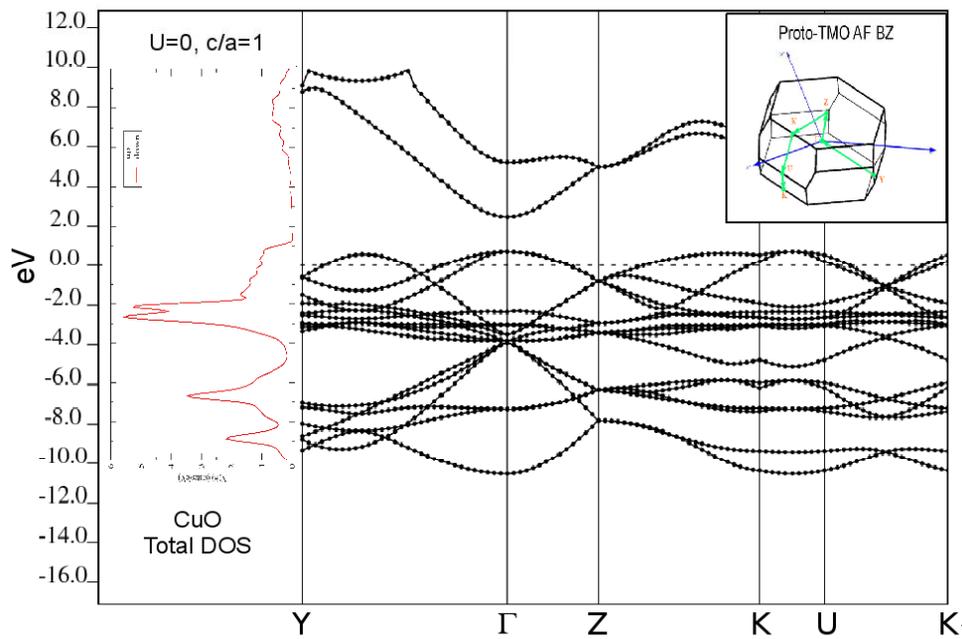
- 2-4 ML epi on STO
- No Fermi Edge
- No Exchange Bias on ferro-SRO ($T_c \sim 100-150$ K)!



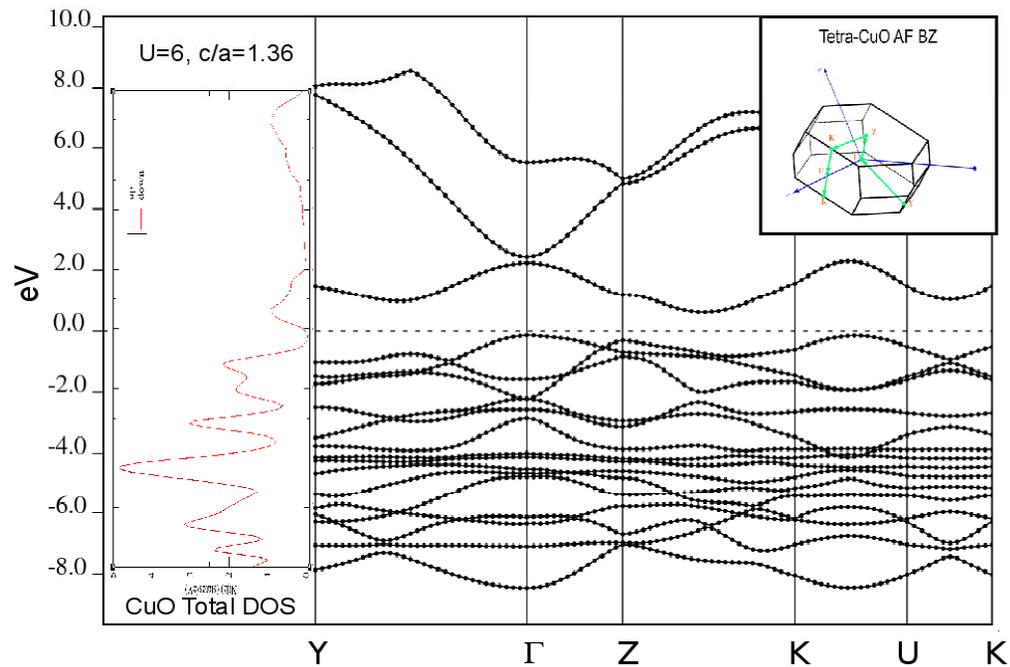
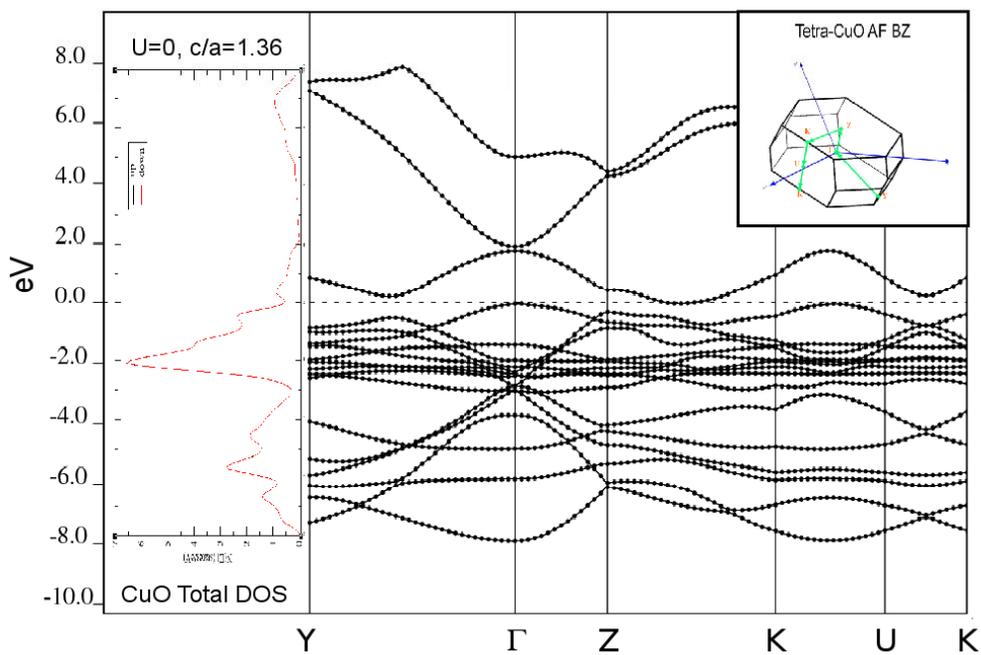
Cu²⁺ 3d Multiplet Splitting (Tetra)



Cubic

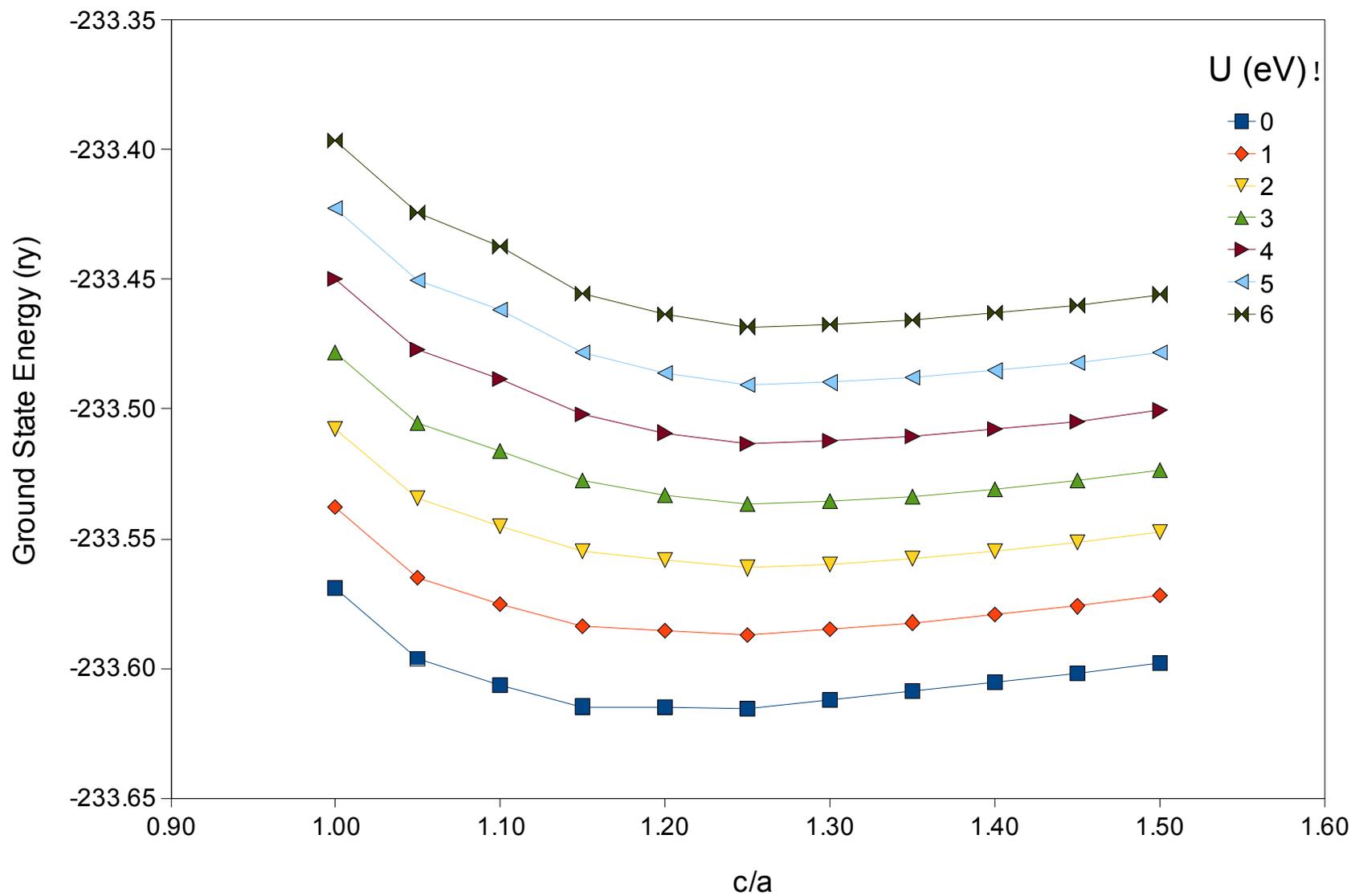


Tetragonal

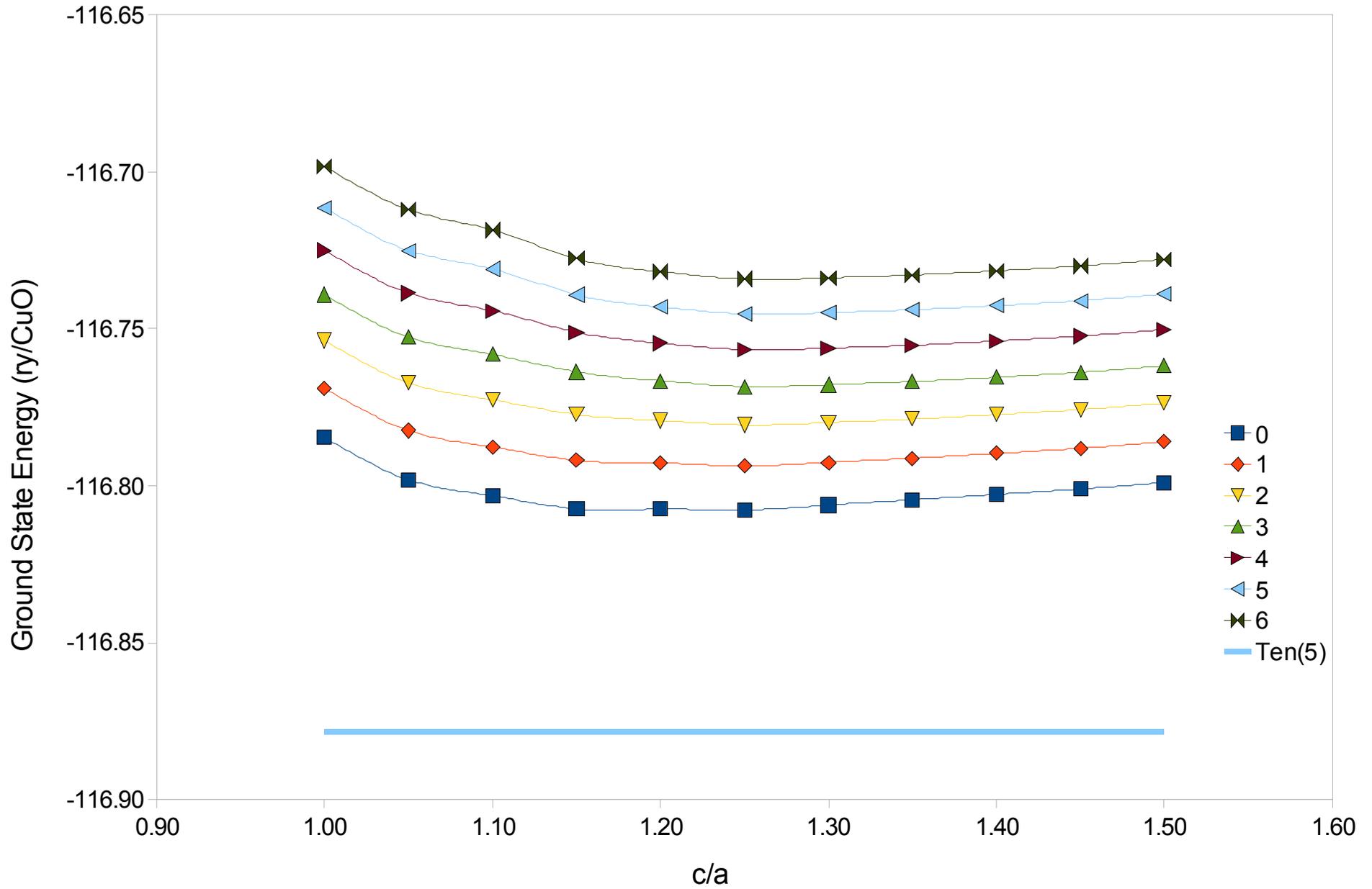


Rocksalt CuO - $a = 3.905$ Angstroms, PP = Cu.pz-3d9_4s2-rrkjus.UPF

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

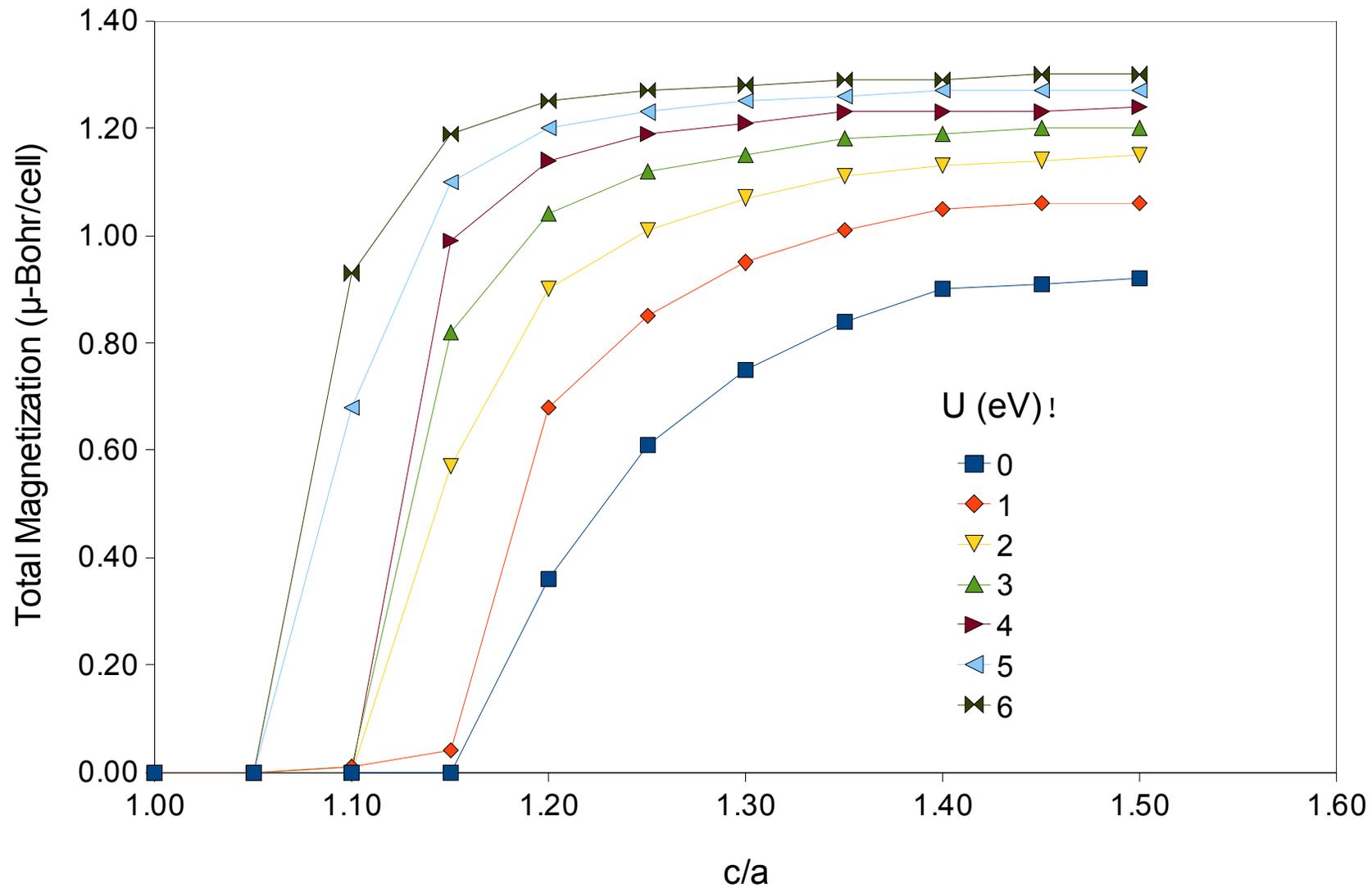


...With Respect to Tenorite



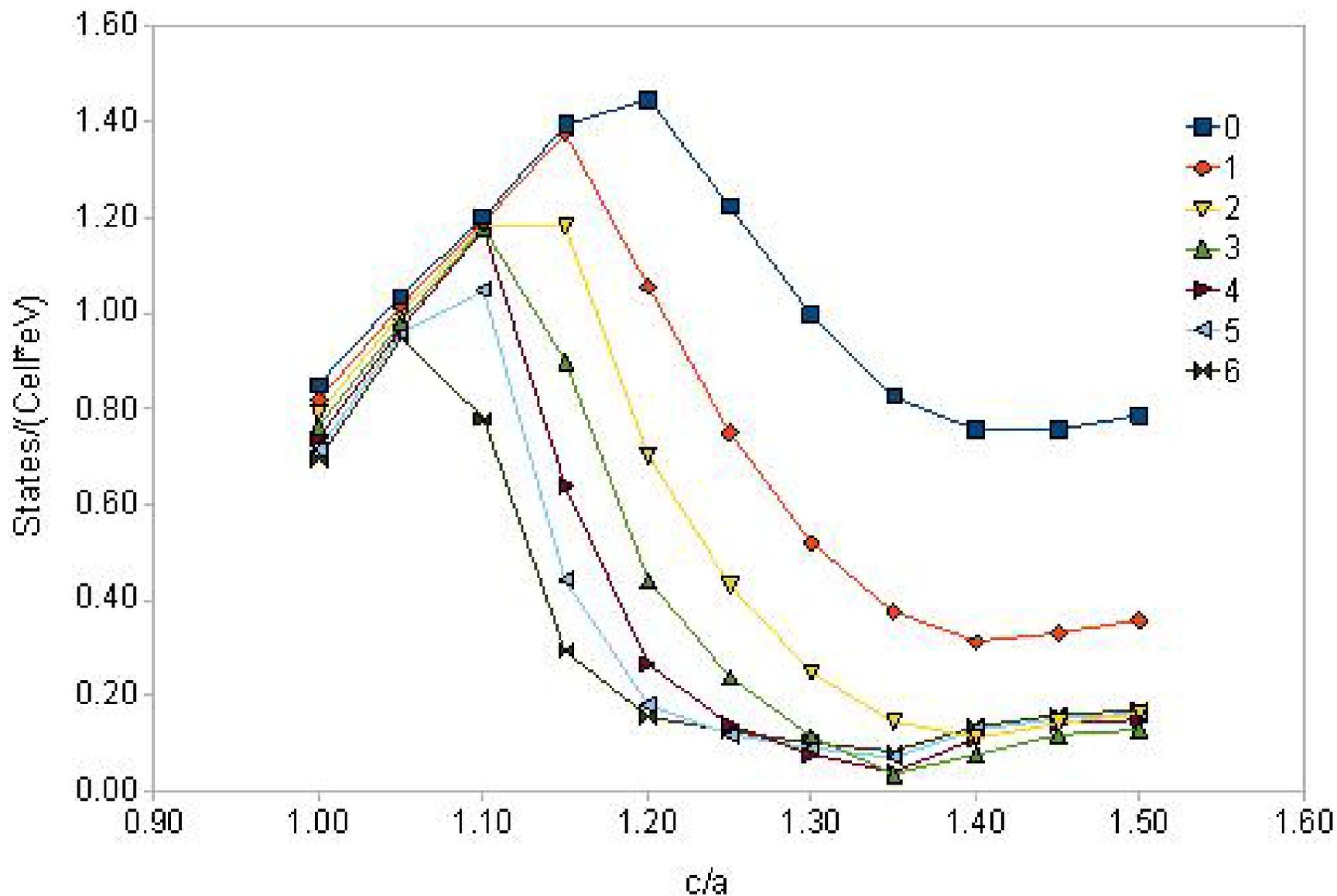
Rocksalt CuO - $a = 3.905 \text{ \AA}$, PP = Cu.pz-3d9_4s2-rrkjus.UPF

Total Magnetization vs c/a & $U(\text{eV})$

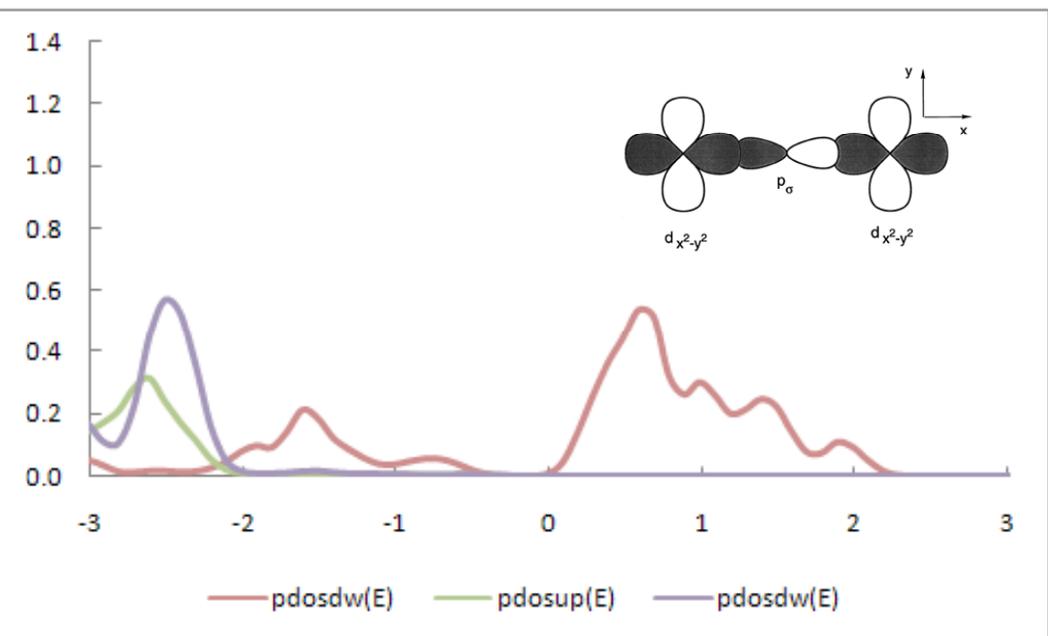
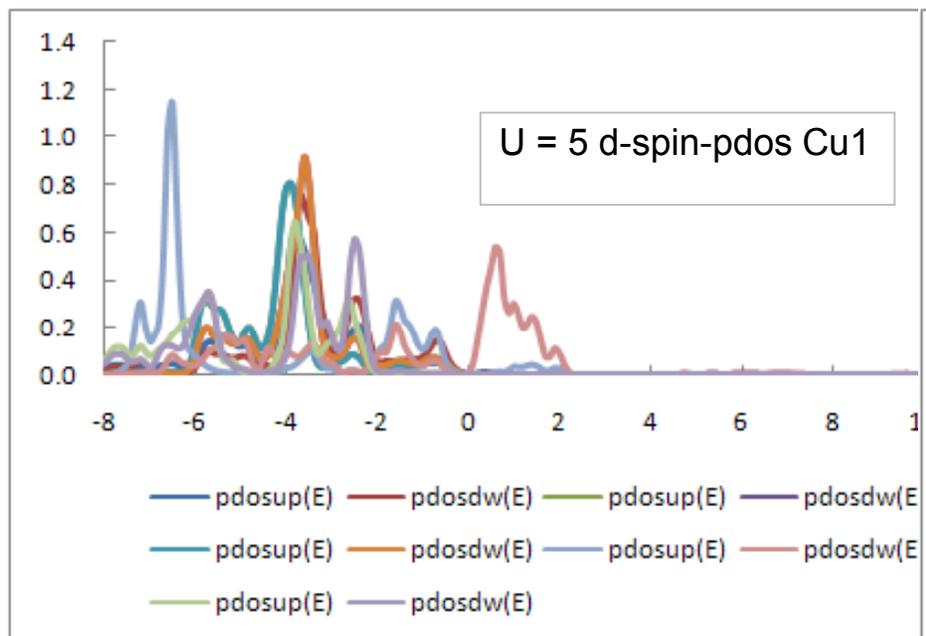
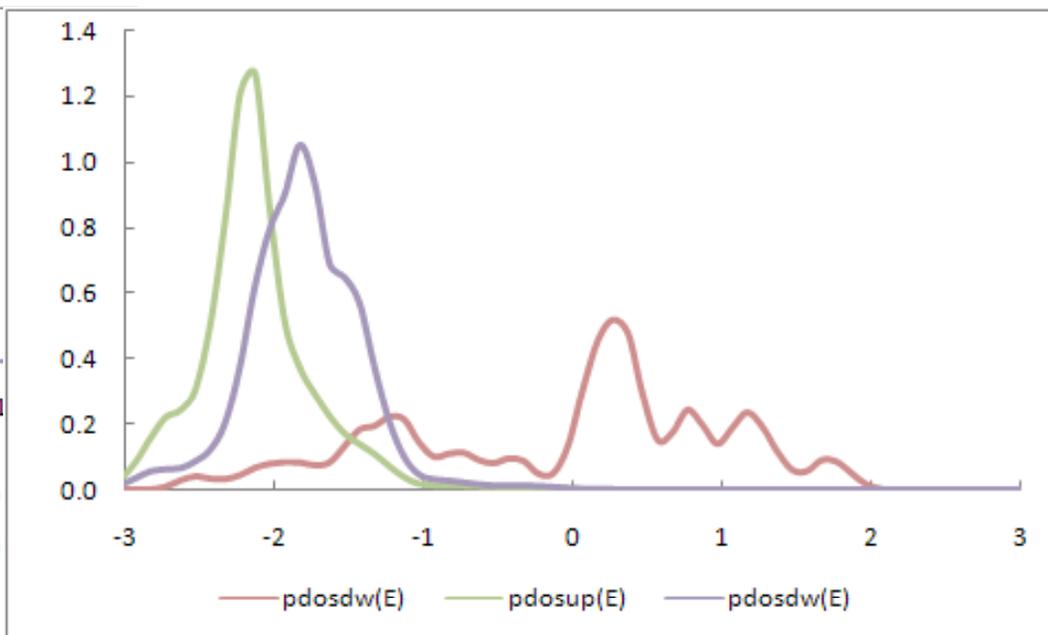
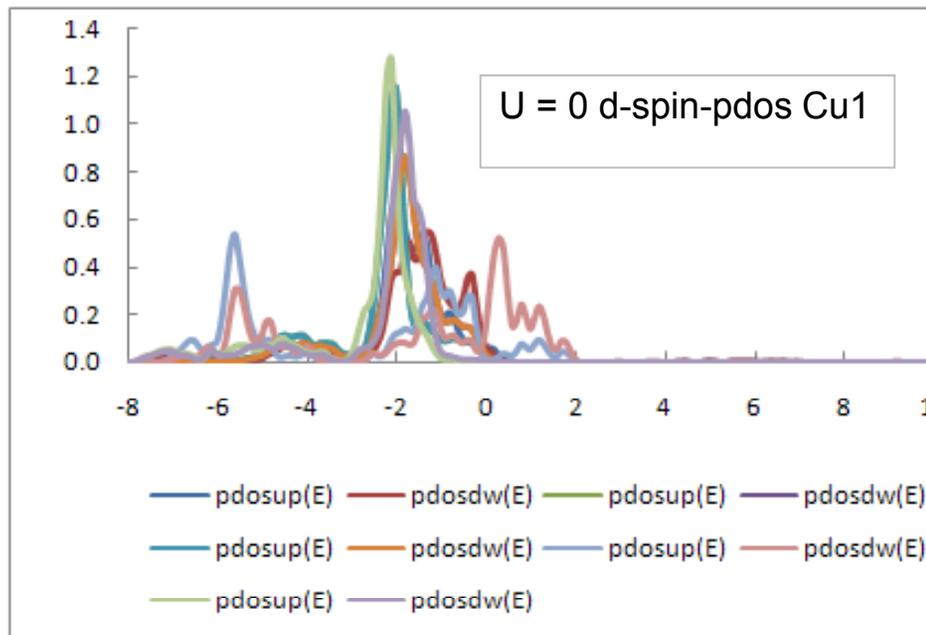


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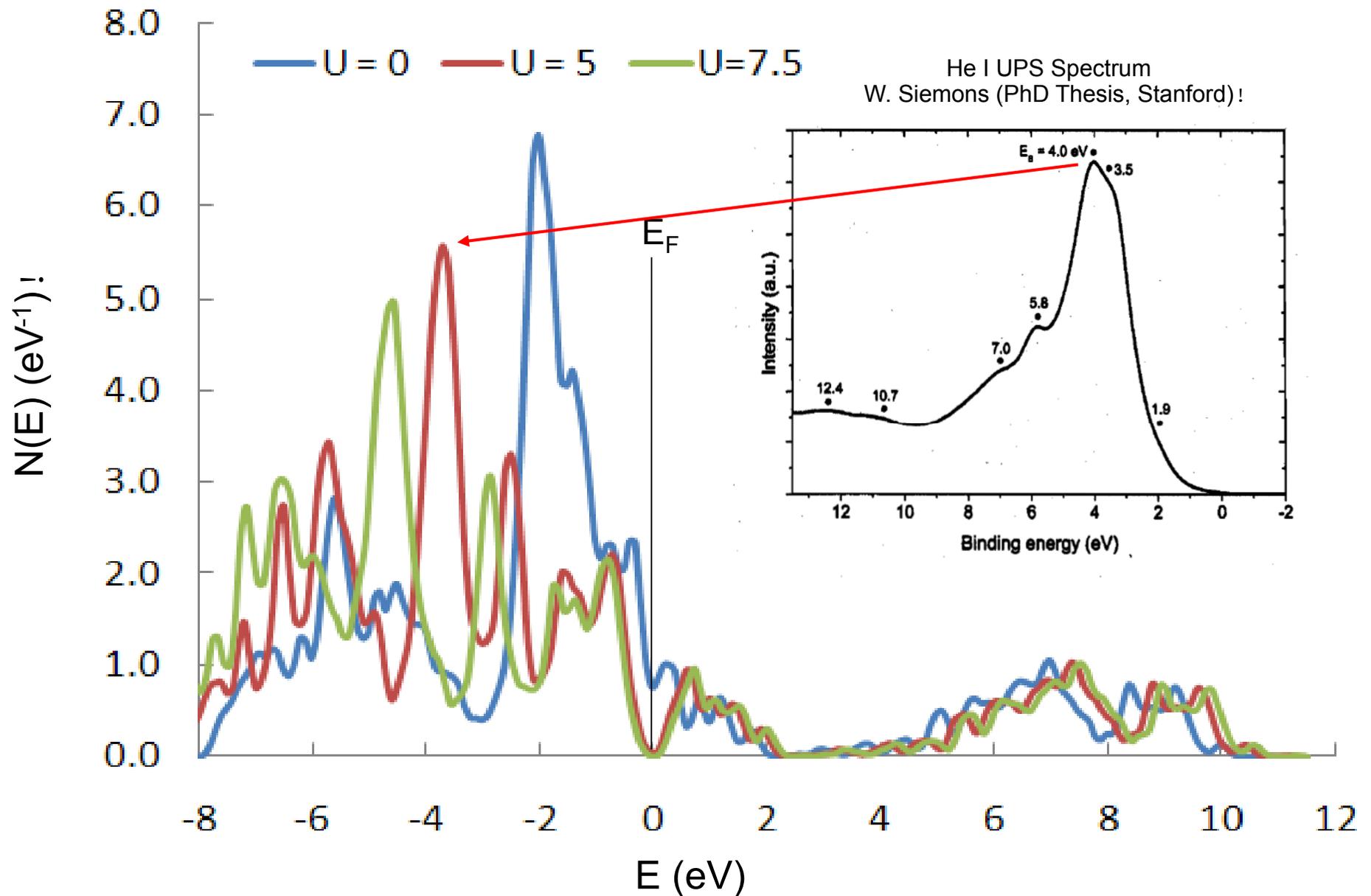
$N(E_f)$ vs c/a & $U(\text{ev})$



Spin Composition of Cu 3d pDOS as fn(Hubbard): $c/a = 1.36$

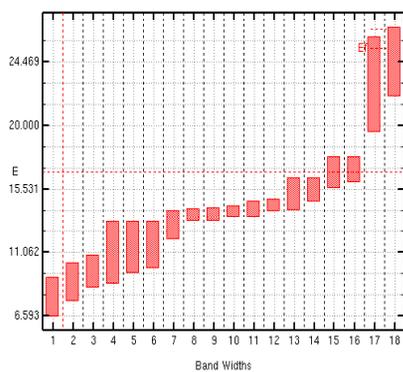


t-CuO Density-of-States

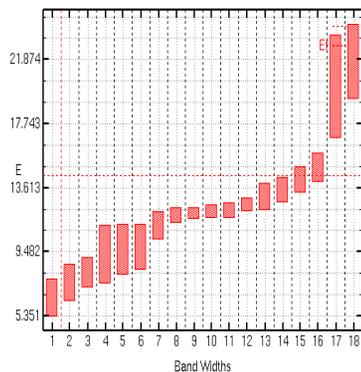


Af-CuO: Spin Up Bands

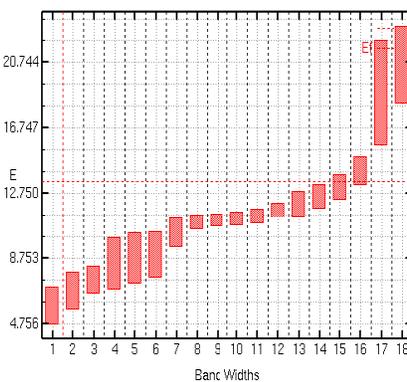
$U = 0$



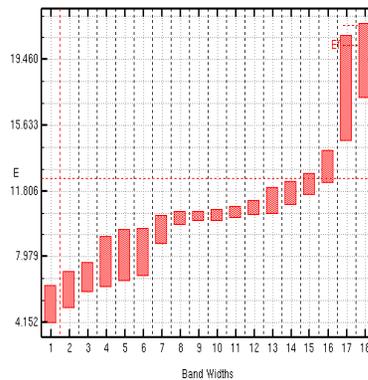
1.0



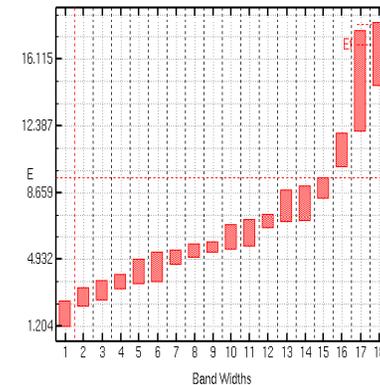
1.1



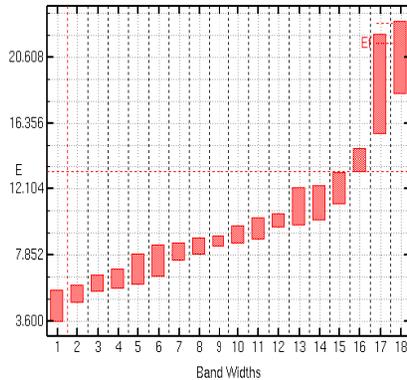
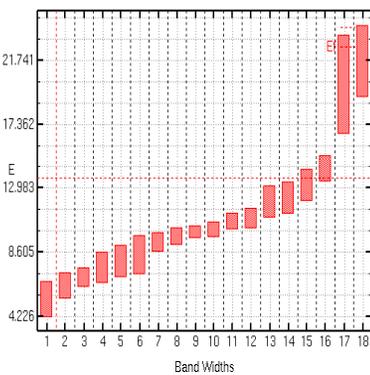
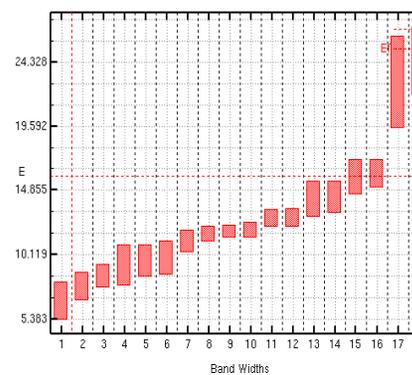
c/a
1.115



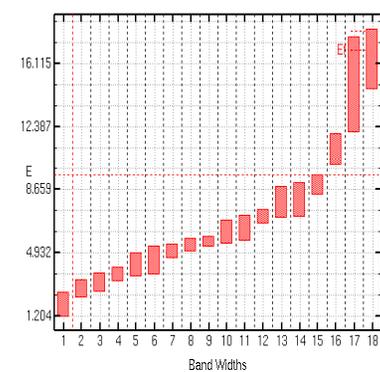
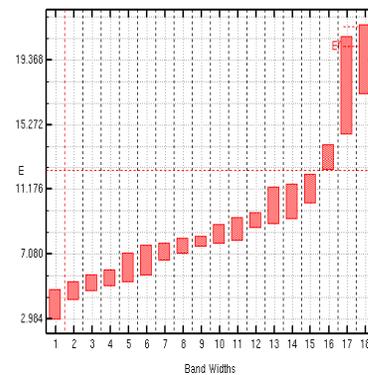
1.2



1.36

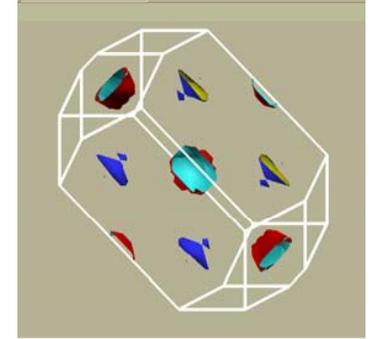
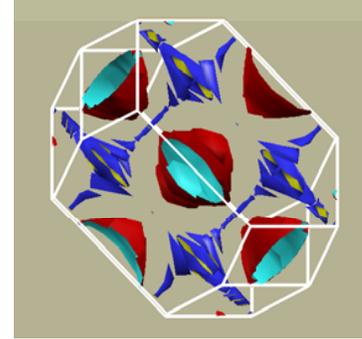
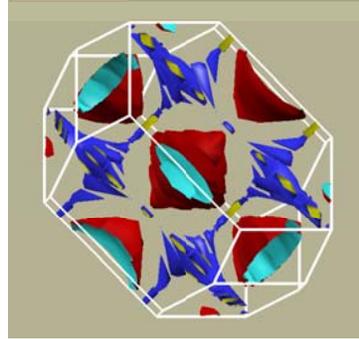
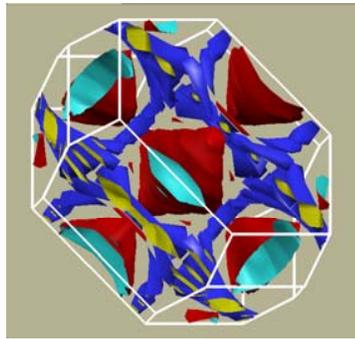
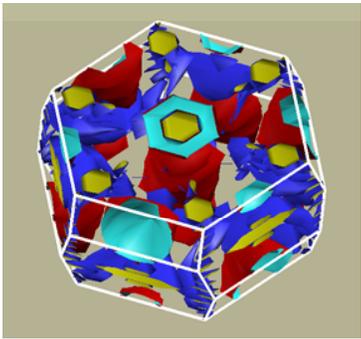


$U = 6$



Af-CuO: FS Spin Up

$U = 0$



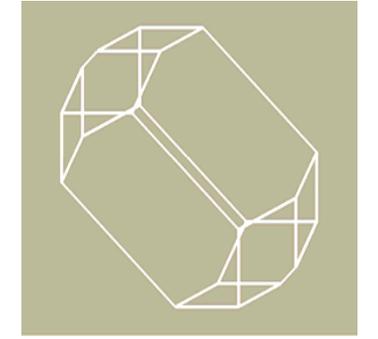
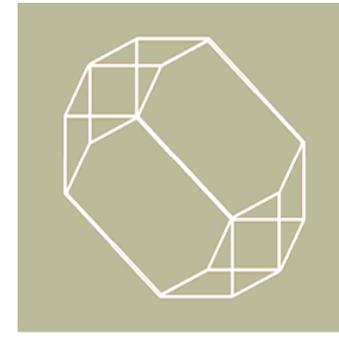
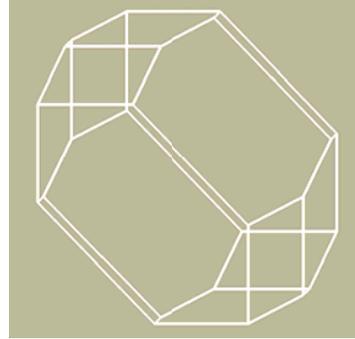
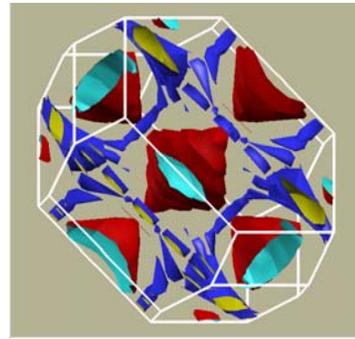
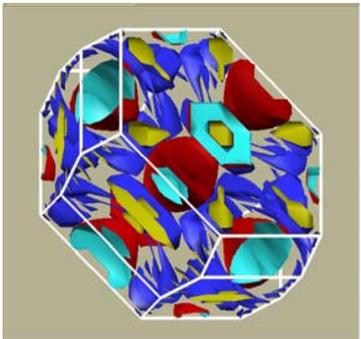
1.0

1.1

c/a
1.115

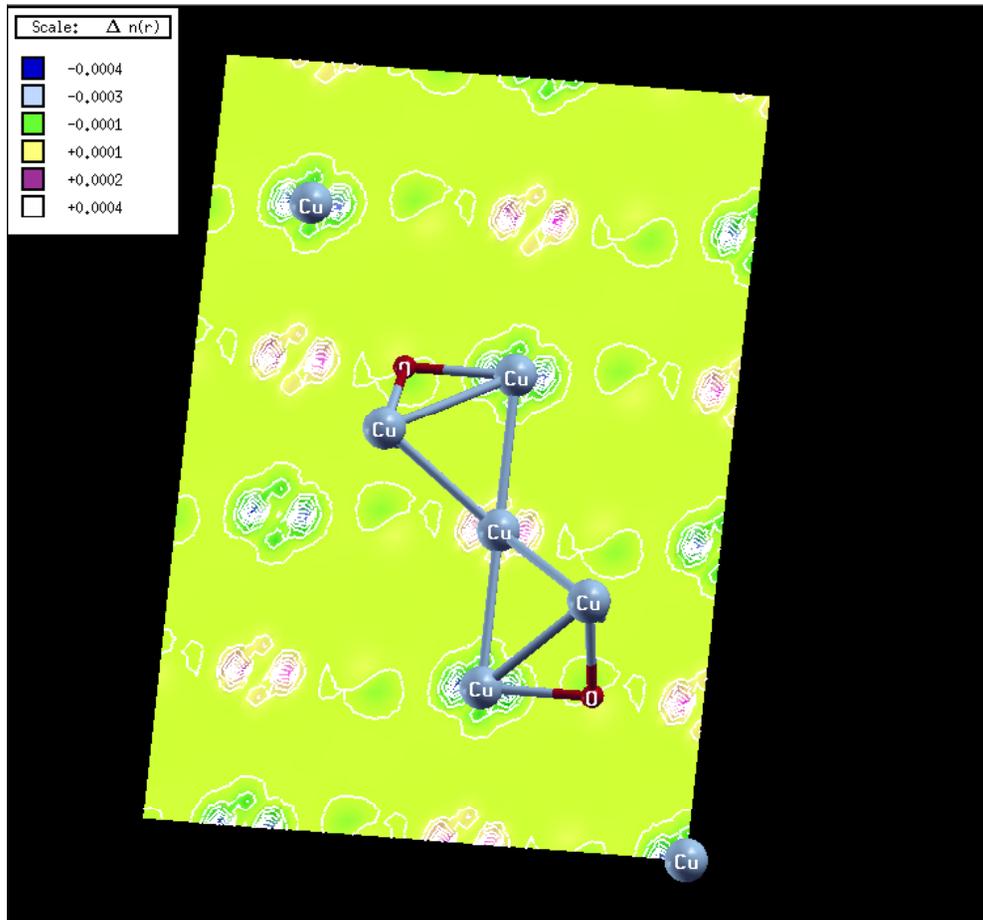
1.2

1.36

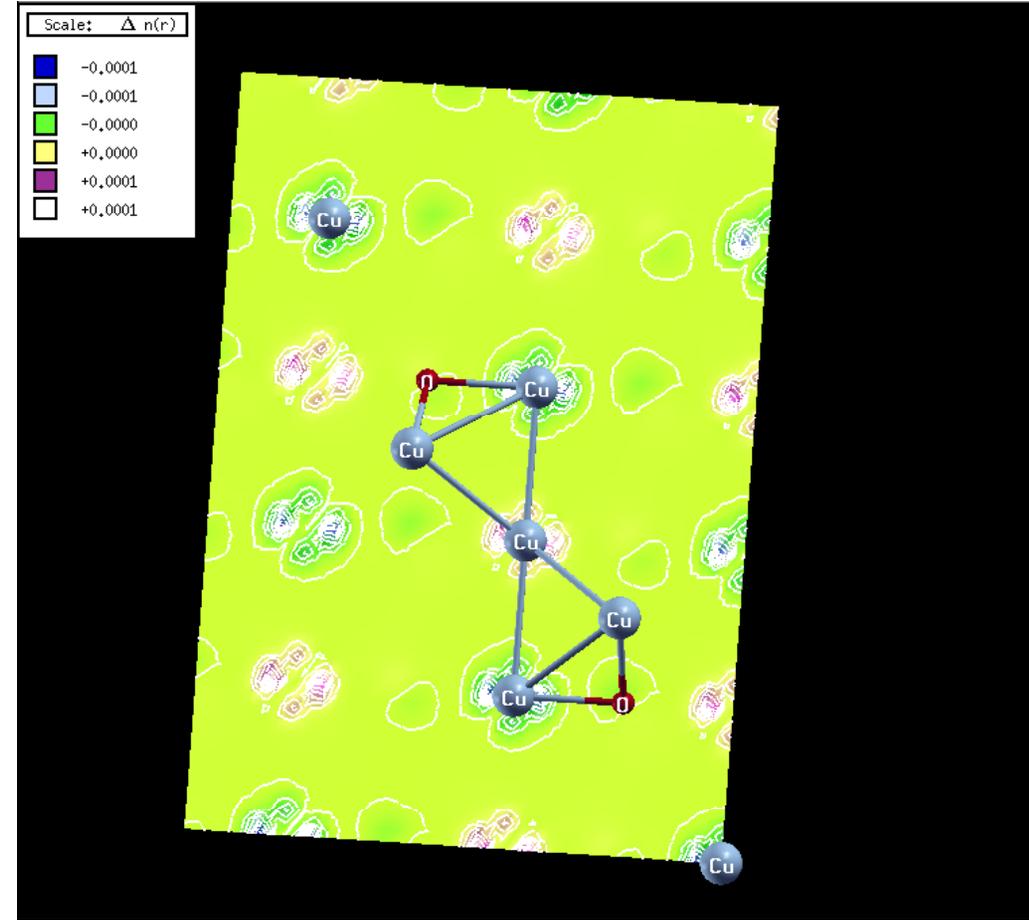


$U = 6$

$$c/a = 1.00$$

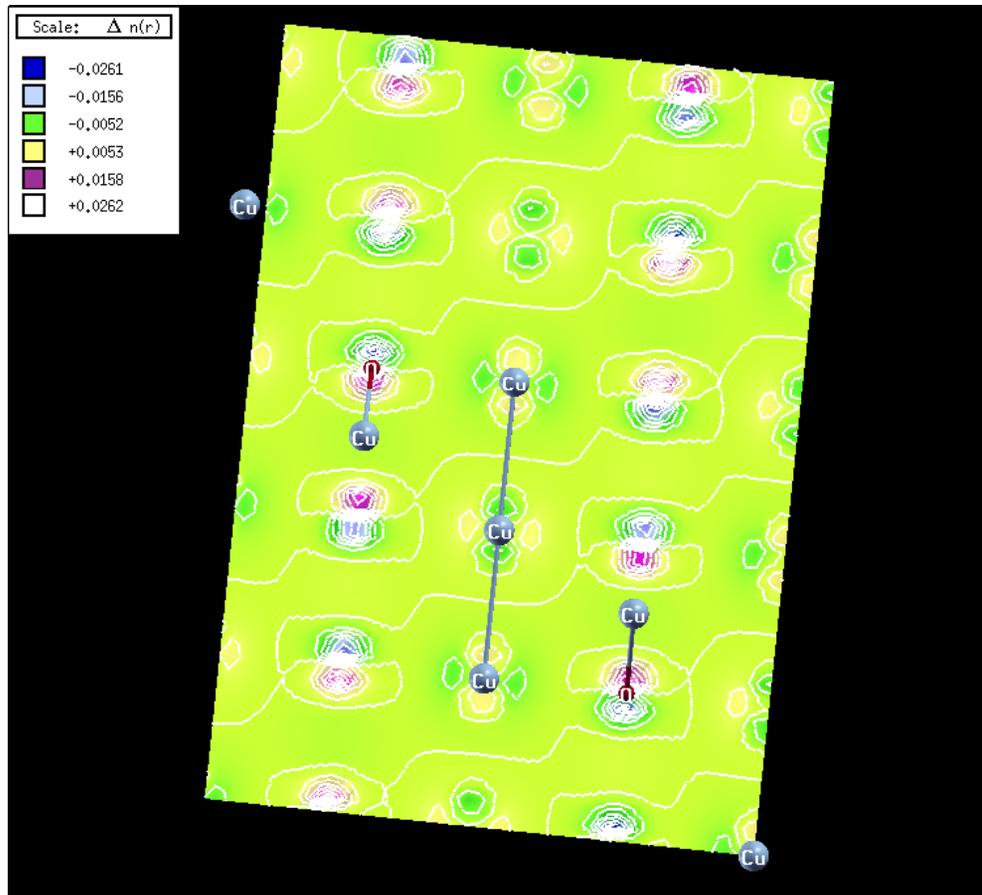


$$U = 0$$

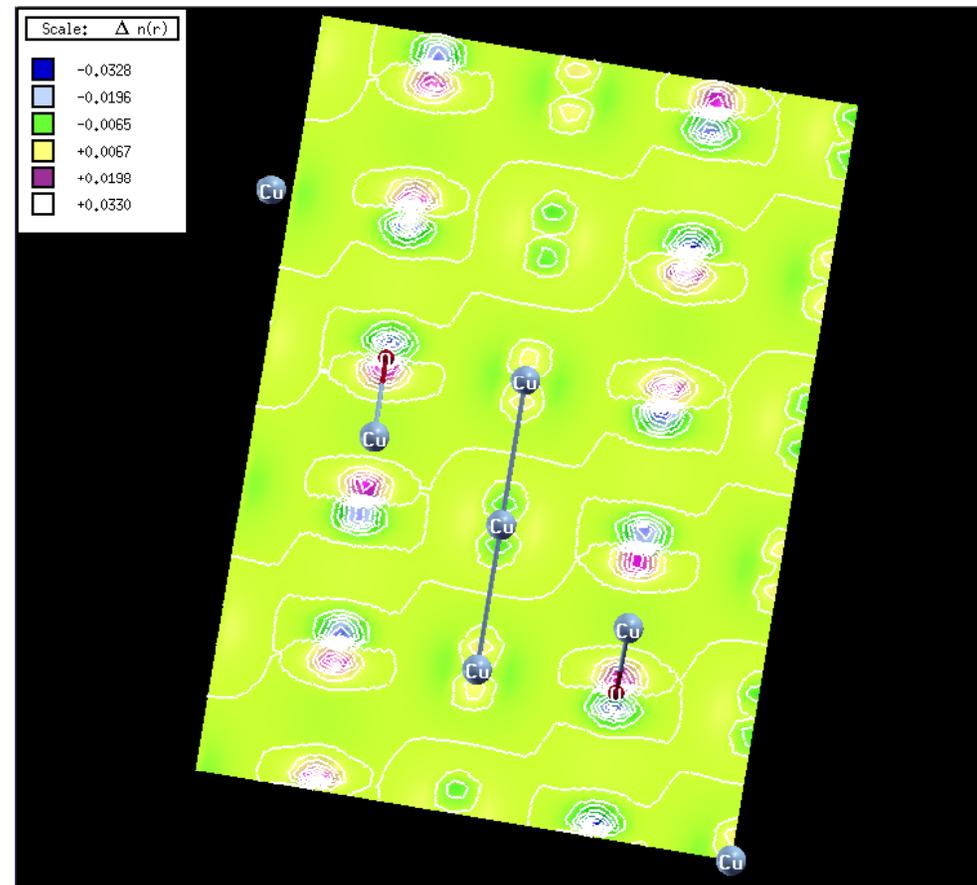


$$U = 6$$

$$c/a = 1.36$$



$$U = 0$$



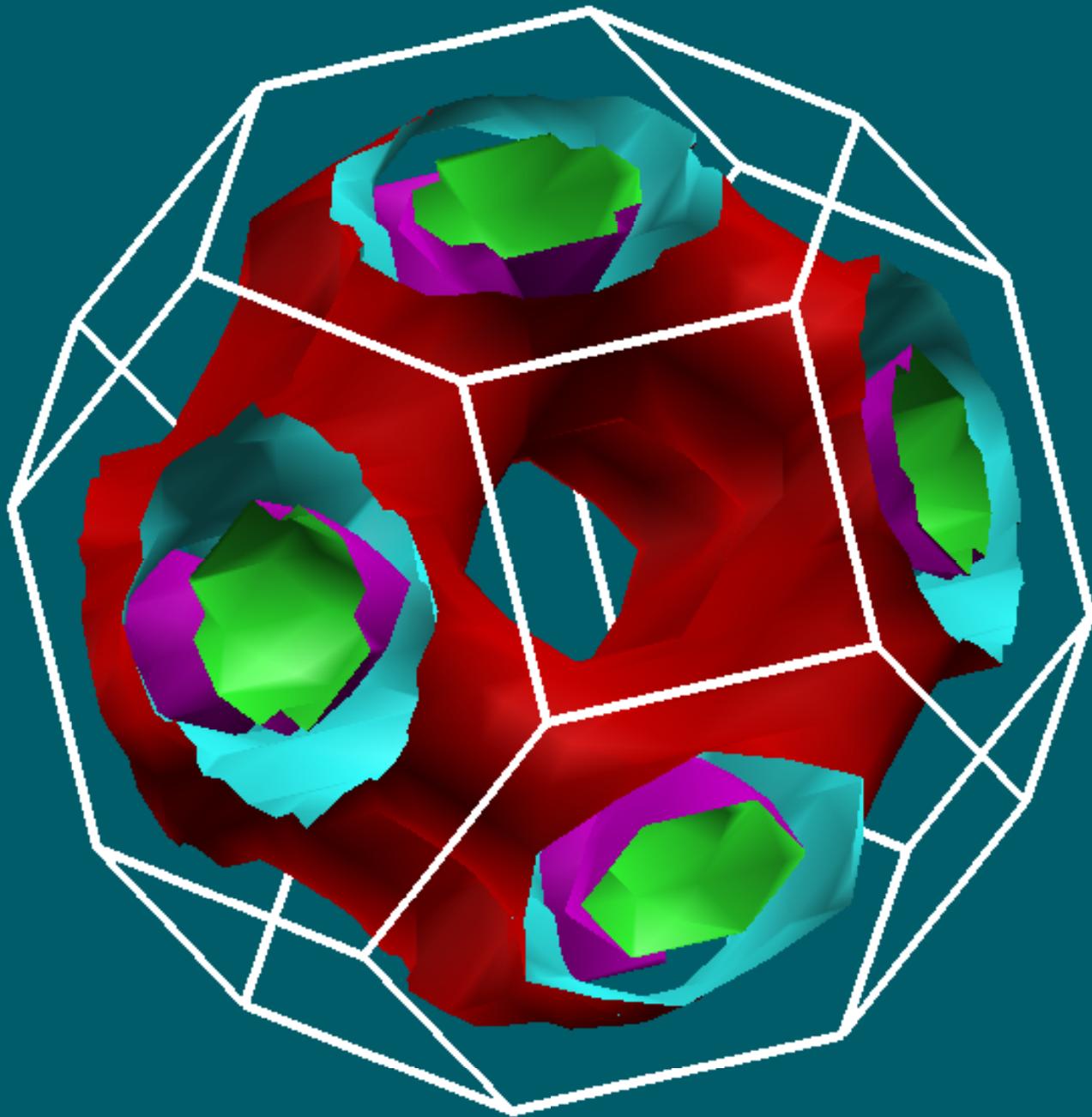
$$U = 6$$

Agenda

- ...Still No Theory
- Structural Issues
- “Experimental Apparatus”
- Band Structure, DOS and Fermiology
- **Superconductivity**
- Conclusions/Homework

Electron-Phonon Coupling - Superconductivity -

- QE package for e-p coupling with spin-polarized bands still “under construction,” so...
- Since the bands near the Fermi level hardly change from $U = 0$ to $U = 6$, let's...
- Just ignore the AF II symmetry and see what happens!



Electron-Phonon Coupling a la Migdal-Eliashberg-McMillan

(plus Allen & Dynes)!

$$H_{el-ph} = \sum_{\mathbf{k}q\nu} g_{\mathbf{k}+\mathbf{q},\mathbf{k}}^{q\nu,mn} c_{\mathbf{k}+\mathbf{q}}^{\dagger m} c_{\mathbf{k}}^n (b_{-\mathbf{q}\nu}^{\dagger} + b_{\mathbf{q}\nu}) \quad (1)$$

$$\alpha^2 F(\omega) = \frac{1}{N(\varepsilon_F)} \sum_{mn} \sum_{q\nu} \delta(\omega - \omega_{q\nu}) \sum_{\mathbf{k}} |g_{\mathbf{k}+\mathbf{q},\mathbf{k}}^{q\nu,mn}|^2 \\ \times \delta(\varepsilon_{\mathbf{k}+\mathbf{q},m} - \varepsilon_F) \delta(\varepsilon_{\mathbf{k},n} - \varepsilon_F), \quad (2)$$

$$\lambda = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega = \sum_{q\nu} \lambda_{q\nu}, \quad (3)$$

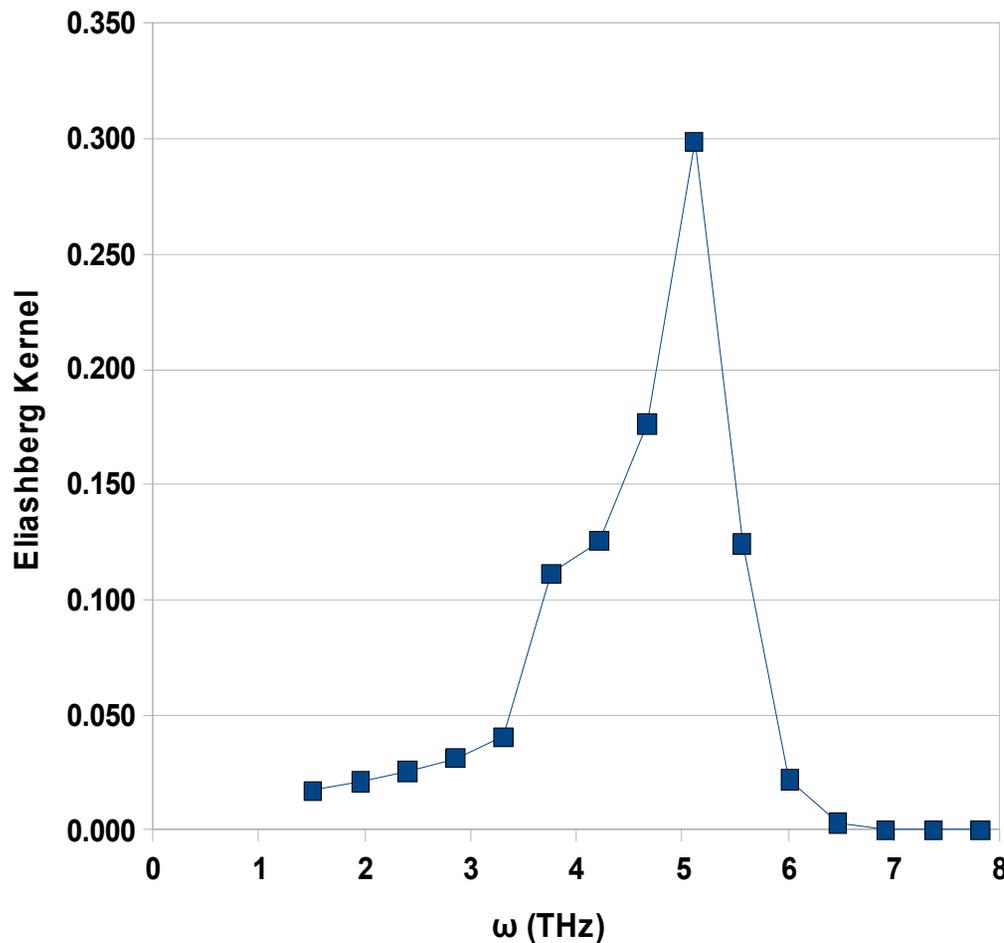
$$\lambda_{q\nu} = \frac{2}{N(\varepsilon_F)\omega_{q\nu}} \sum_{mn} \sum_{\mathbf{k}} |g_{\mathbf{k}+\mathbf{q},\mathbf{k}}^{q\nu,mn}|^2 \\ \times \delta(\varepsilon_{\mathbf{k}+\mathbf{q},m} - \varepsilon_F) \delta(\varepsilon_{\mathbf{k},n} - \varepsilon_F). \quad (4)$$

Wierzbowska, et al, arXiv:cond-mat/0504077 (2006) (Nb)

Non-Magnetic Cubic Rocksalt CuO

-- Electron-Phonon Properties --

$\alpha^2F(\omega)$



$\sigma = 0.04$

- $\lambda \sim 0.6 - 0.7$
- Other sc's...

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

	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	-

Agenda

- ...Still No Theory
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Conclusions & Homework

Conclusions

- c-rs-CuO is metallic and thus a proxy for HTSC cuprates.
- e-p $\lambda \sim 0.6 - 0.7$ consistent with $T_C \sim 20 - 50$ K.
- t-rs-CuO becomes a MH-CTI for $c/a > \sim 1.3$.
- $c/a < 1.3$, t-rs-CuO is “self-doped” metal.
- Exhibits “instabilities” in GSE possibly sc related.
- DFT (LDA+U) + proxy structures a useful exploratory tool for nano-material discovery.

Homework

- Compute e-p coupling λ as $f(c/a, U)$ for t-rs-CuO.
- Determine condensate symmetry.
- Compute T_N , μ^* , BCS prefactor, then T_C .
- Compute isotope shift.
- Calculate Lindhardt function.
- Look for anharmonicities a la Newns & Tsuei
- Calculate optical & transport properties as $f(c/a)$.

Dank je wel !