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

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- Ted Geballe
- Bob Hammond
- Mac Beasley
- Gert Koster
- Wolter Siemons

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Con grazie mille e speciale a:
- Paolo Gianozzi, Udine
- Matteo Cococcioni, U Minn
- Nicola Marzari, MIT
- Axel Kohlmeyer, U Penn
- Evyaz Isaev, MISA
- Tone Kokalj, Ljubljana

...*e tutto di consorzio*
"Quantum Espresso," ICTP

22 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!

Agenda

- …Still No Theory
- Structural Issues
- “Experimental Apparatus”
- Band Structure, DOS and Fermiology
- Superconductivity
- The da Vinci Code
- Conclusions/Homework

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

Theory of Everything

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

- Hydrogen atom
- Methane molecule
- Water
- Air
- Rocks
- Concrete
- Steel
- Glass
- Plastic
- Buildings
- Cities
- Continents

- Proteins
- DNA
- Viruses
- Bacteria
- Yeast
- Slime mold
- Butterflies
- Sharks
- Rats
- Lawyers
- Ebola virus
- Legislatures
- Civilizations

- Flowers
- Trees
- Cows
- Cheese
- Sauce Bernais
- Computers
- Television
- Cars
- Jets
- Lawnmowers
- Sewage
- Spotted owls

...

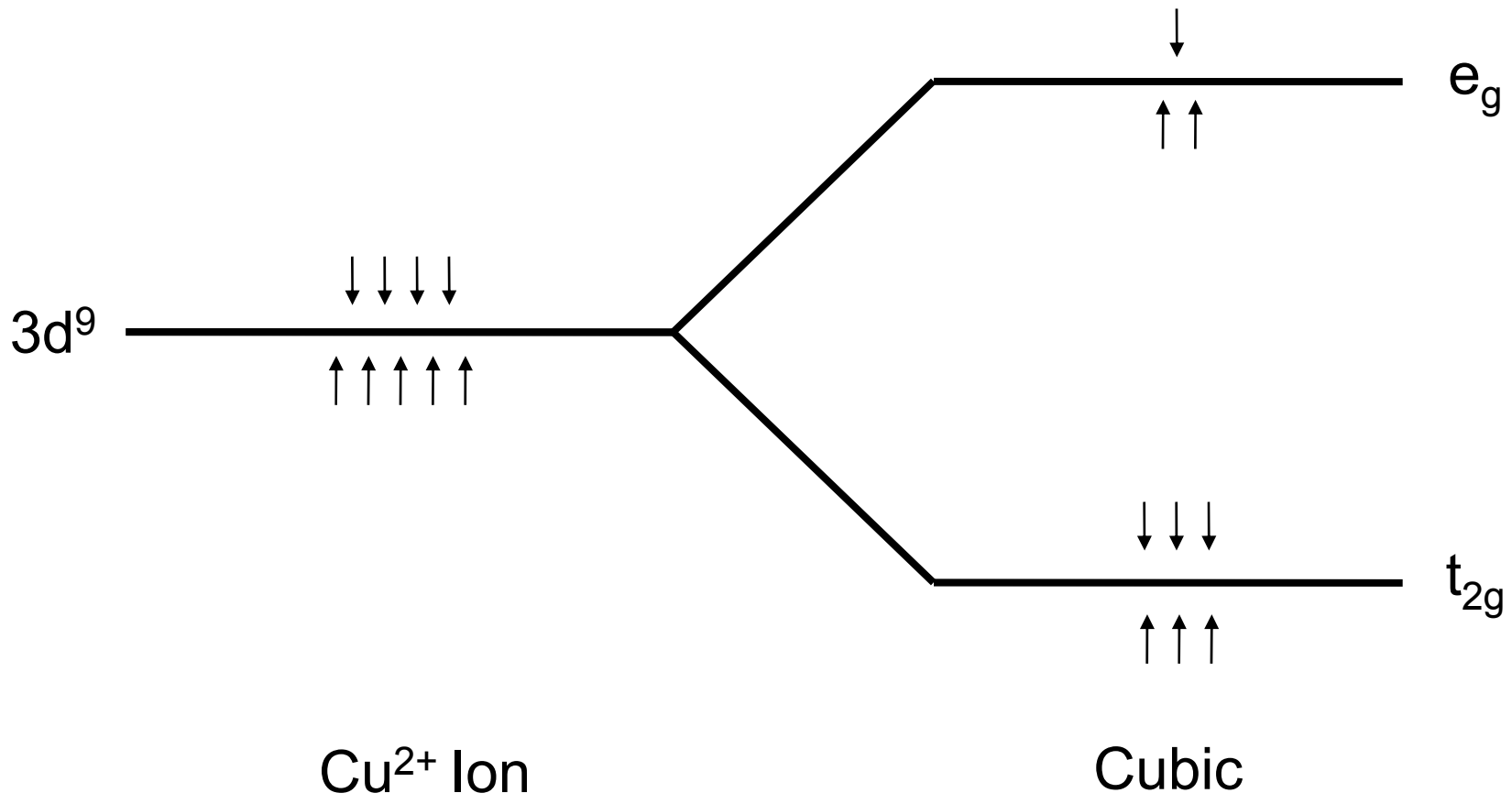
Should use the many body Dirac equation!

And Add Maxwell, Boltzman and Gibbs, and Newton

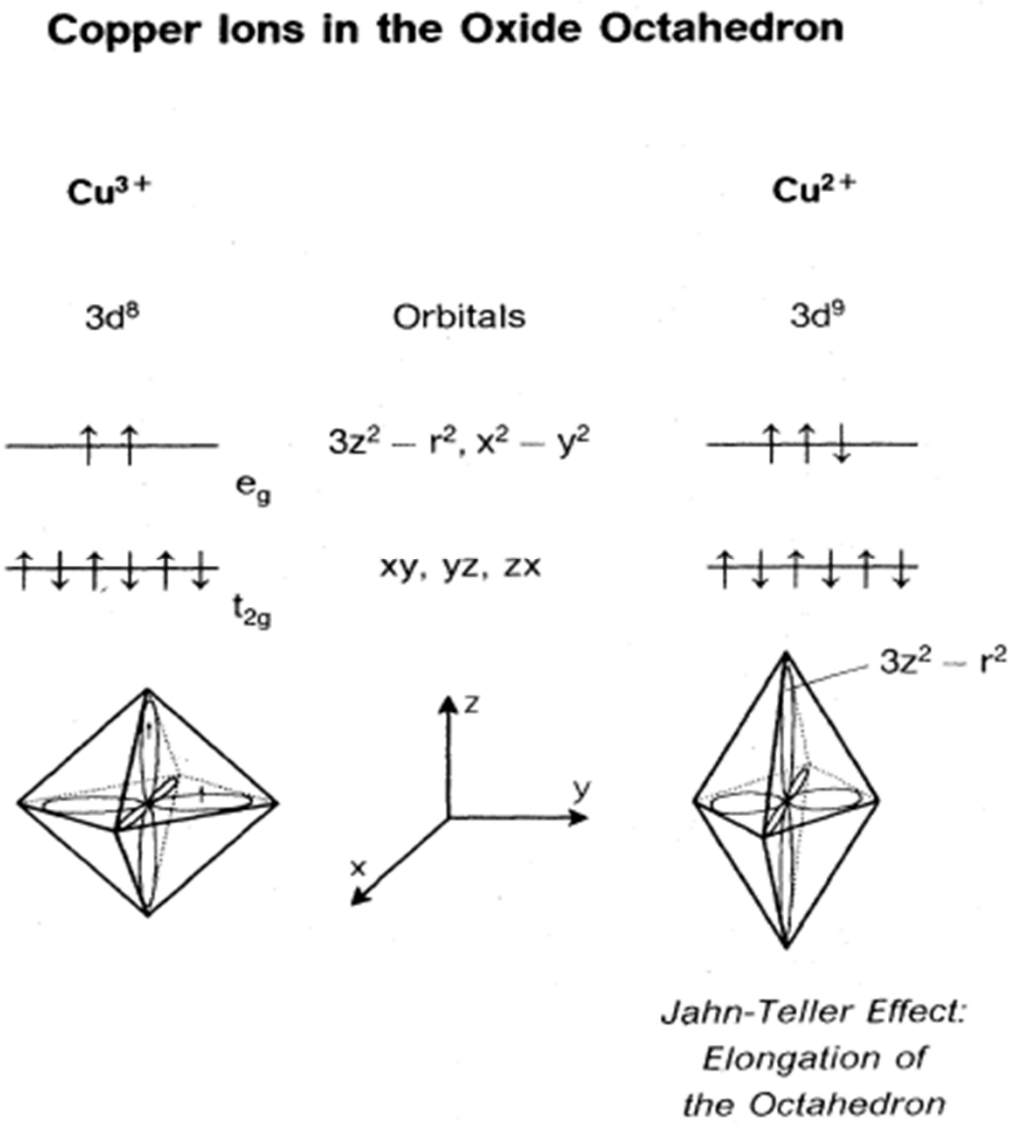
The crunch comes when Σ_i with i >= 3 -> "thermodynamic limit."

"Size Matters !"

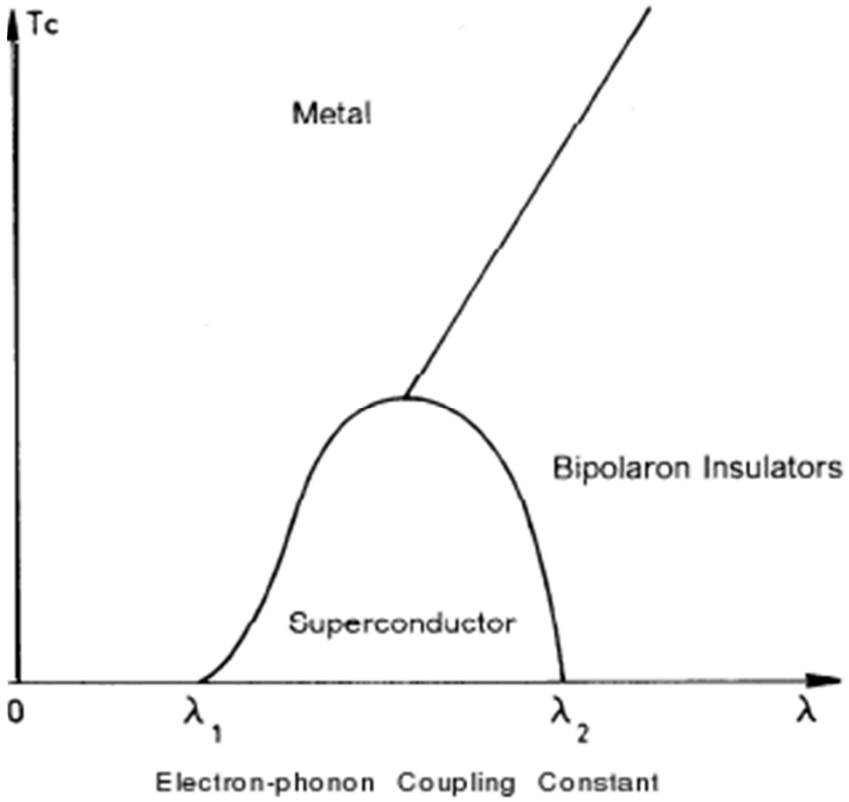
Cu^{2+} 3d Multiplet Splitting (Cubic)



Bednorz-Mueller Nobel Lecture



Jahn-Teller Effect: Elongation of the Octahedron



After Chakravarty, (1979)

Hubbard Theory

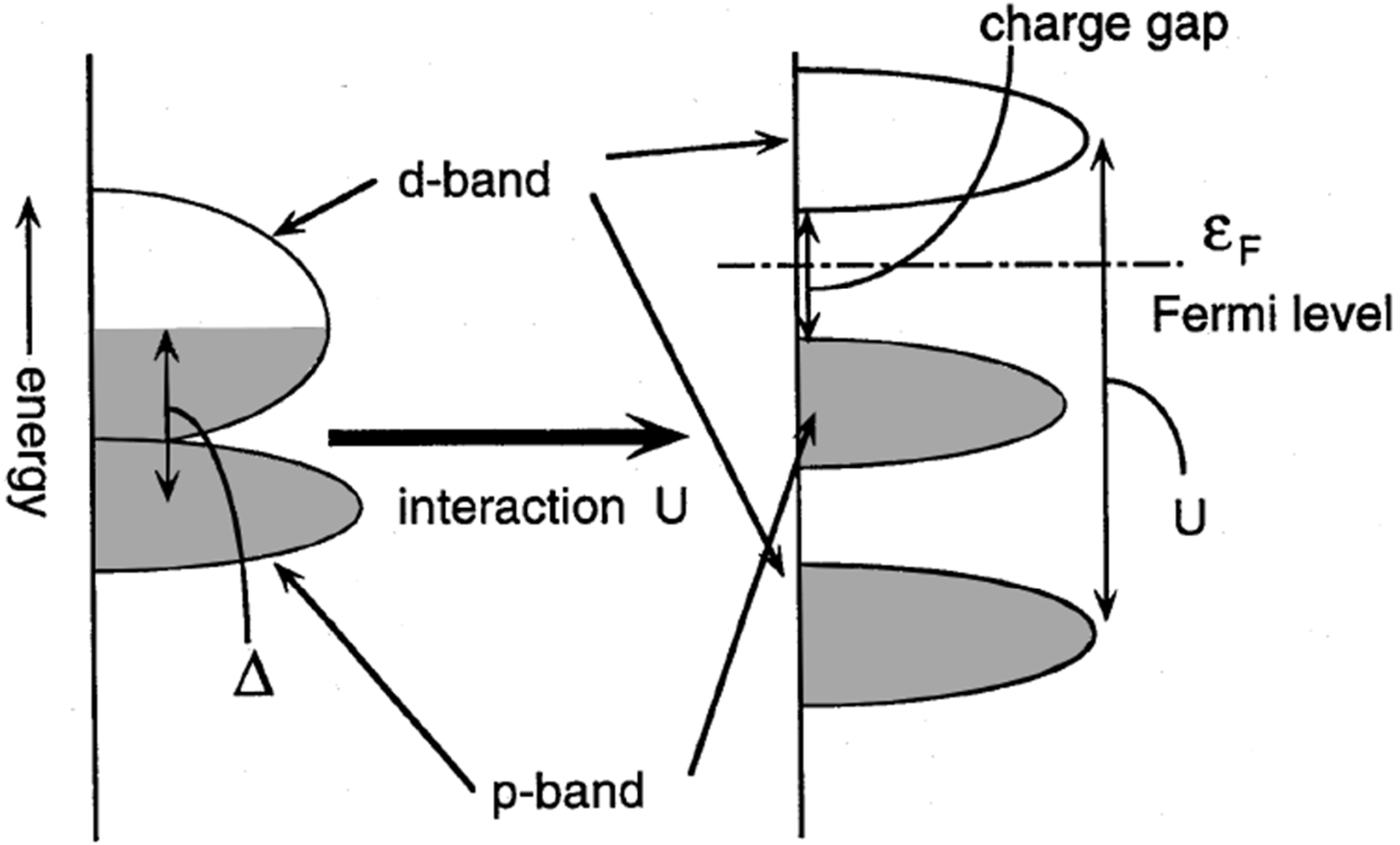
$$H = \sum_{\langle ij \rangle, \sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} n_{i\downarrow} n_{i\uparrow} + \frac{V}{2} \sum_{\langle ij \rangle, \sigma, s} n_{i\sigma} n_{js}$$

One-electron "band" term

On-site "Hubbard" double occupation coulomb repulsion

Off-site repulsion

Charge Transfer Insulator



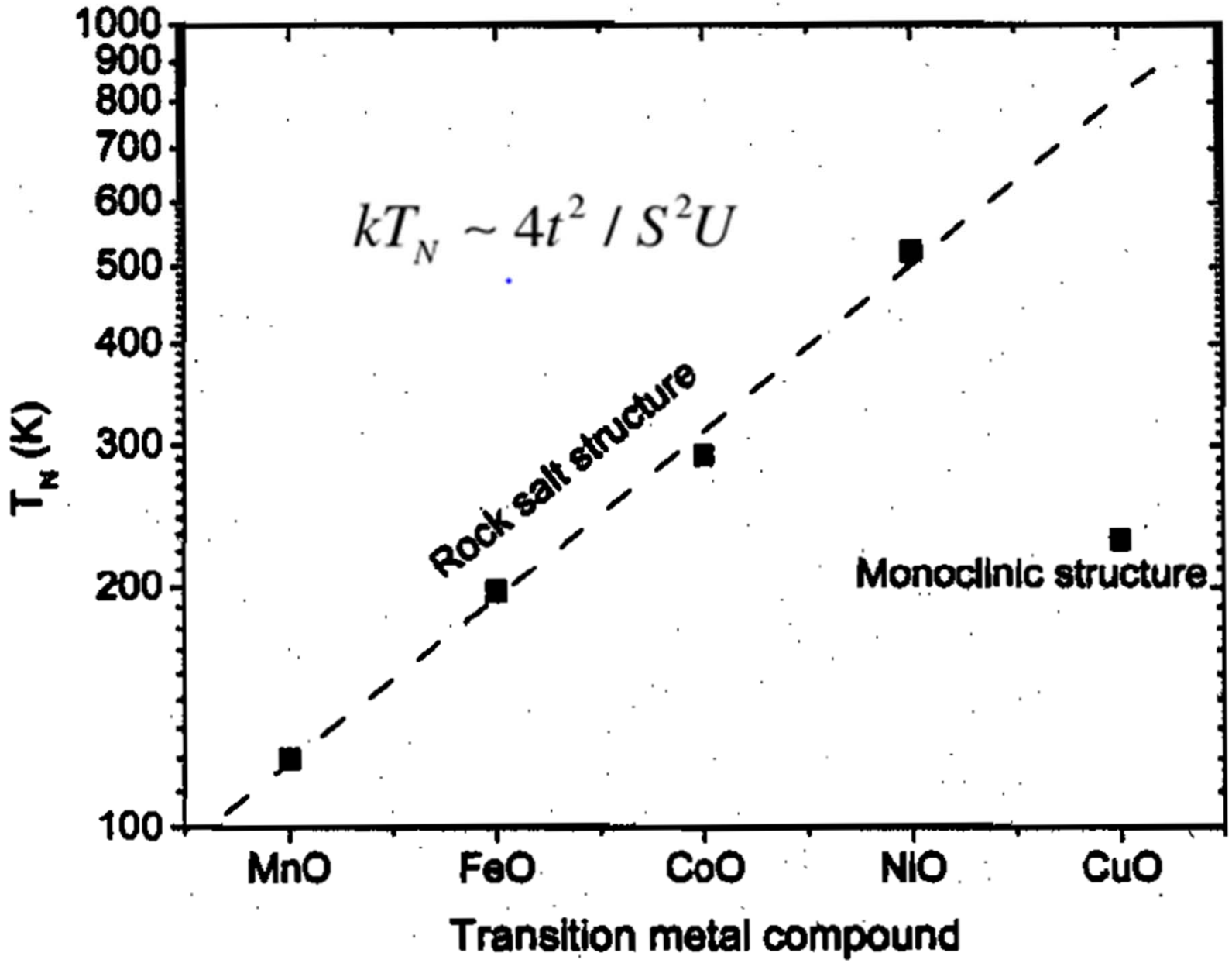
After Imada, et al, RMP 70, 1039 (1998)

Cubic Rocksalt Divalent TMOs

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)

Néel Temperature vs. TMO Atomic Number



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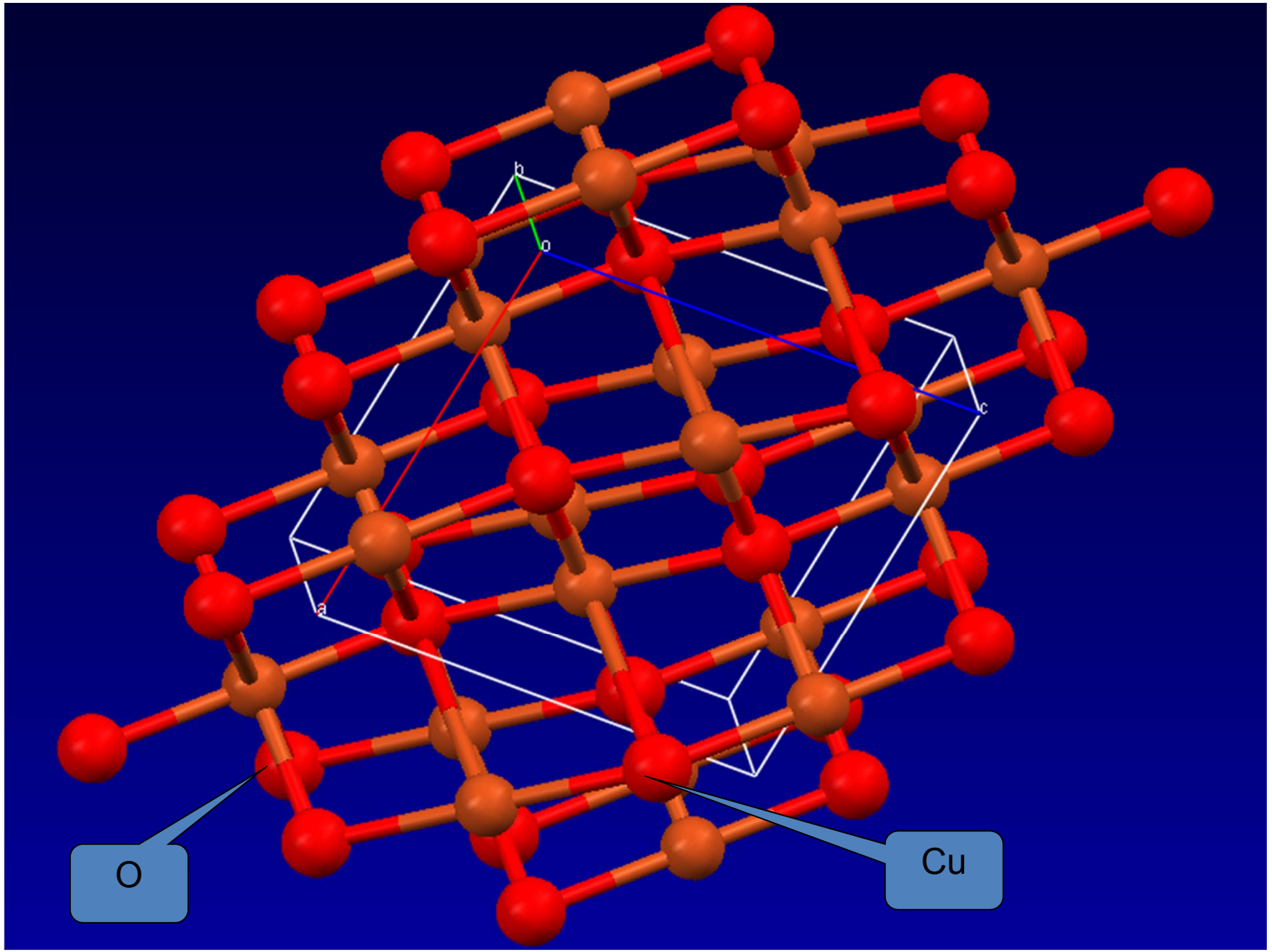
Tenorite (Monoclinic CuO)



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

Experimental Equipment (Software)

- QUANTUM-ESPRESSO Suit of Codes
  - DFT (LDA+U) plus electron-phonon
  - Graphics by Tone Kolalj (XCrysDen)
  - www.quantum-espresso.org
- "Dial-in" Parameters
  - G^2 = 40 Ry ρ = 320 Ry
  - Convergence ≤ 10^{-6} Ry
  - "Smearing" = Methfessel-Paxton
  - Psuedopotentials: 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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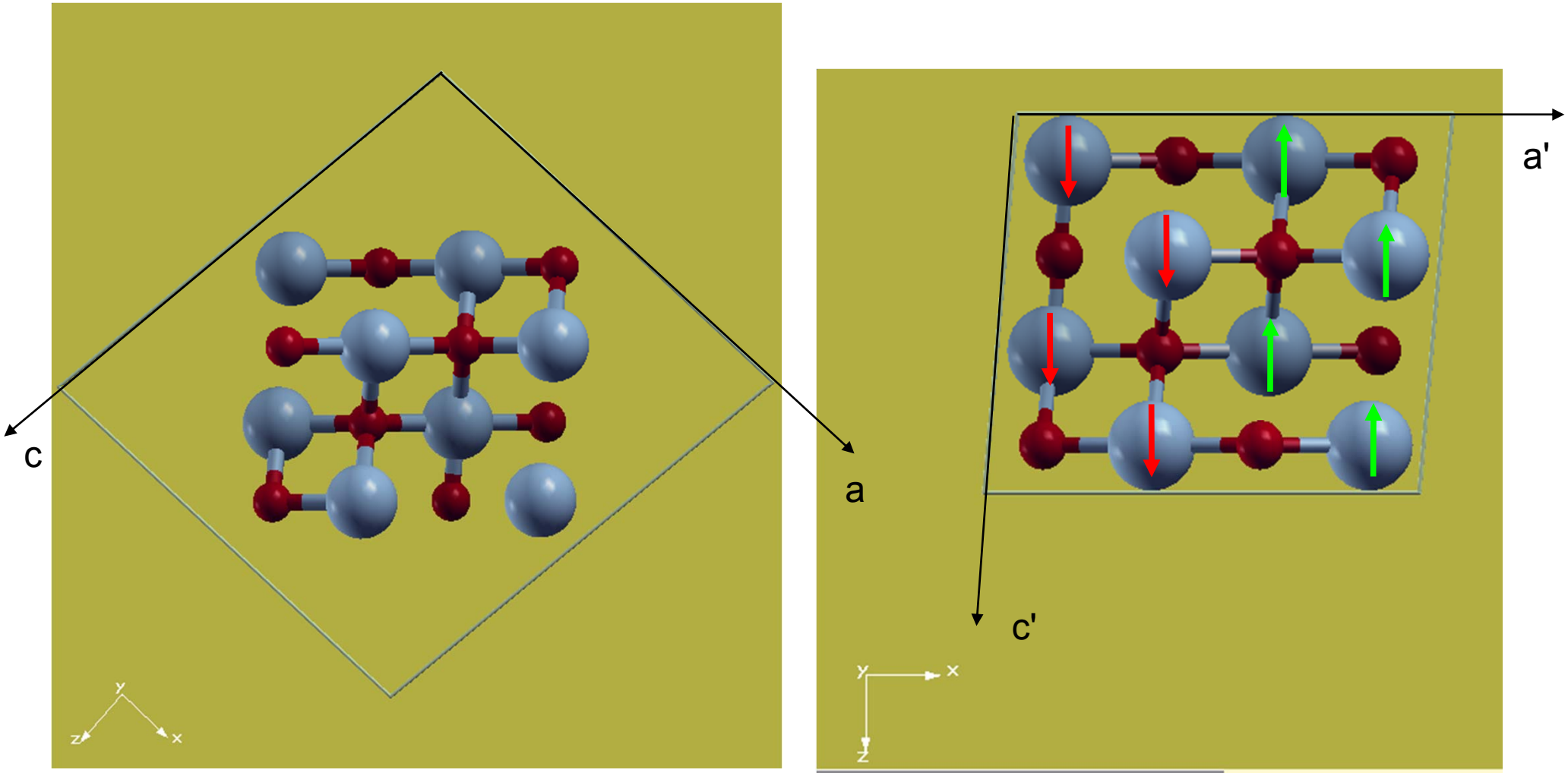
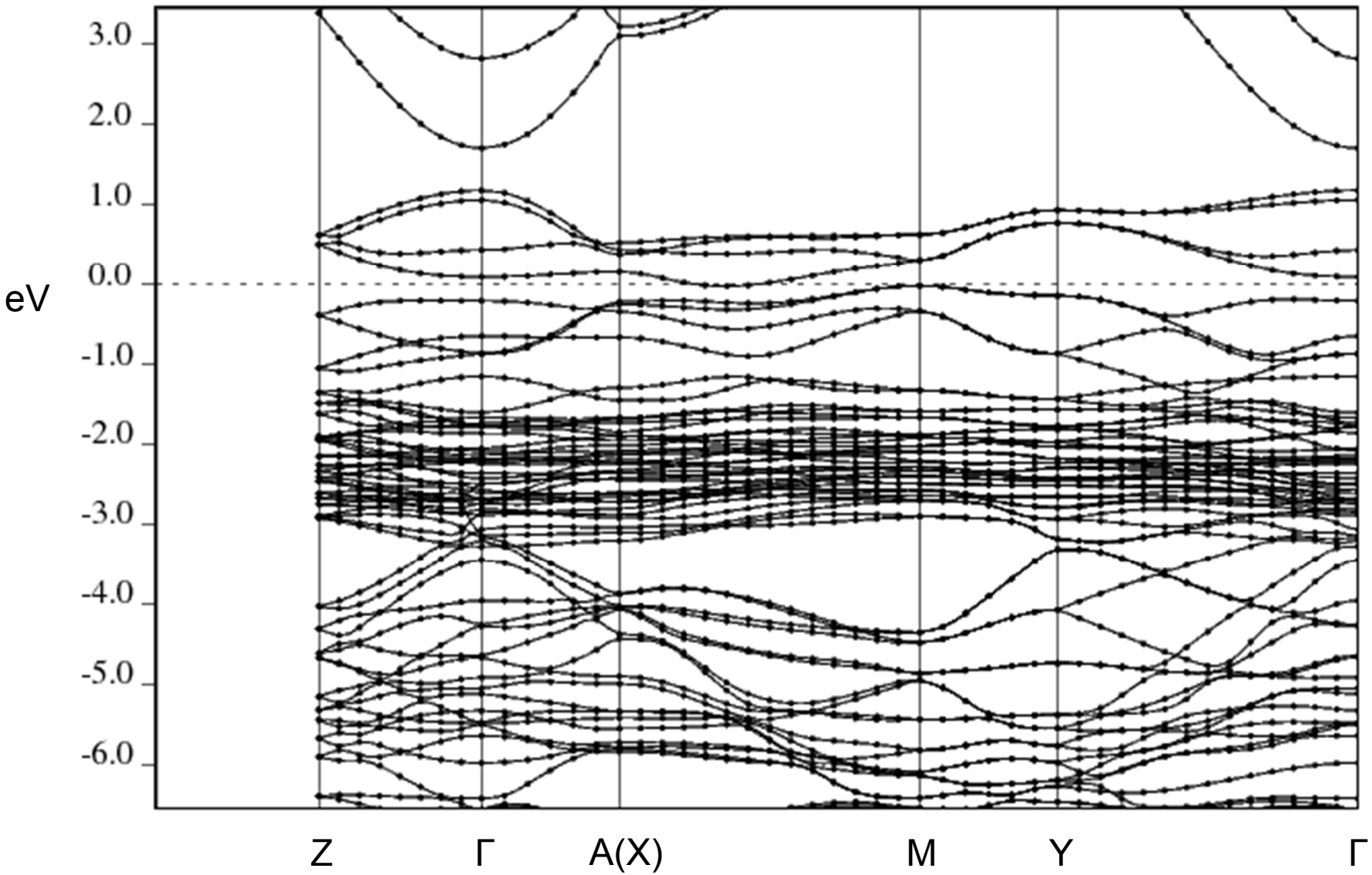
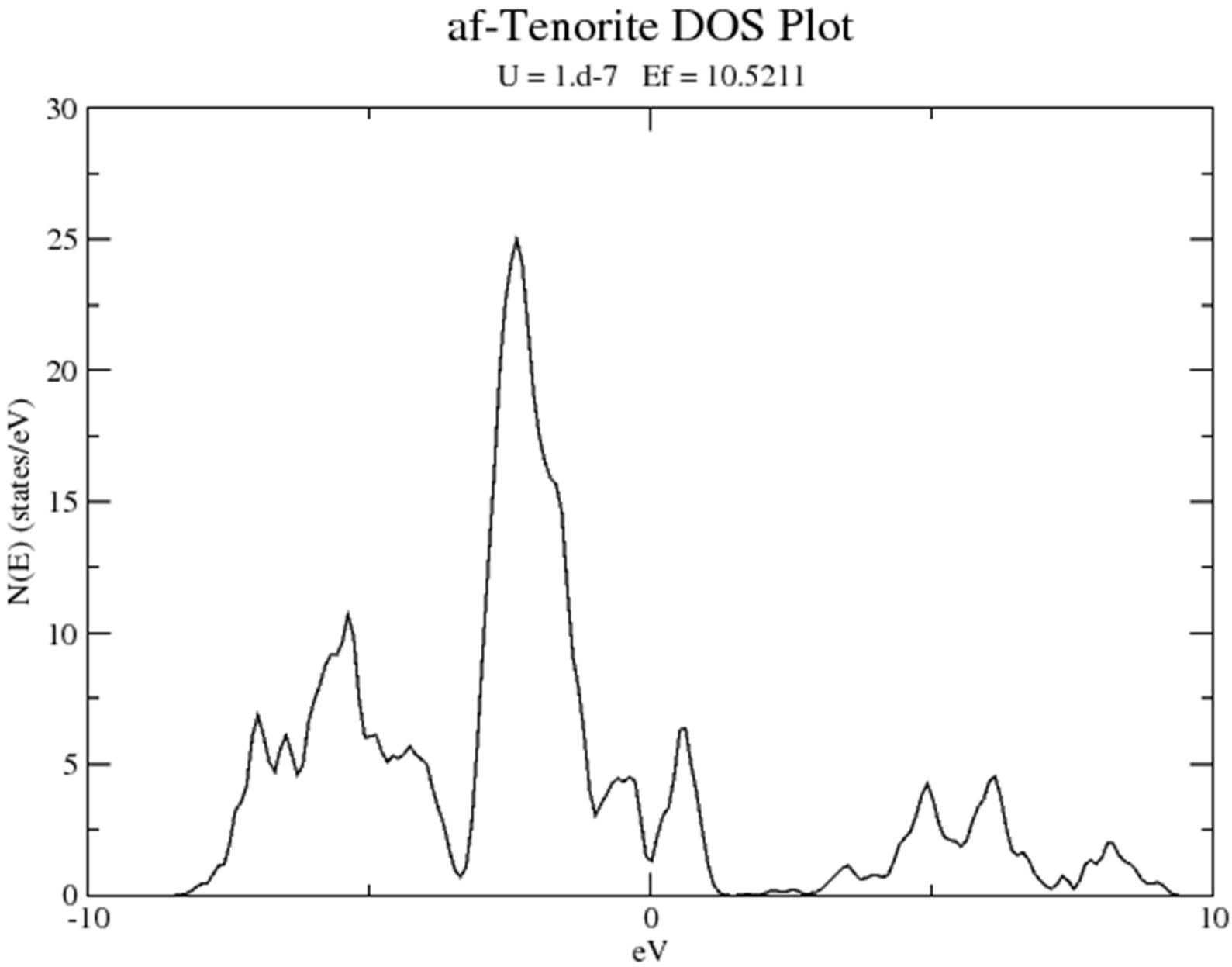
nm & af Unit Cells

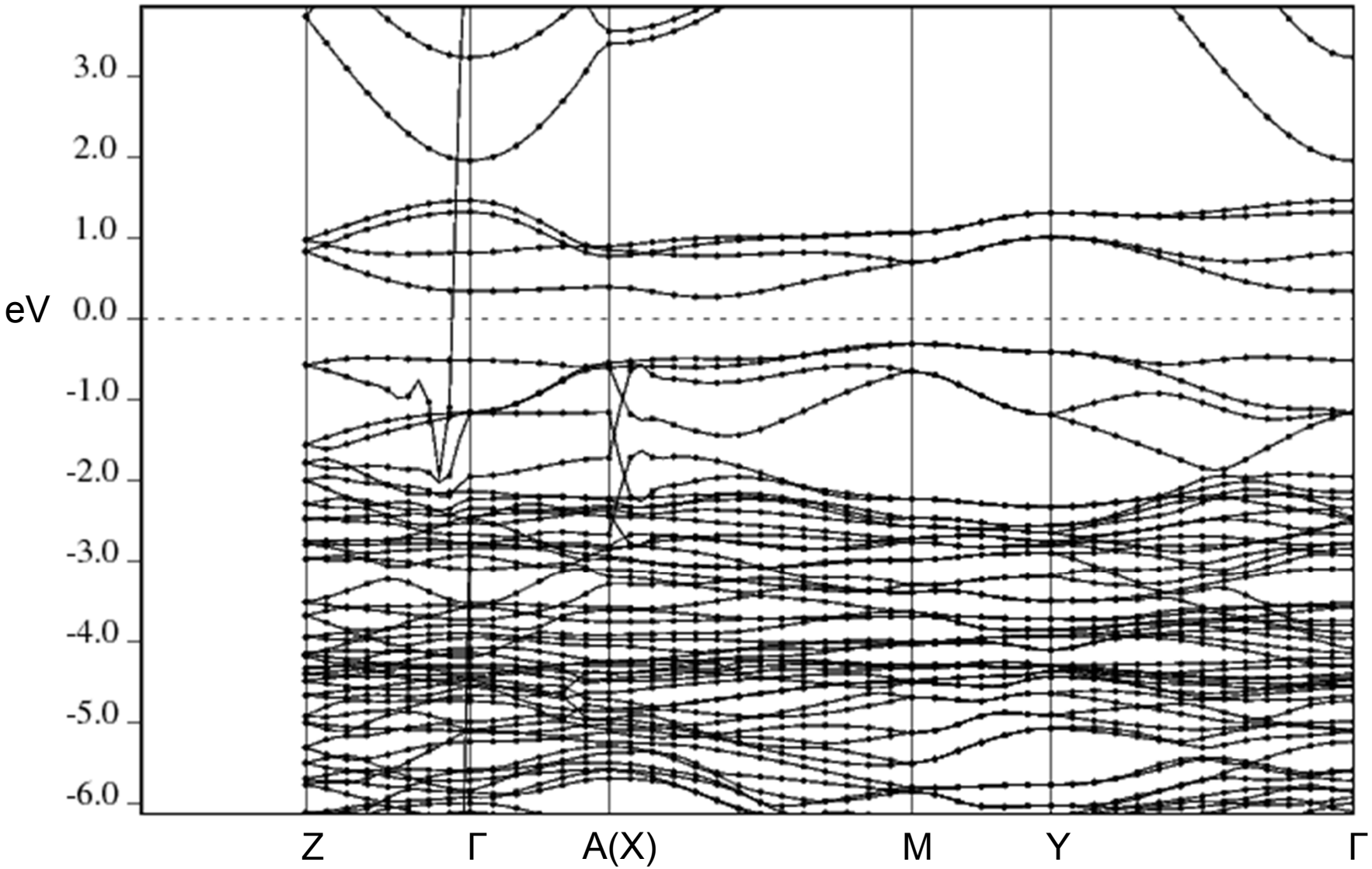


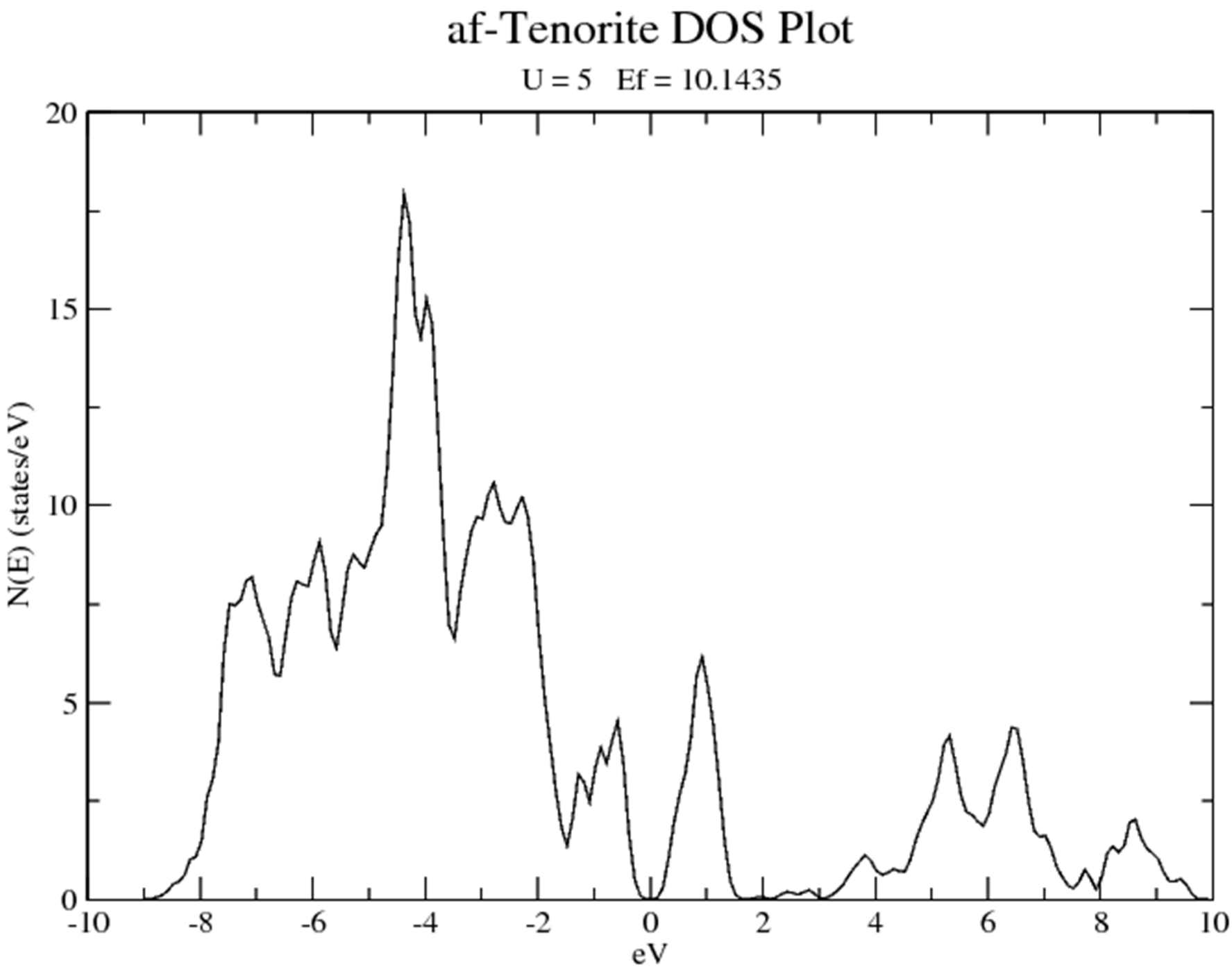
Tenorite (U = 0)



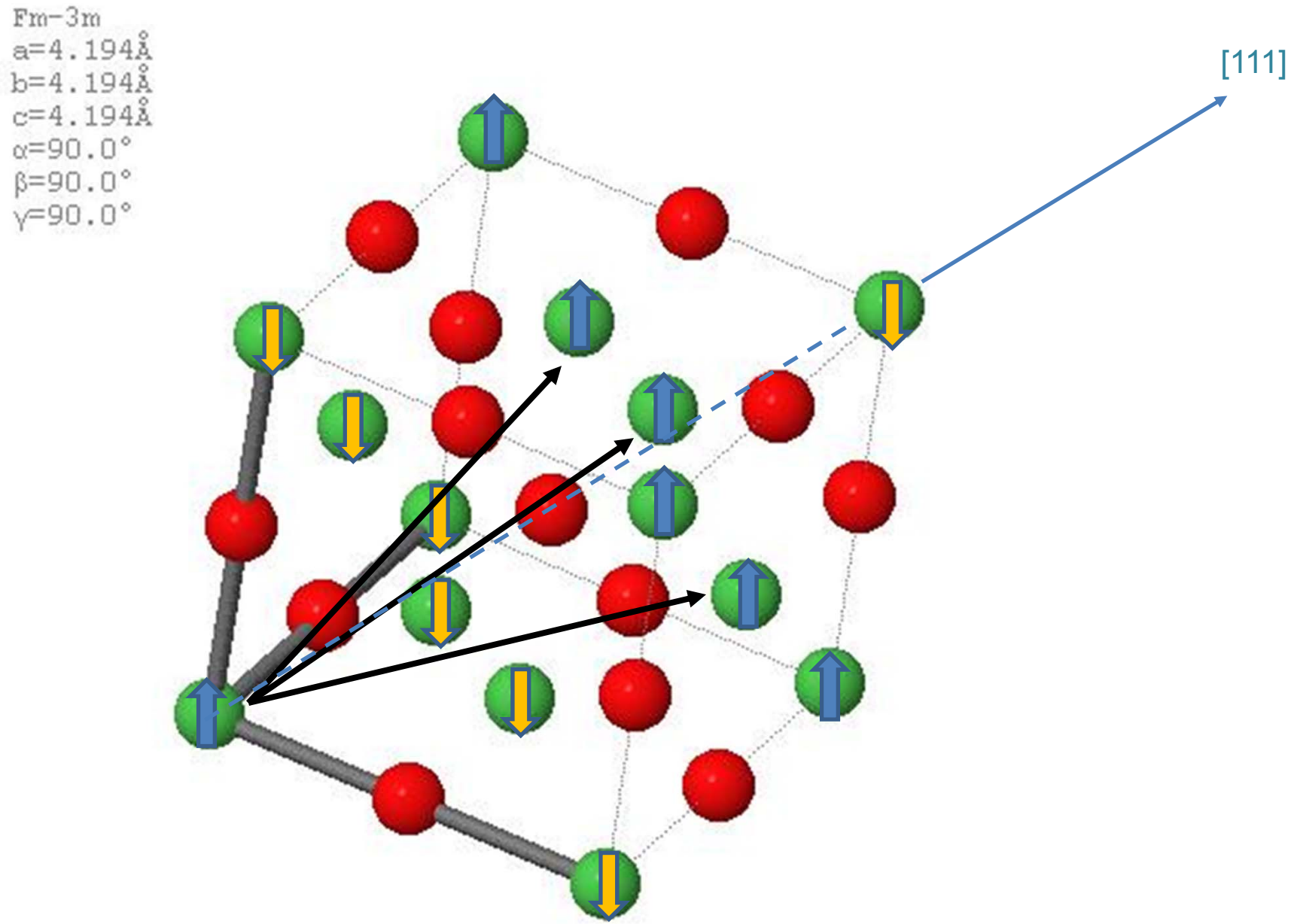

af-Tenorite DOS Plot
U = 1.d-7 Ef = 10.5211
N(E) (states/eV)
30
25
20
15
10
5
0
-10
0
10
eV

Tenorite (U = 5)

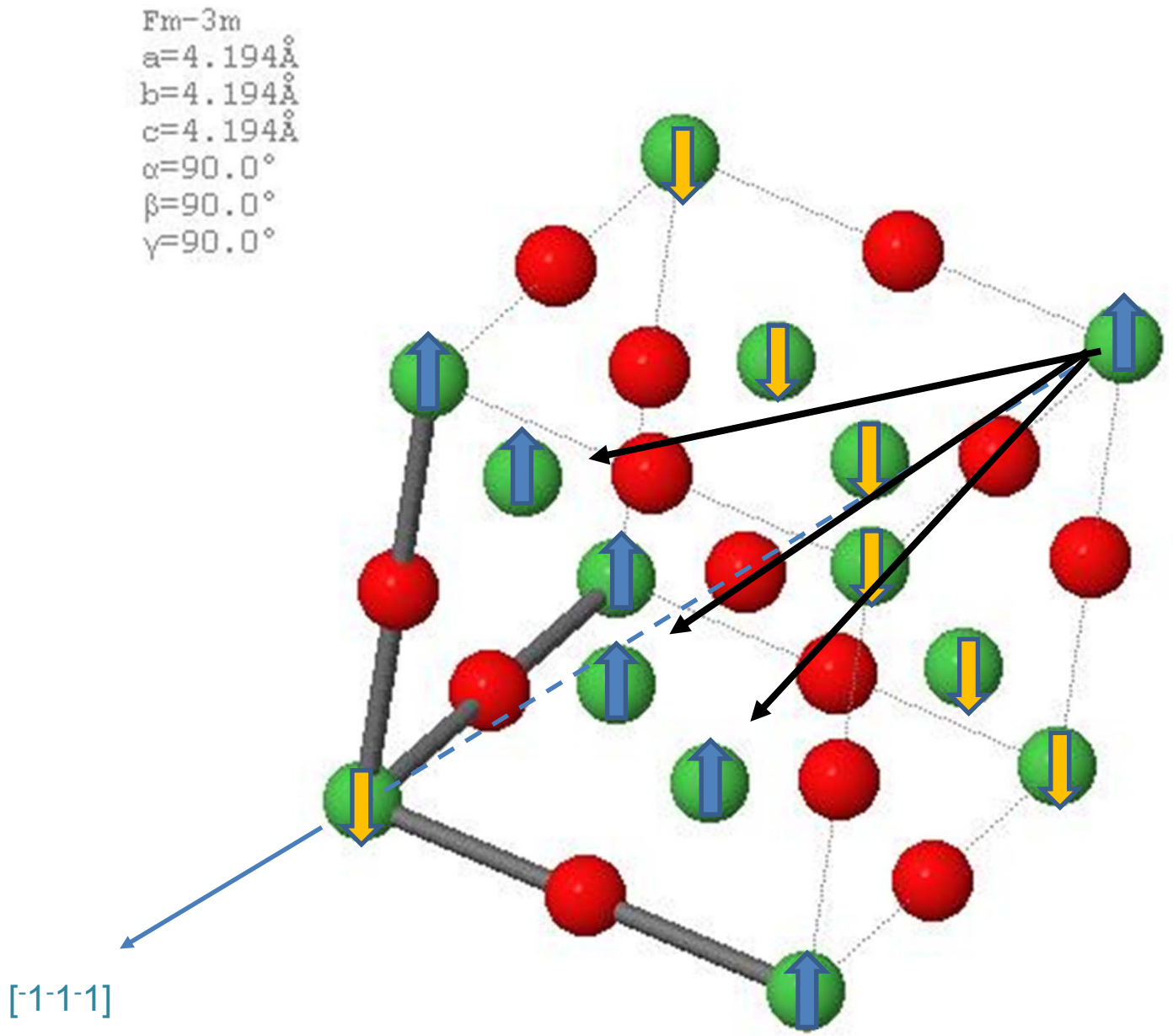



af-Tenorite DOS Plot
U = 5 Ef = 10.1435
N(E) (states/eV)
eV
20
15
10
5
0
-10
-8
-6
-4
-2
0
2
4
6
8
10

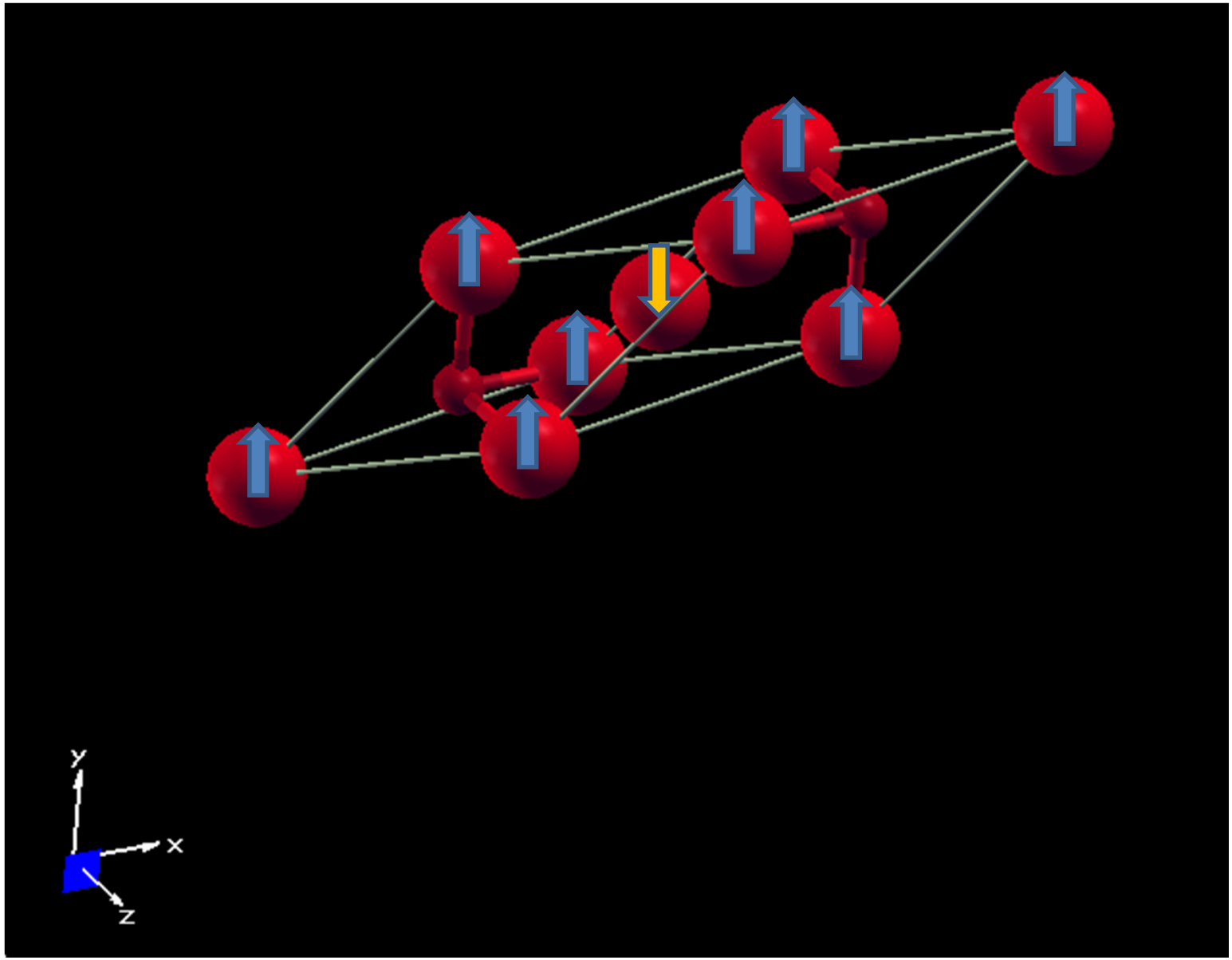
Proto-TMO AF Rock Salt



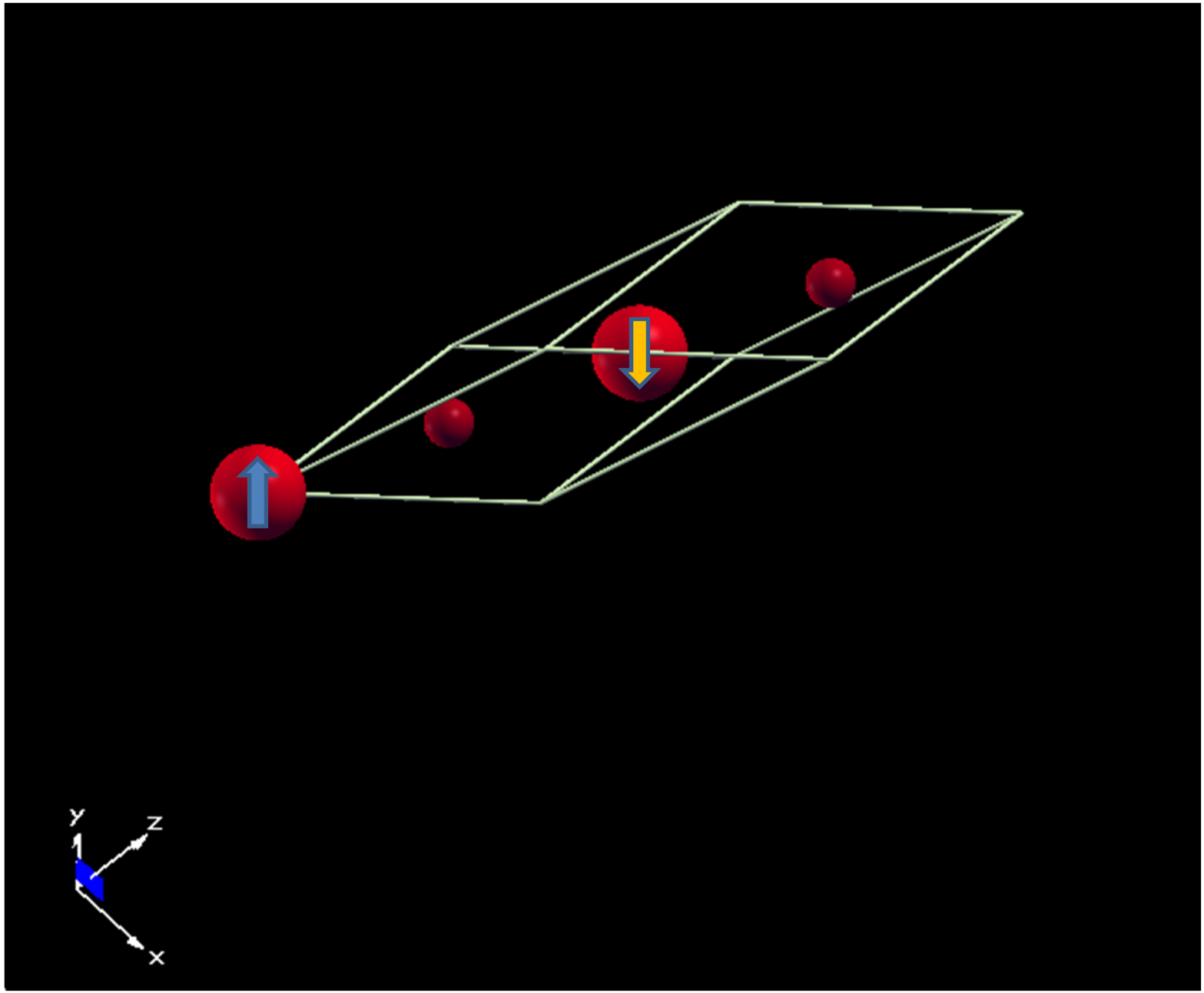
Proto-TMO AF Rock Salt



AF Type II Primitive Cell



Basic Asymmetric AF Cell



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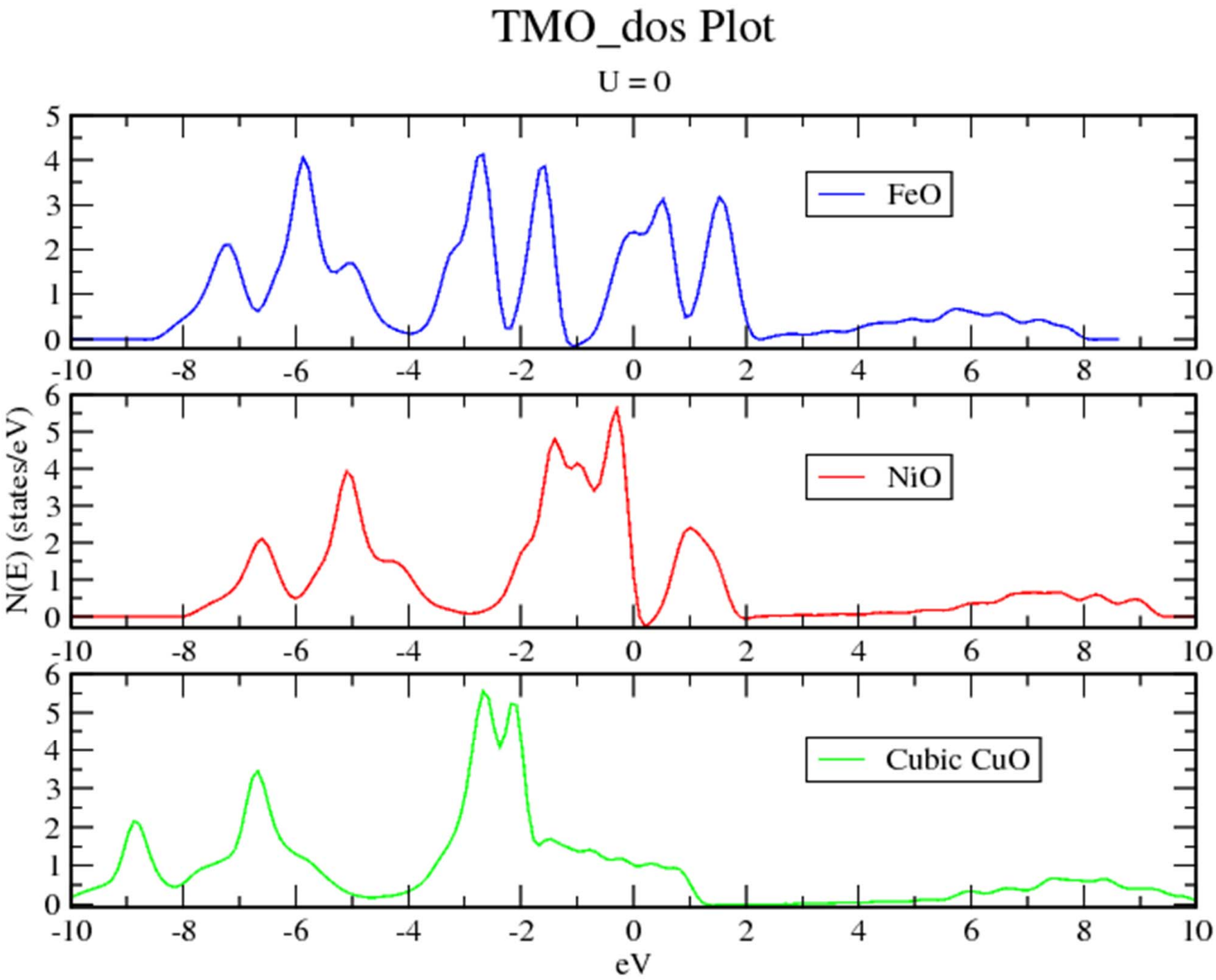
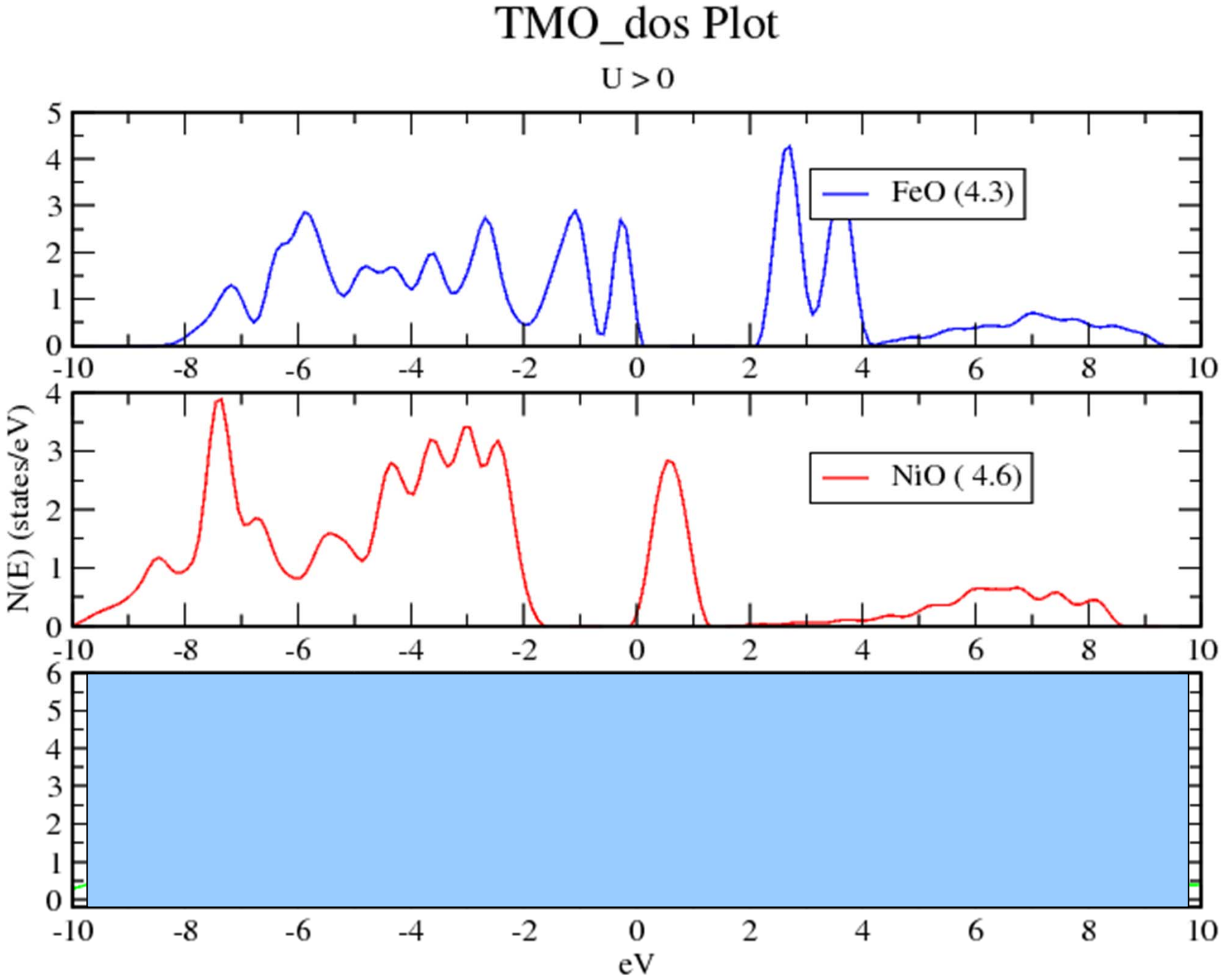
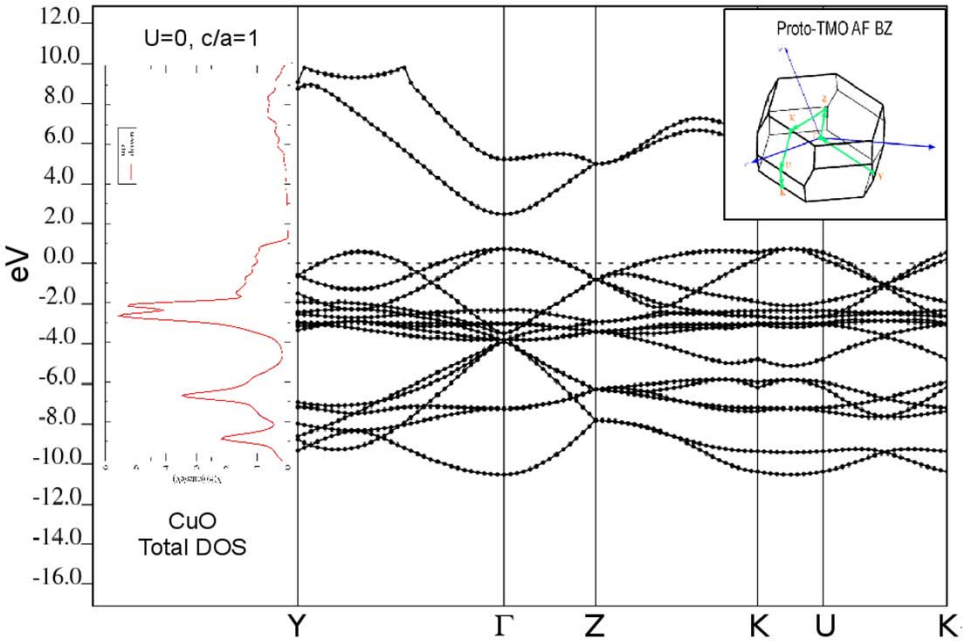
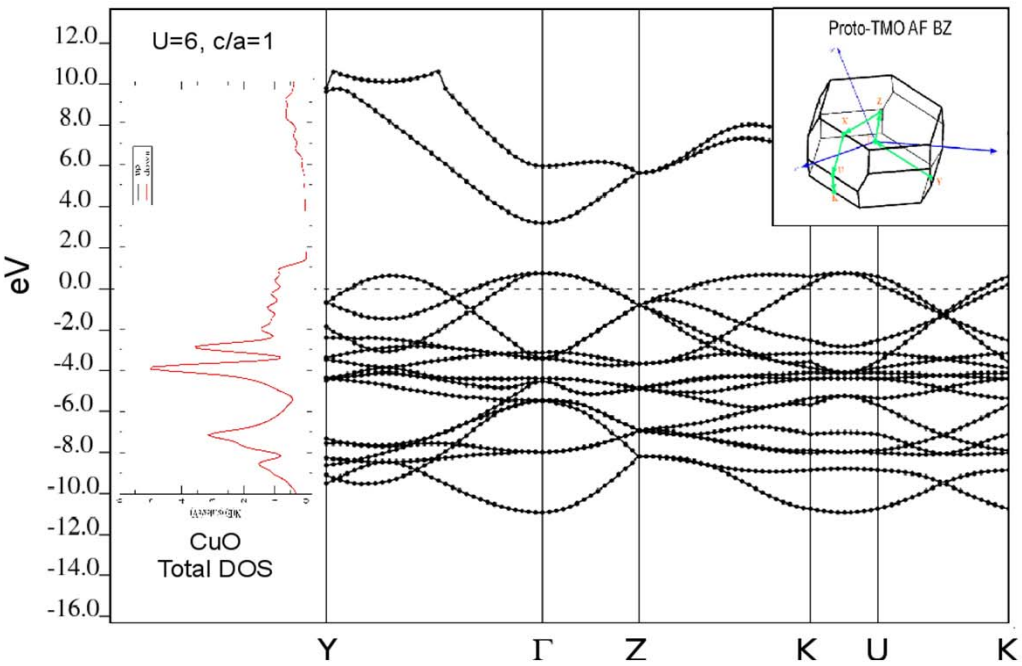
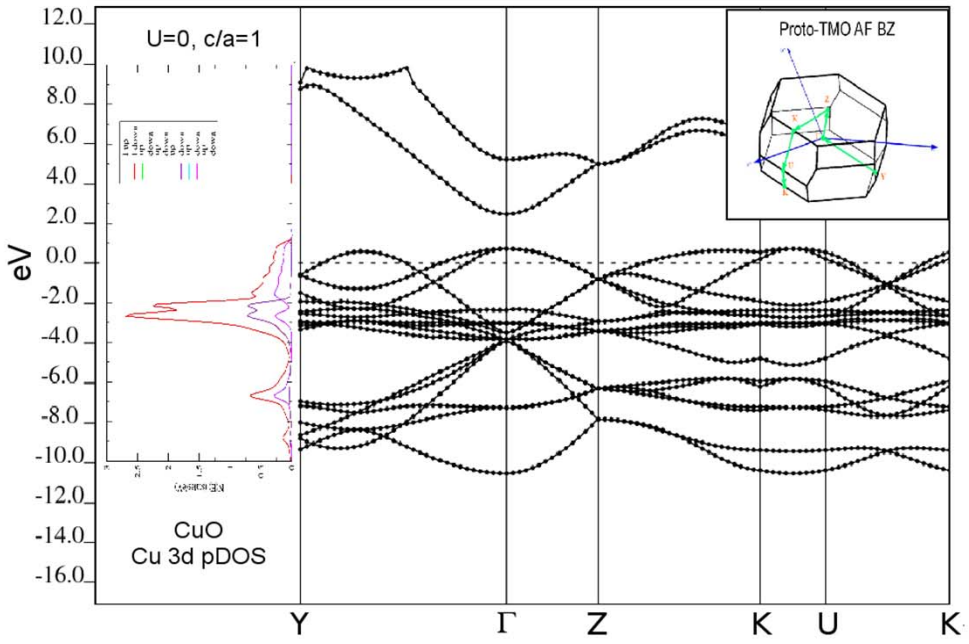

TMO_dos Plot
U = 0
FeO
NiO
Cubic CuO
N(E) (states/eV)
eV

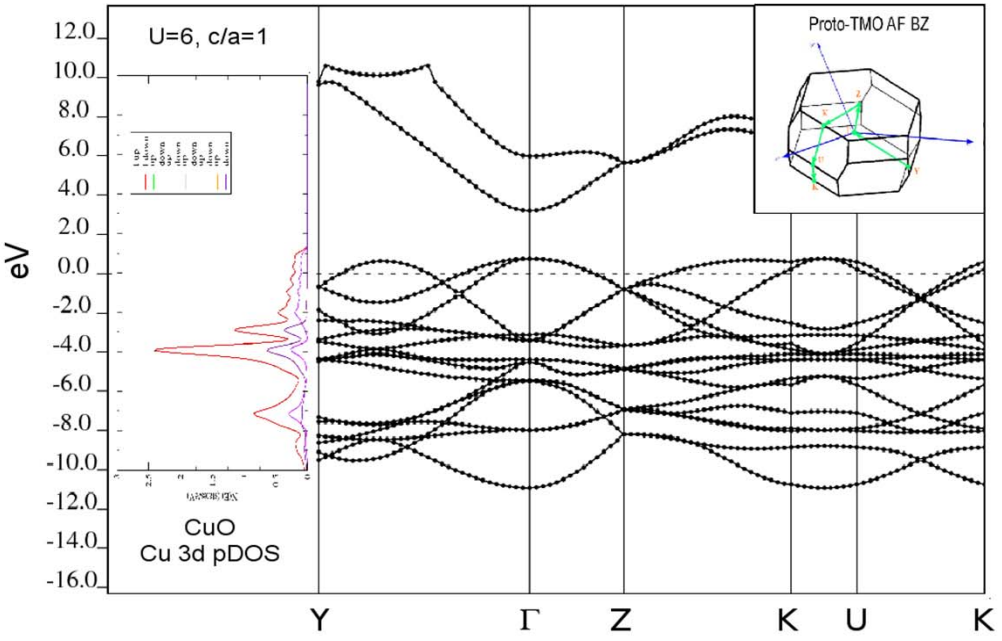

TMO_dos Plot
U > 0
FeO (4.3)
NiO (4.6)
N(E) (states/eV)
eV

Cubic Rocksalt CuO

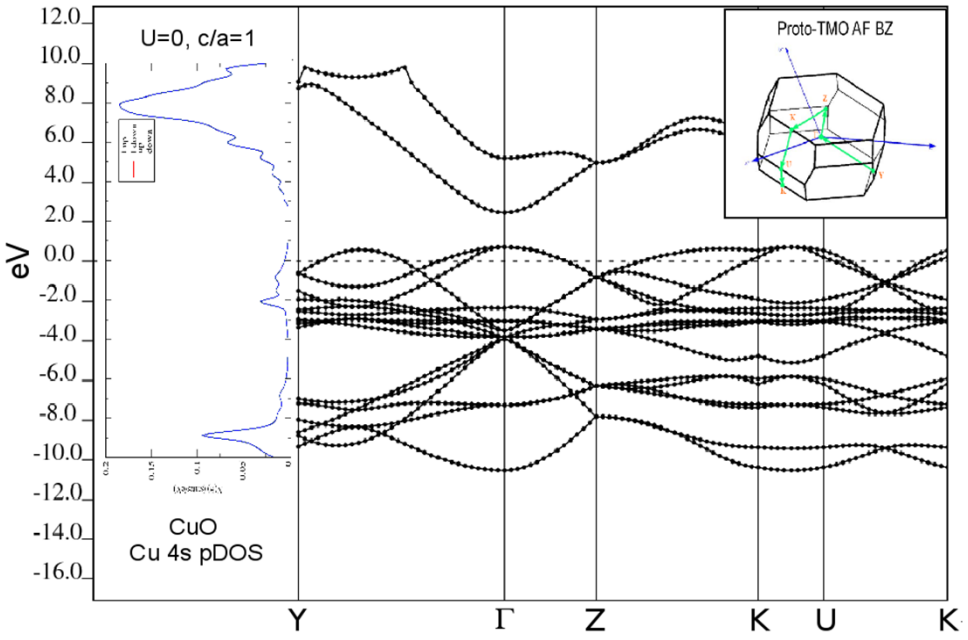


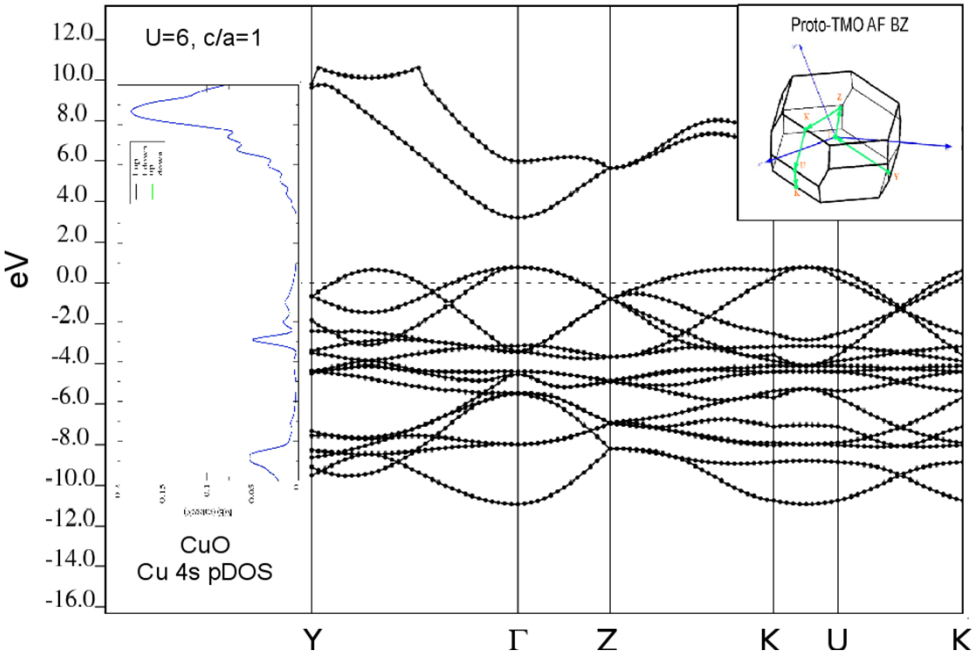


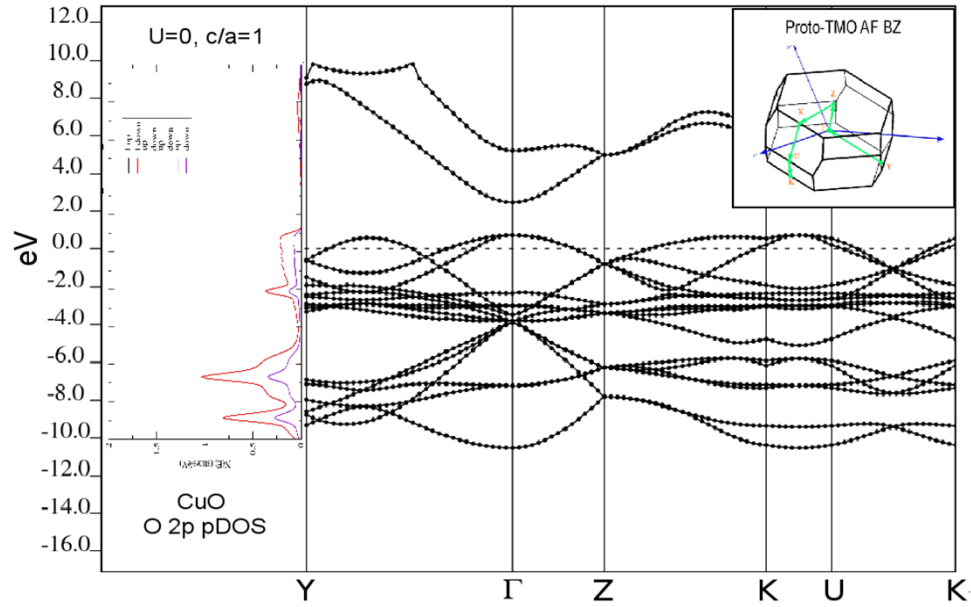


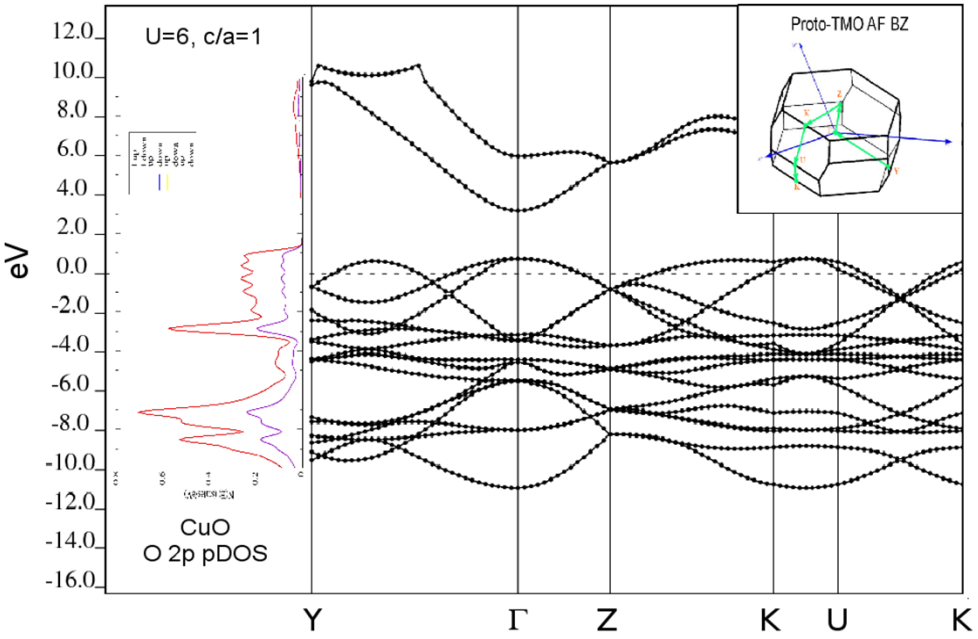


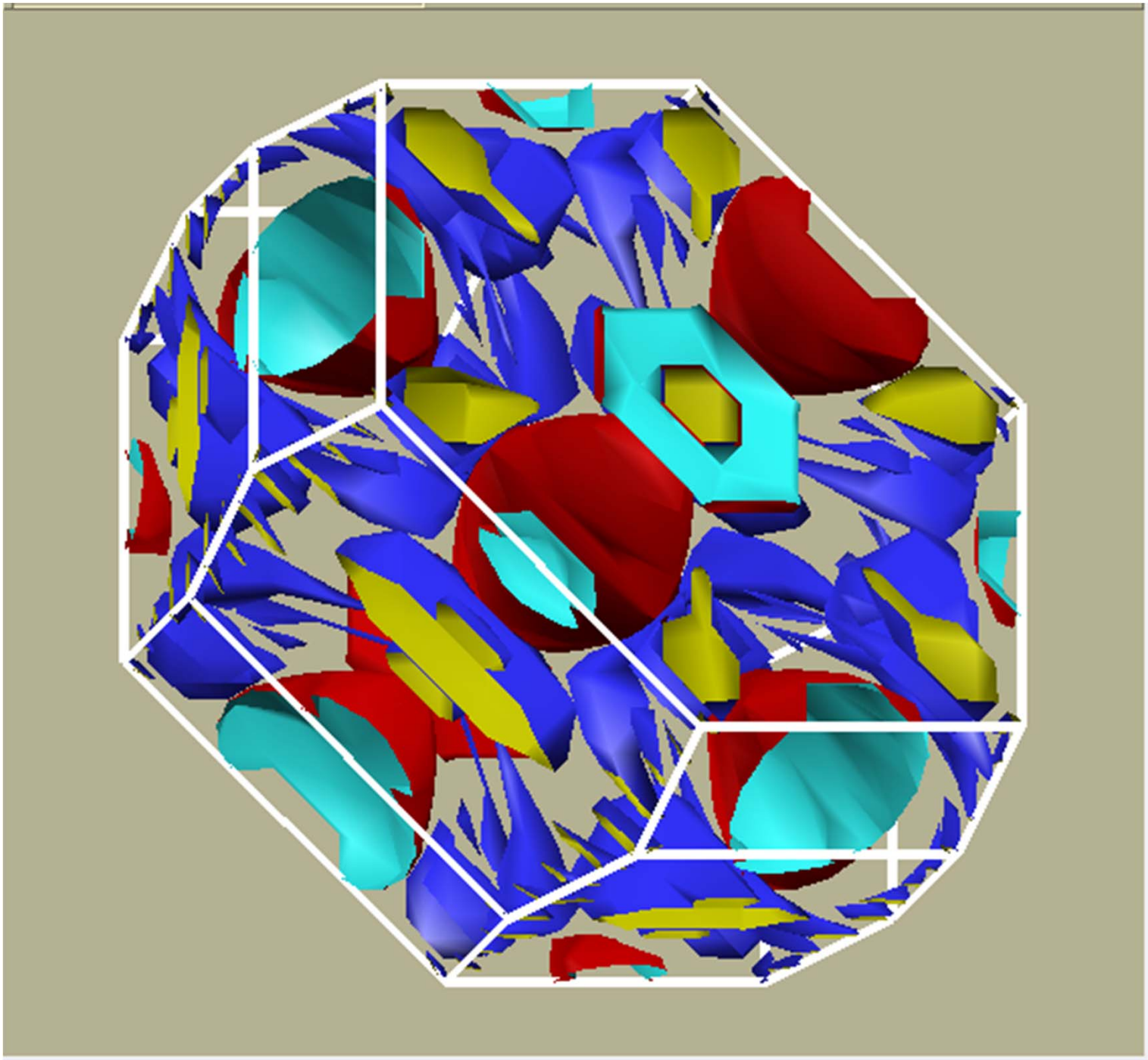
Cubic Rocksalt CuO (Cu 4s & O2p)

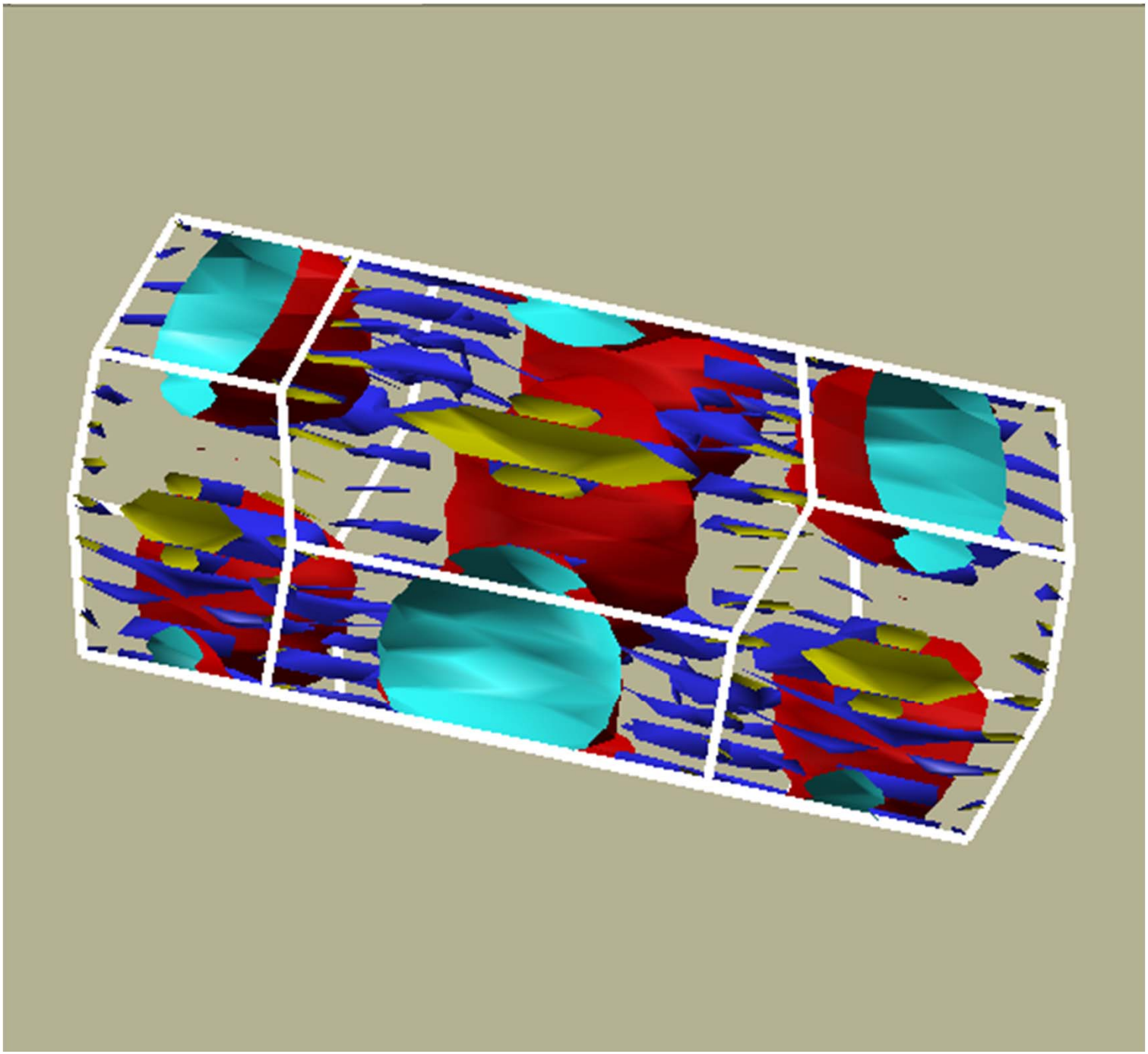












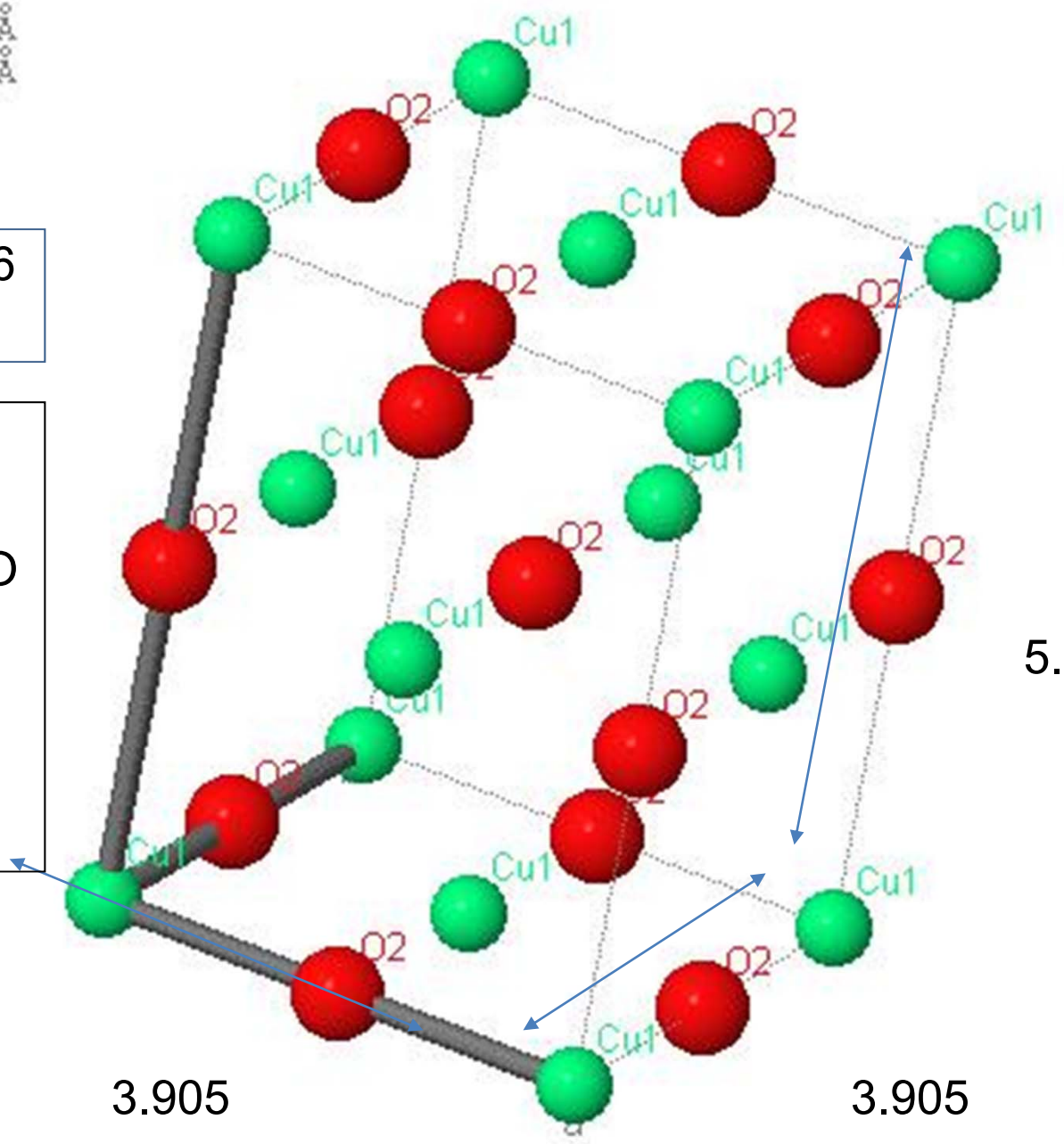
Tetragonal CuO

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

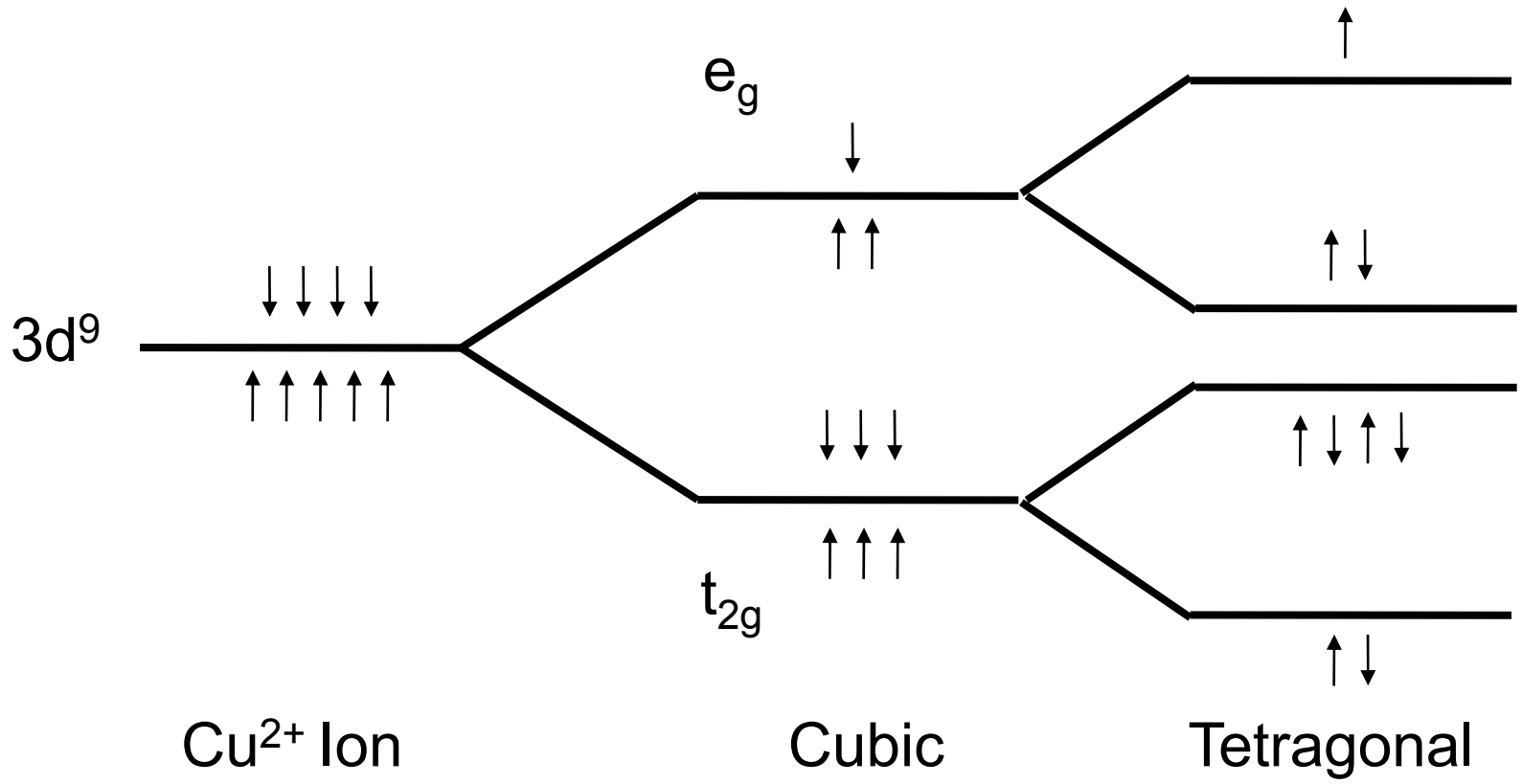
c/a = 1.36

<u>Measurements (Wolter Siemons)</u>

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

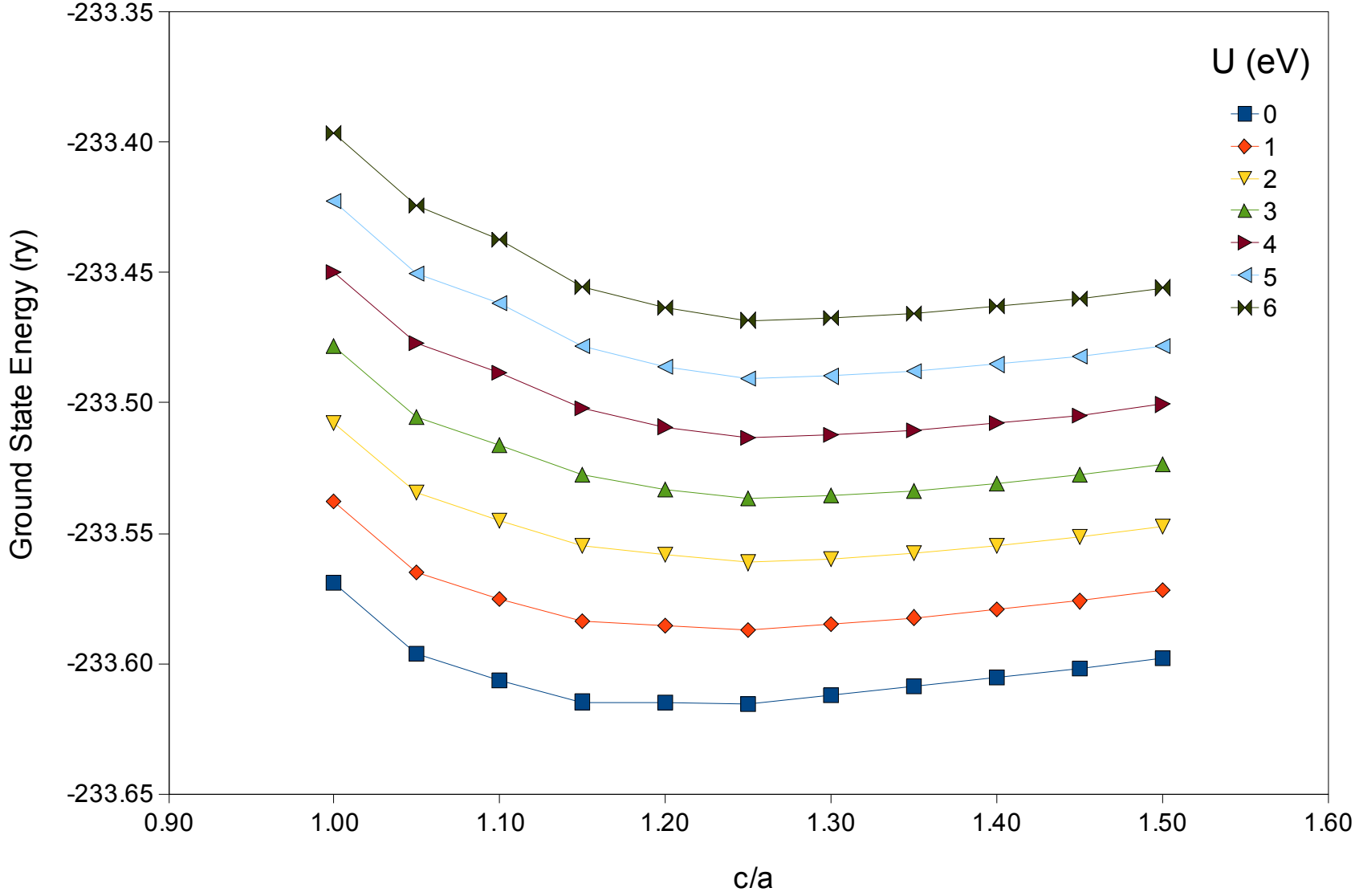


Cu2+ 3d Multiplet Splitting (Tetra)

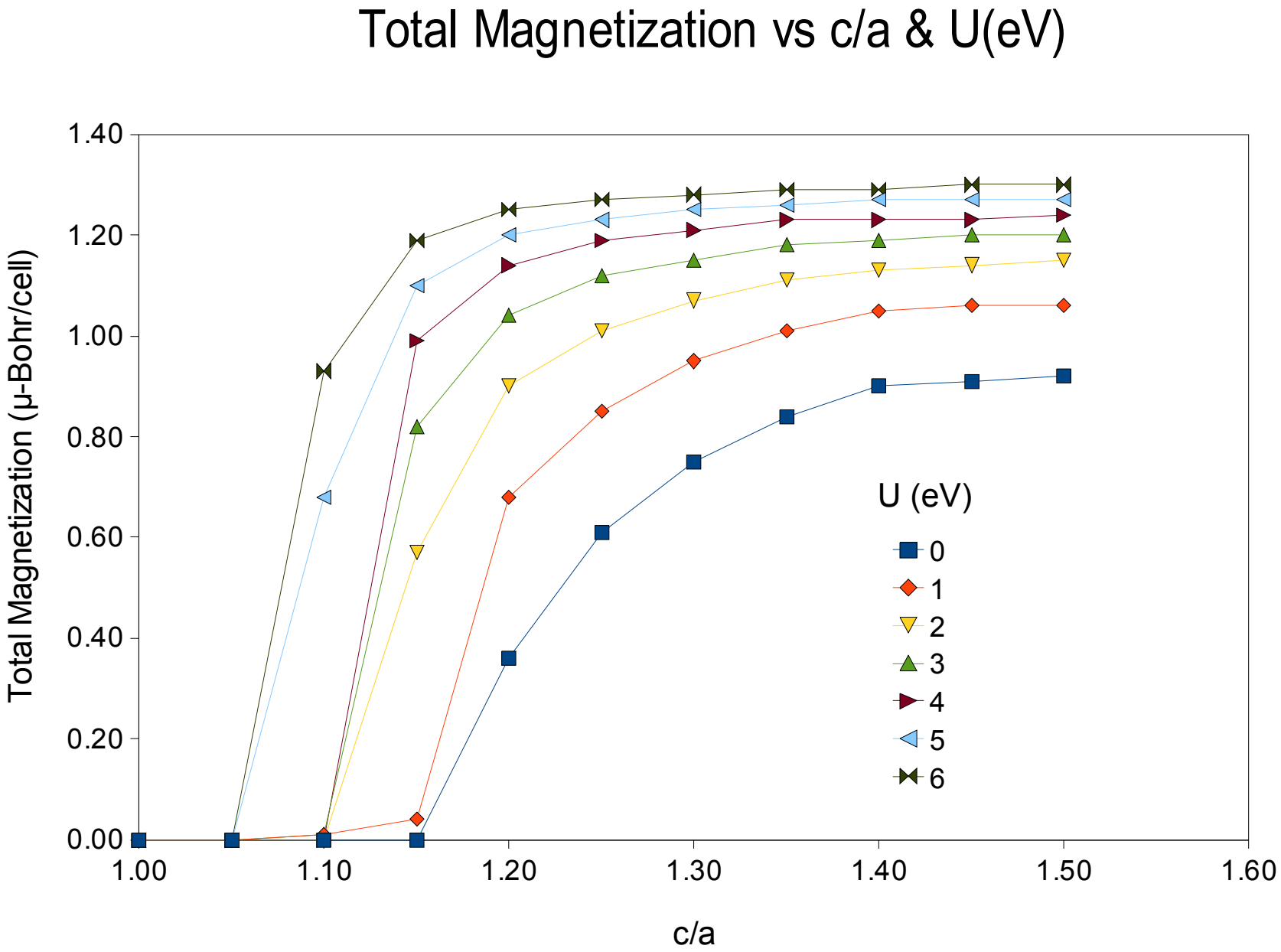


Rocksalt CuO - a = 3.905 Angstroms, PP = Cu.pz-3d9_4s2-rrkjus.UPF

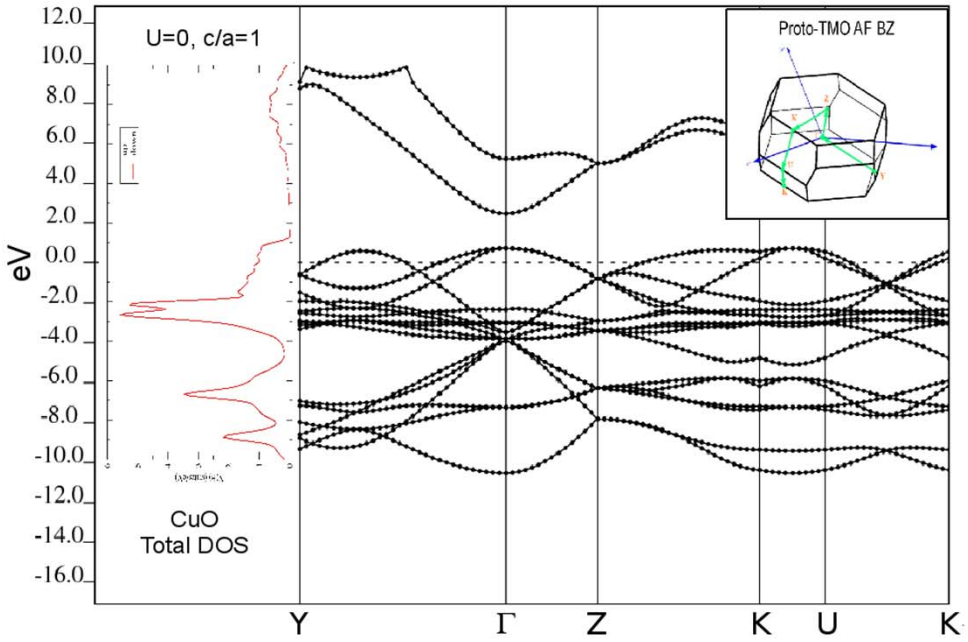
Ground State Energy vs c/a & U(ev)

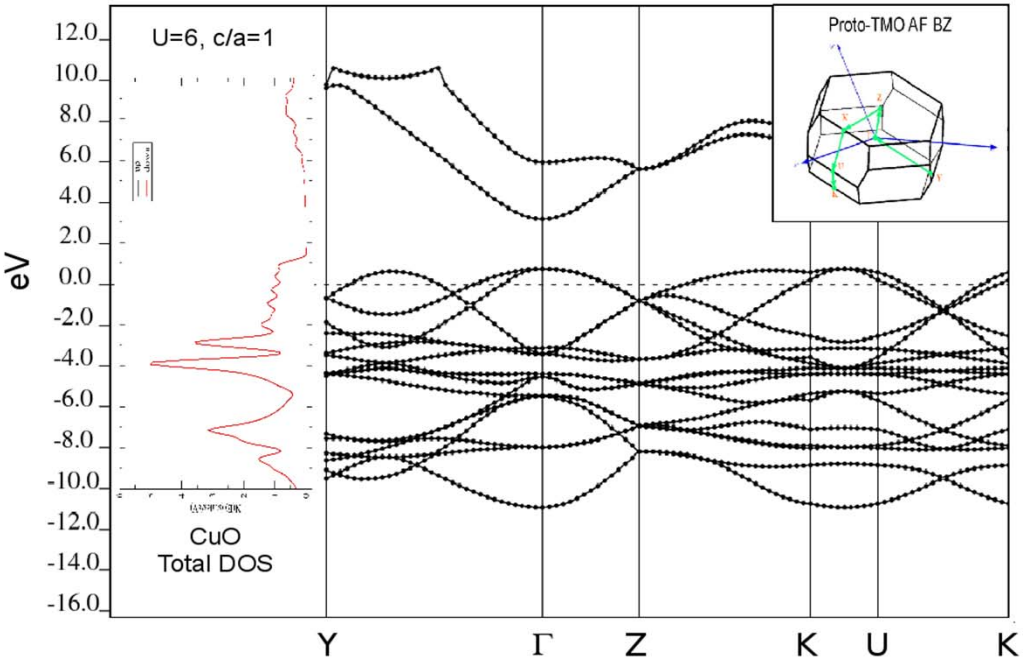


Rocksalt CuO - a = 3.905 Å, PP = Cu.pz-3d9_4s2-rrkjus.UPF

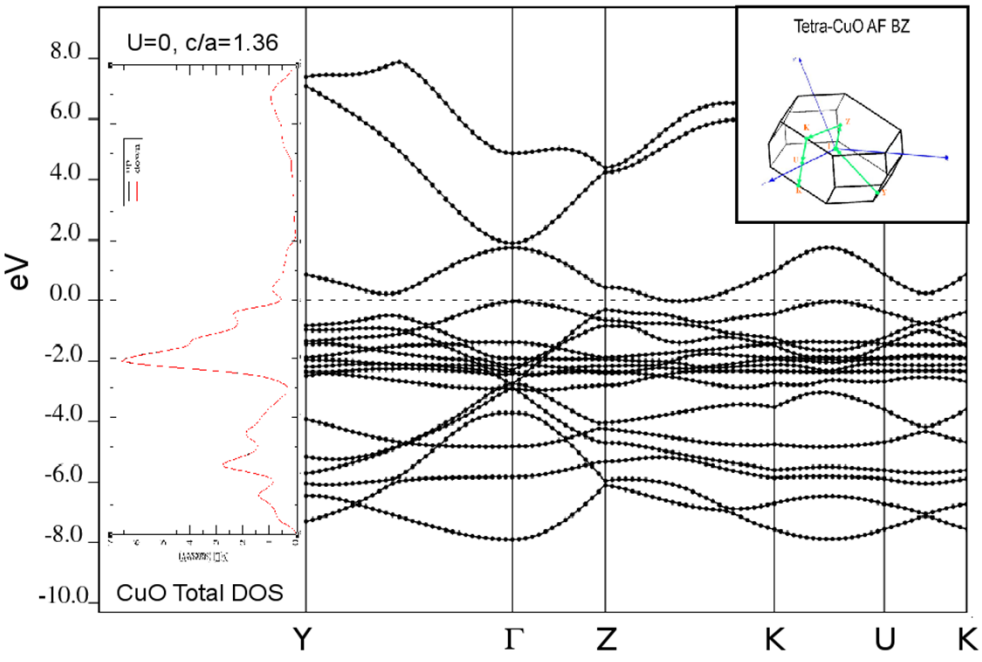


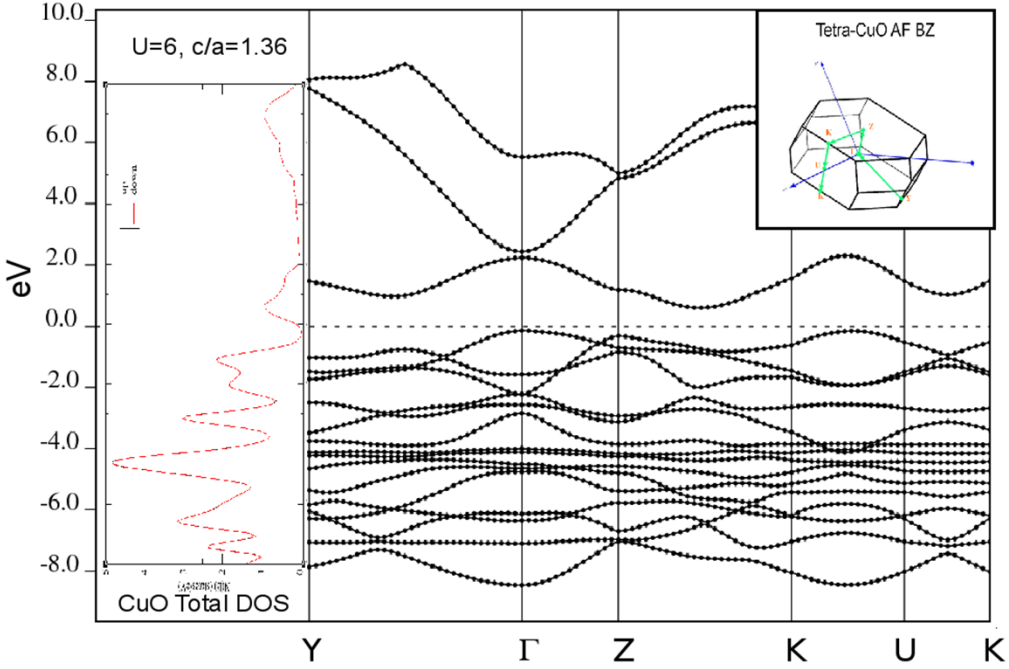
Cubic



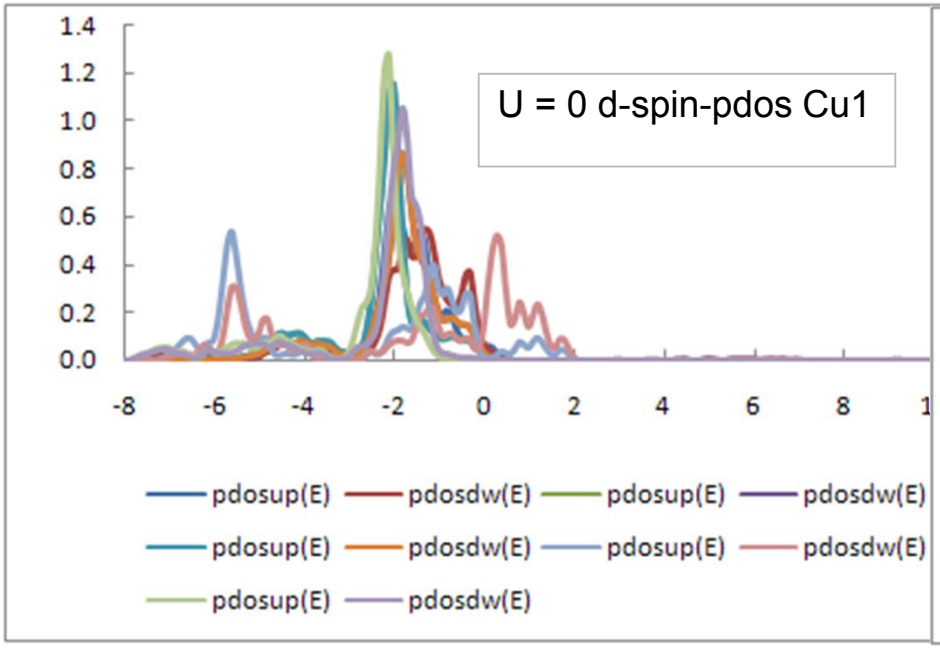


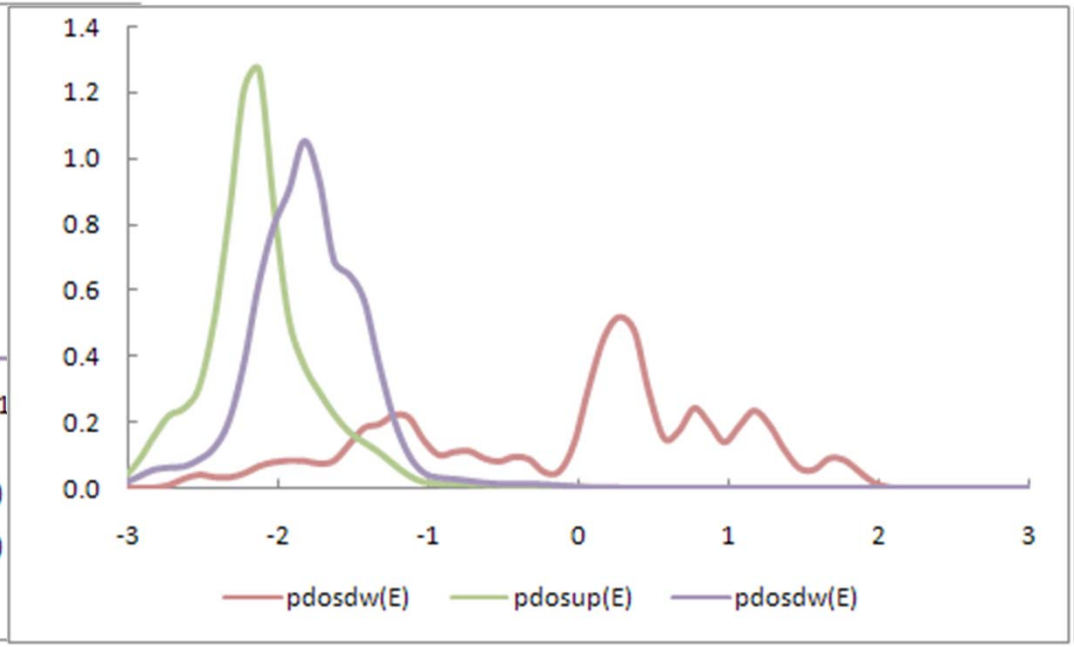
Tetragonal

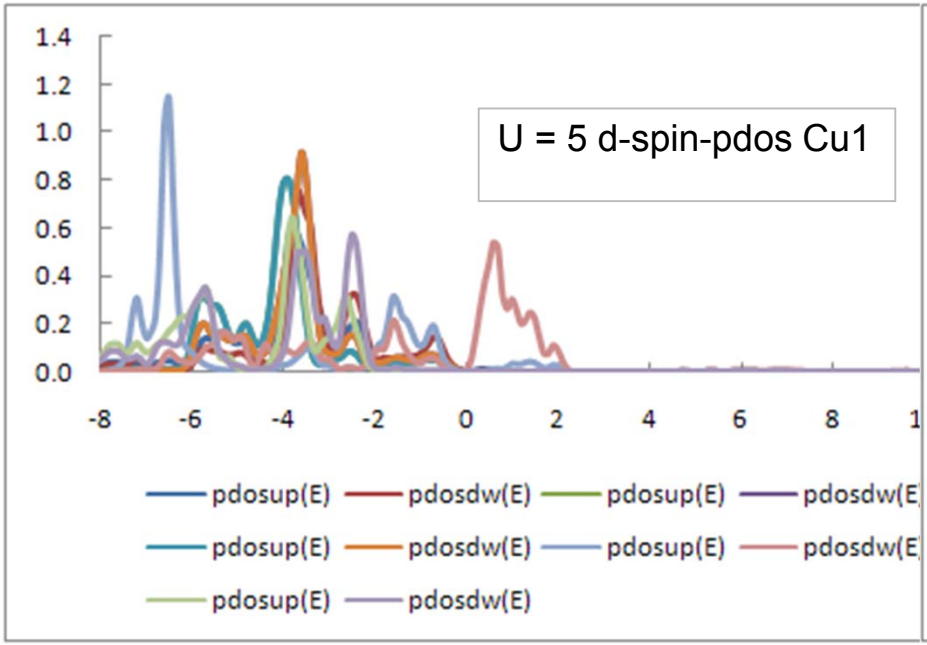


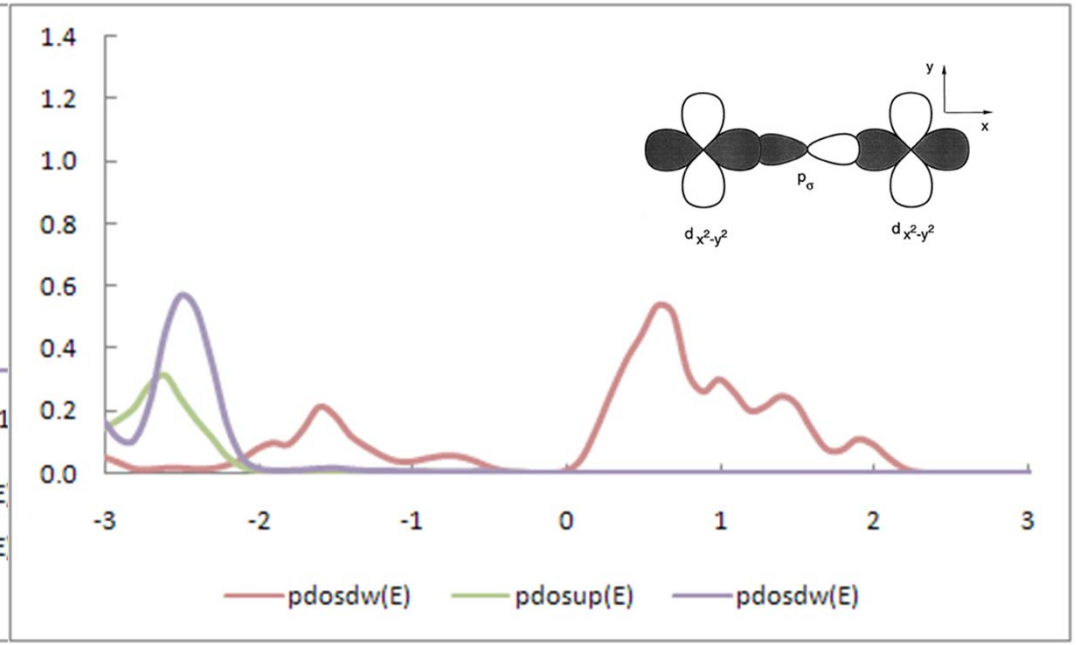


Spin Composition of Cu 3d pDOS as fn(Hubbard): c/a = 1.36

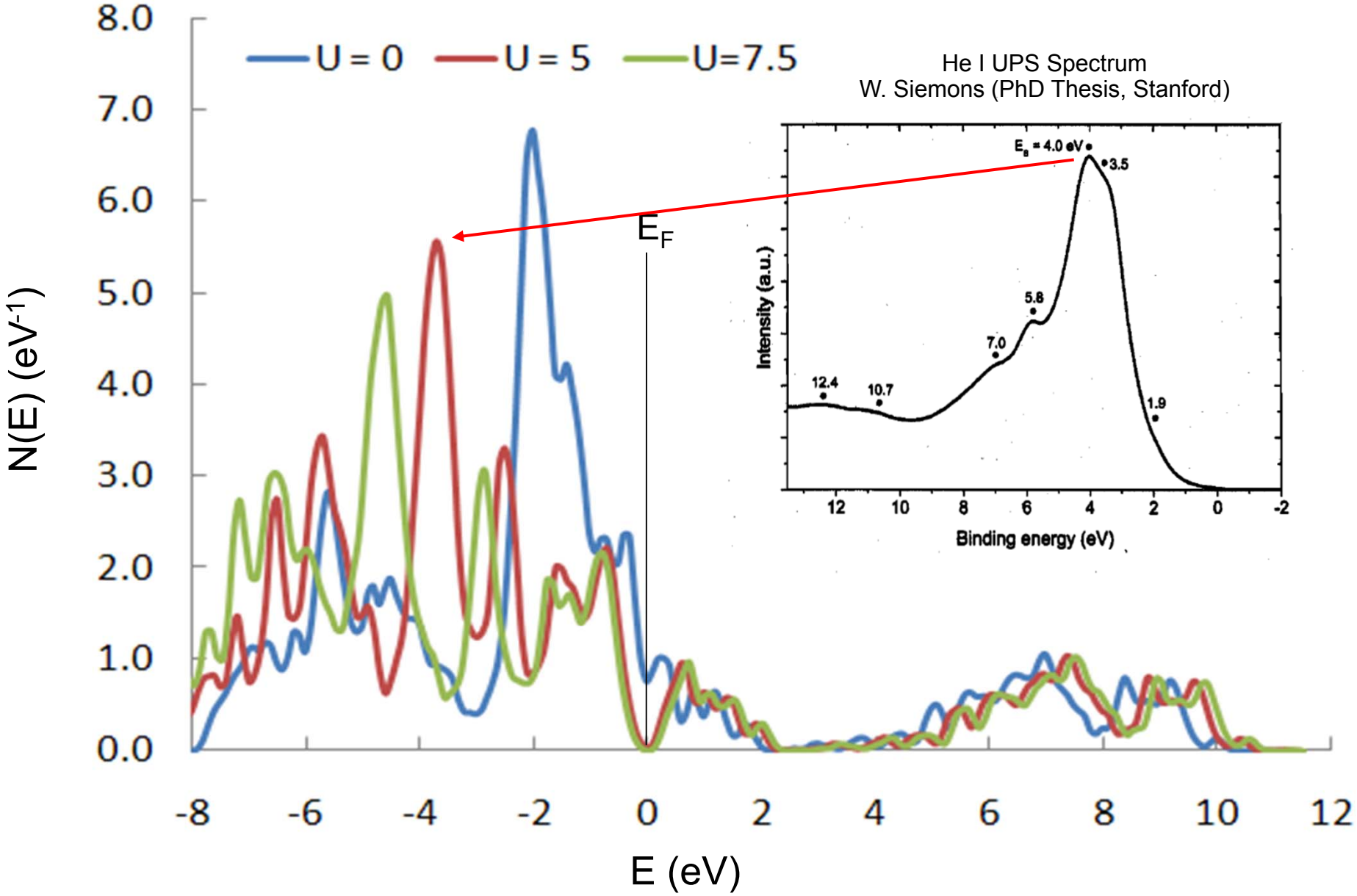






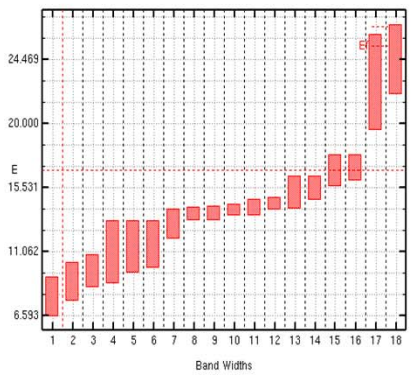


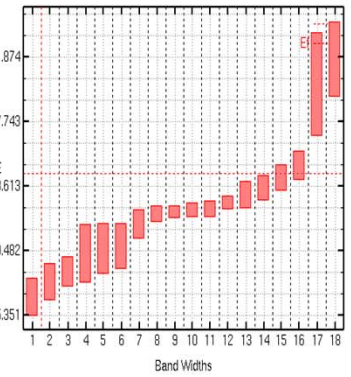
t-CuO Density-of-States

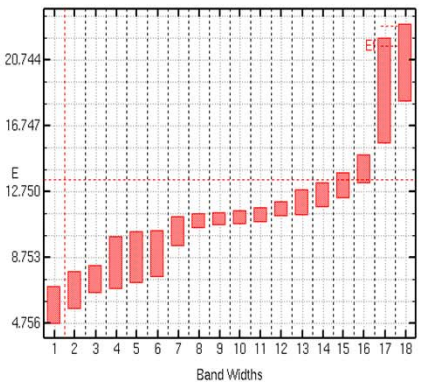


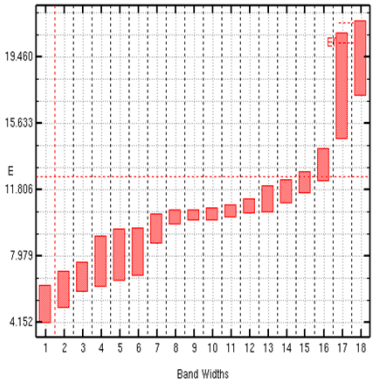
Af-CuO: Spin Up Bands

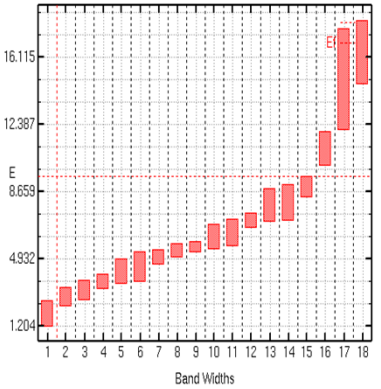
U = 0





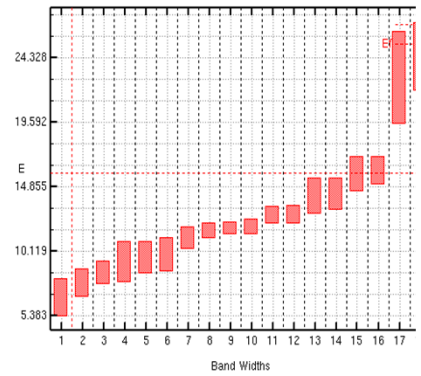


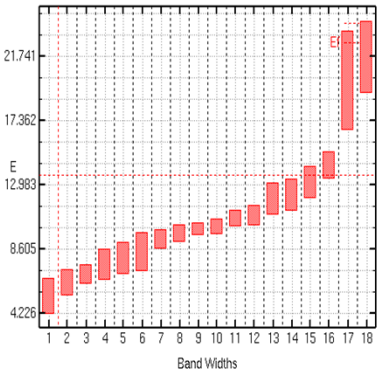


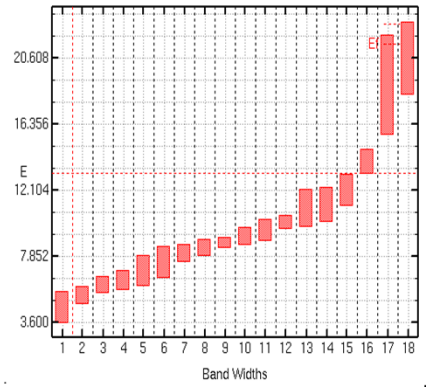


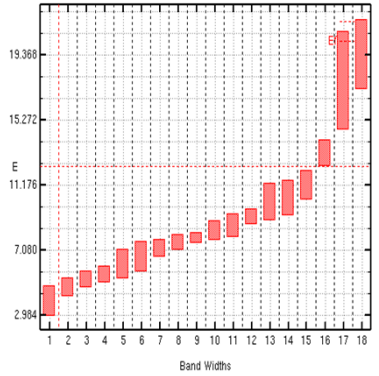
c/a

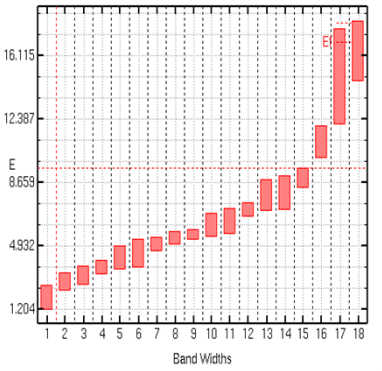
1.0 1.1 1.115 1.2 1.36







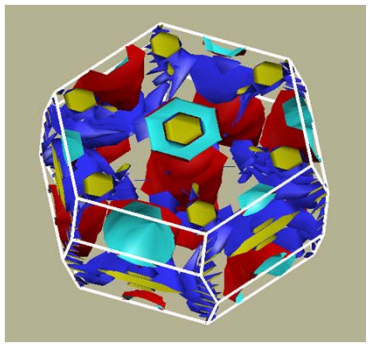
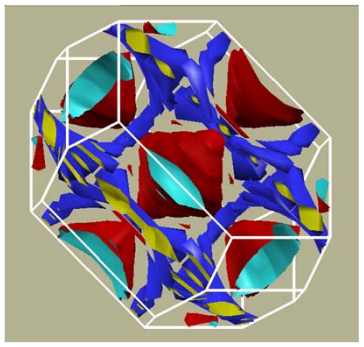
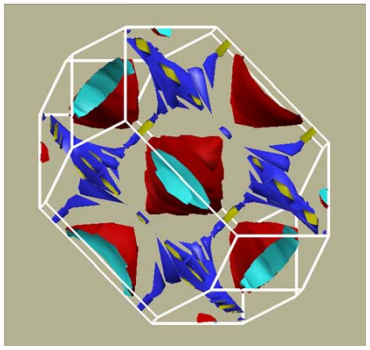
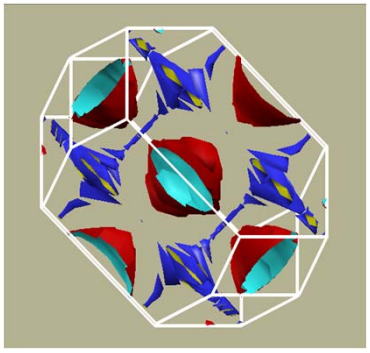
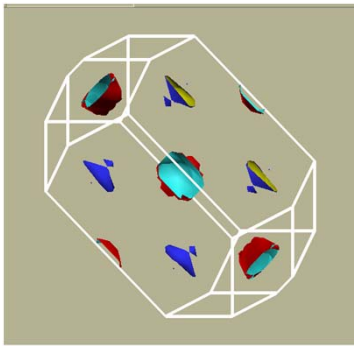




U = 6

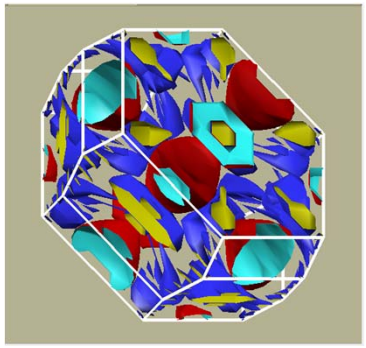
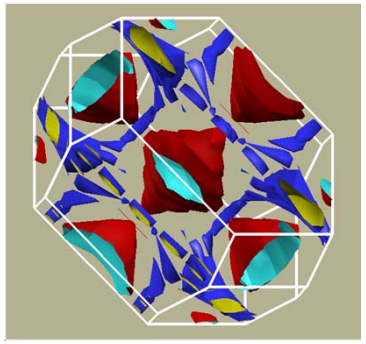
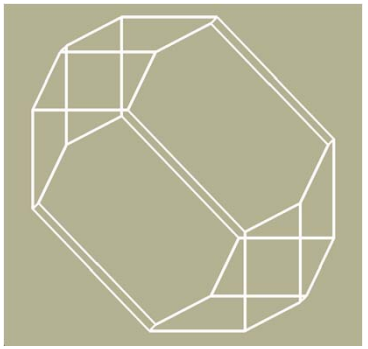
Af-CuO: FS Spin Up

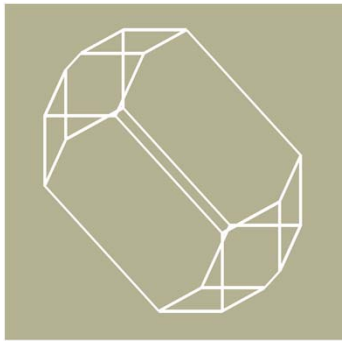
U = 0

c/a

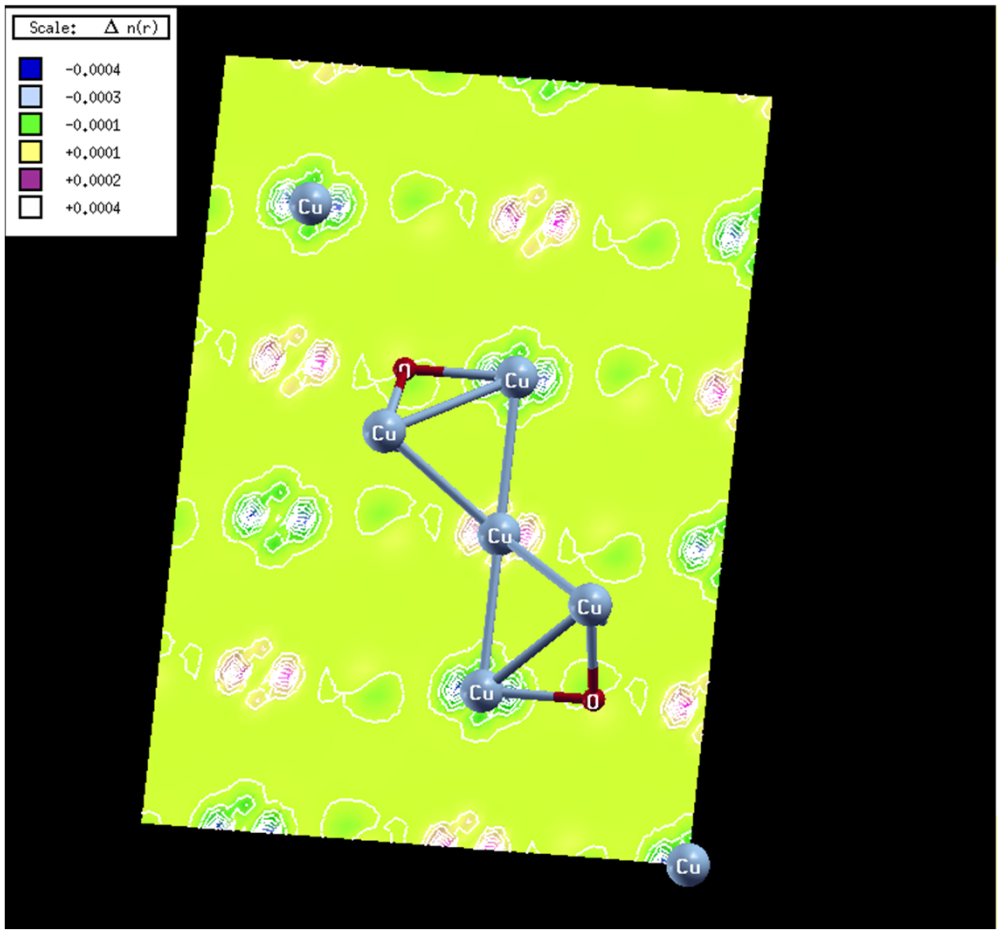
1.0 1.1 1.115 1.2 1.36

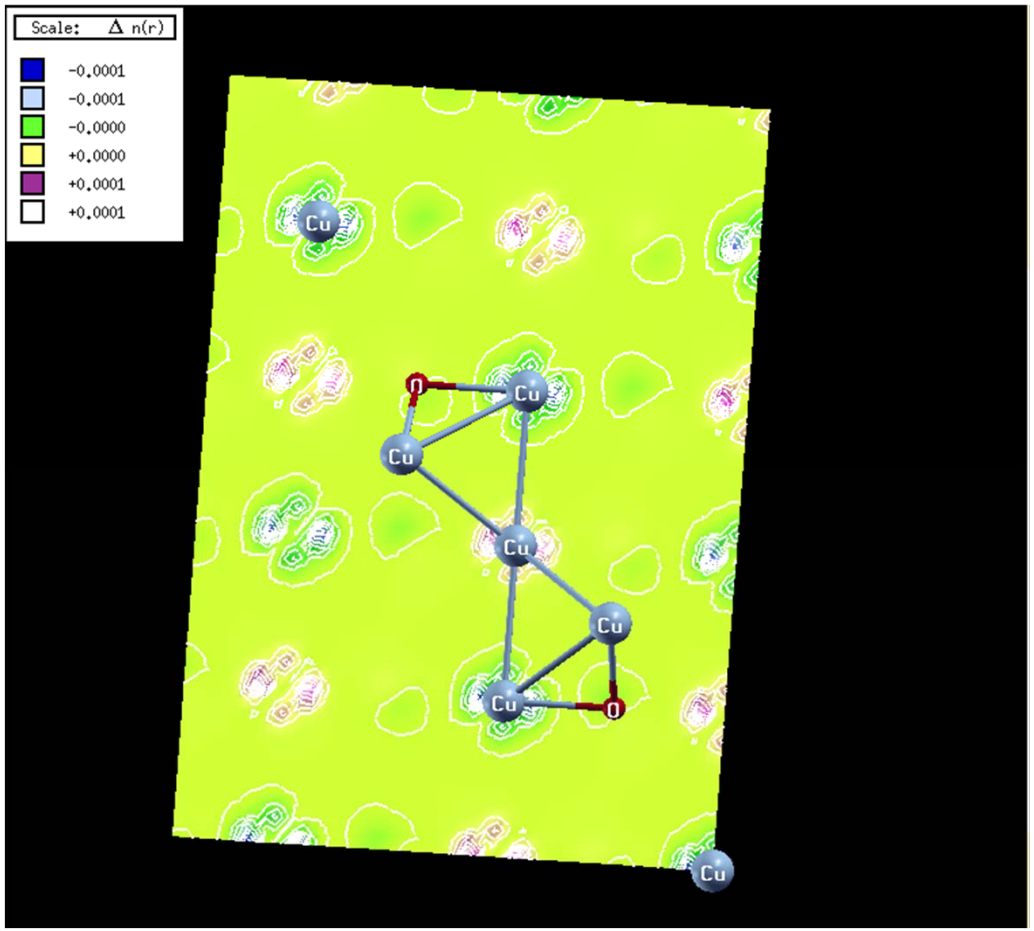


U = 6

c/a = 1.00

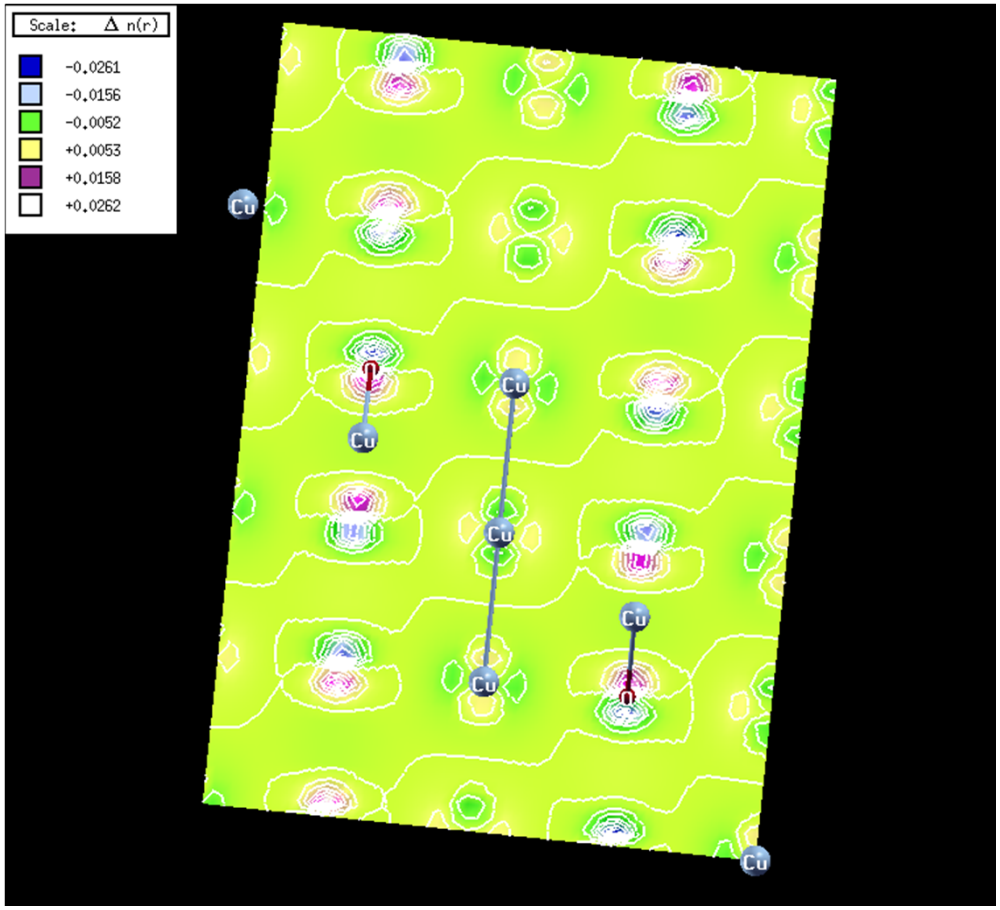

Scale: Δ n(r)
-0.0004
-0.0003
-0.0001
+0.0001
+0.0002
+0.0004
Cu
O

U = 0

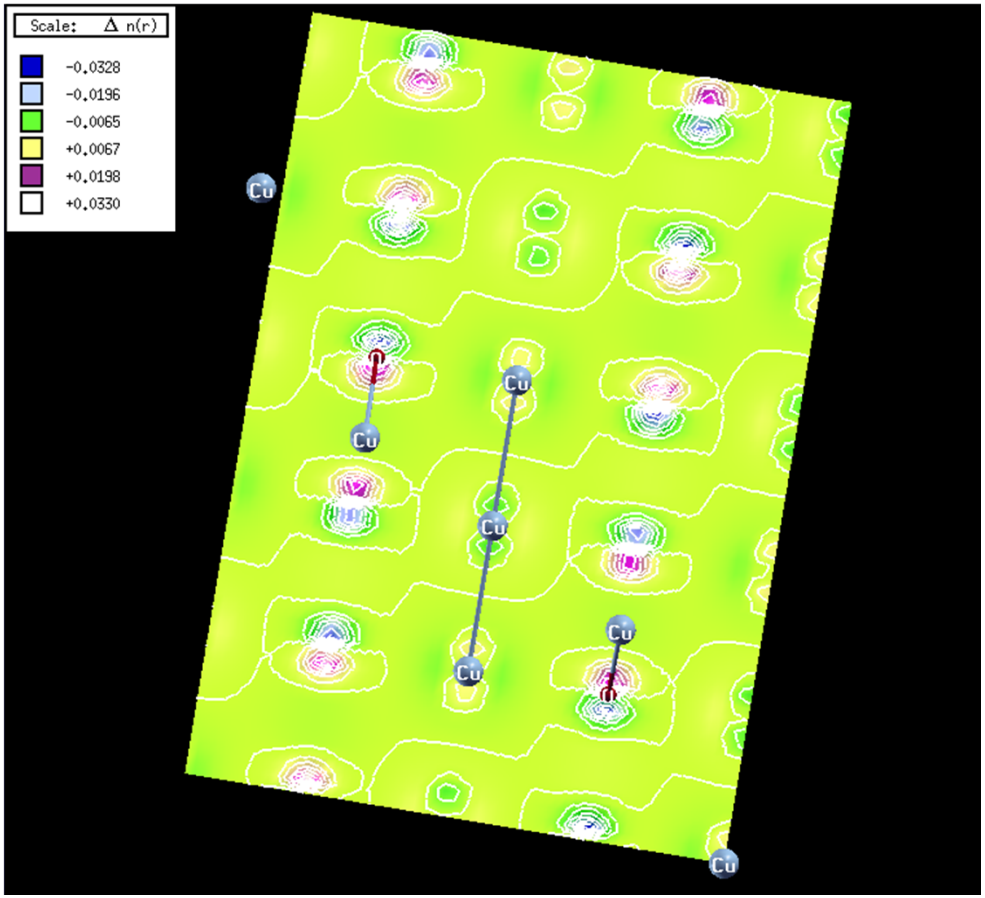

Scale: Δ n(r)
-0.0001
-0.0001
-0.0000
+0.0000
+0.0001
+0.0001
Cu
O

U = 6

c/a = 1.36


Scale: Δ n(r)
-0.0261
-0.0156
-0.0052
+0.0053
+0.0158
+0.0262
Cu
Cu
Cu
Cu
Cu
Cu
Cu

U = 0


Scale: Δ n(r)
-0.0328
-0.0196
-0.0065
+0.0067
+0.0198
+0.0330
Cu
Cu
Cu
Cu
Cu
Cu
Cu

U = 6

Agenda

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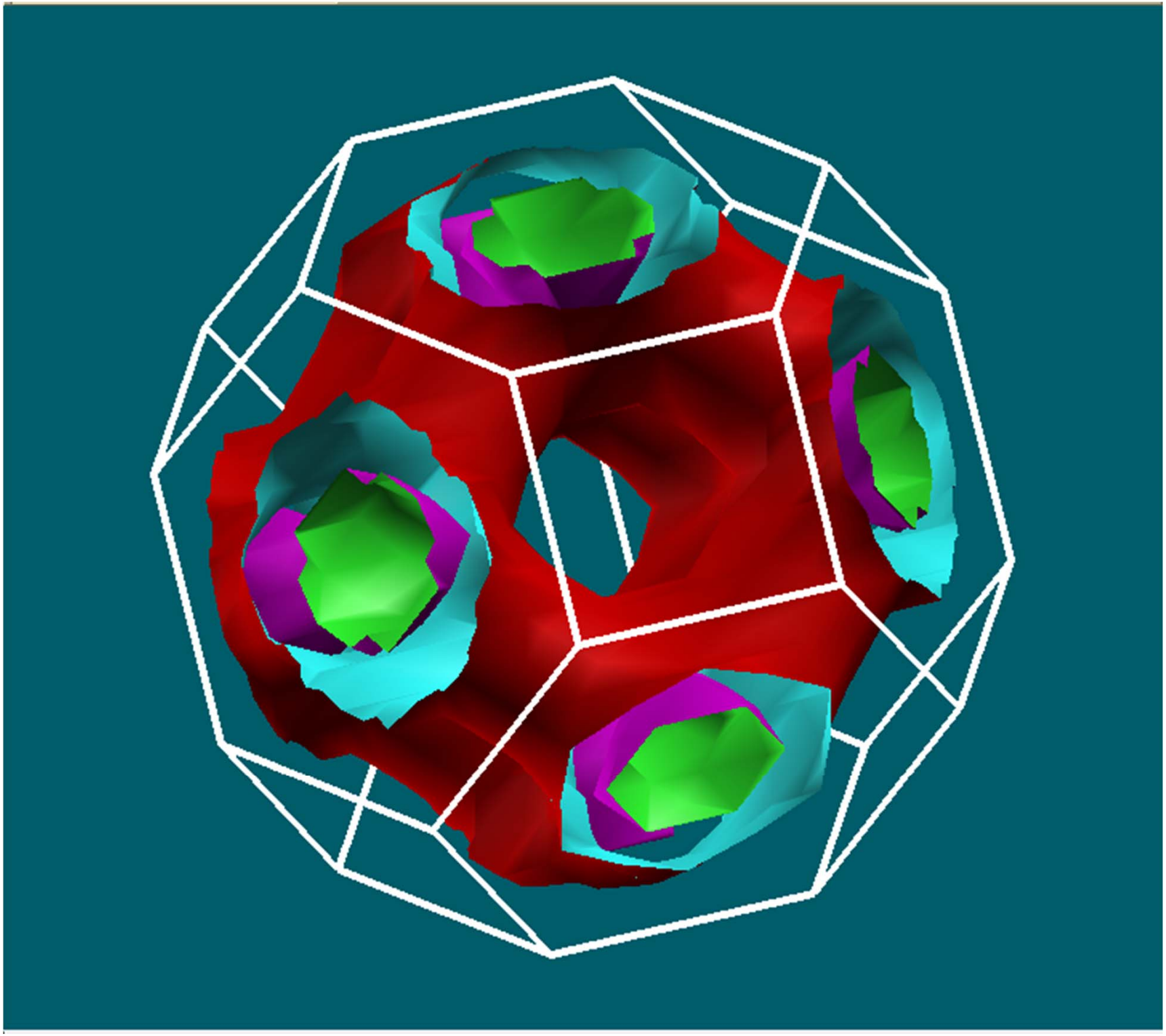
Electron-Phonon Coupling - Superconductivity -

- 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)

$$H_{el-ph} = \sum_{\mathbf{k}\mathbf{q}\nu} g^{\mathbf{q}\nu,mn}_{\mathbf{k}+\mathbf{q},\mathbf{k}}\, c^{\dagger m}_{\mathbf{k}+\mathbf{q}} c^{n}_{\mathbf{k}}\, (b^{\dagger}_{-\mathbf{q}\nu} + b_{\mathbf{q}\nu}) \qquad (1)$$

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

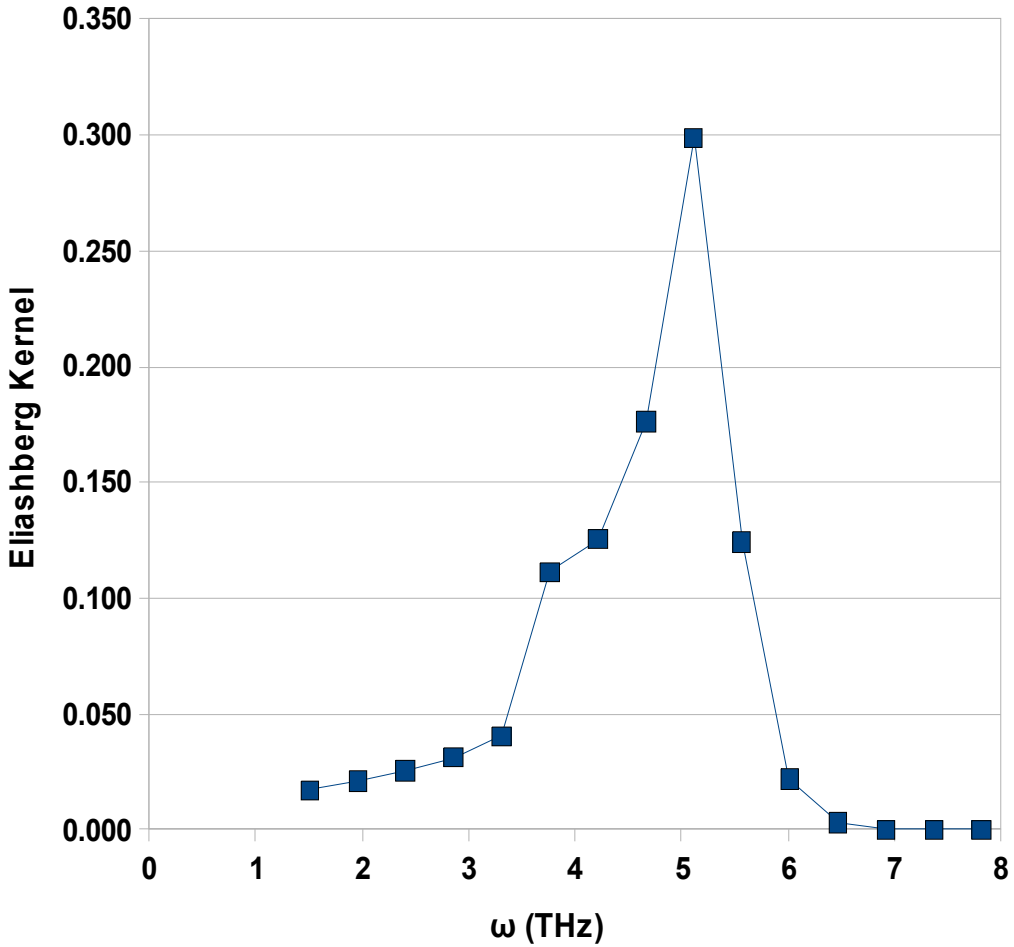
$$\lambda = 2\int \frac{\alpha^2 F(\omega)}{\omega} d\omega = \sum_{\mathbf{q}\nu} \lambda_{\mathbf{q}\nu}, \qquad (3)$$

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

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…

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

$$\lambda k\Theta \ll E_F$$

	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	-

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Does the DaVinci Code Hold the Key to Room Temperature Superconductivity?

Paul M. Grant

Visiting Scholar, Stanford

IBM Research Staff Member Emeritus

EPRI Science Fellow (Retired)

Principal, W2AGZ Technologies

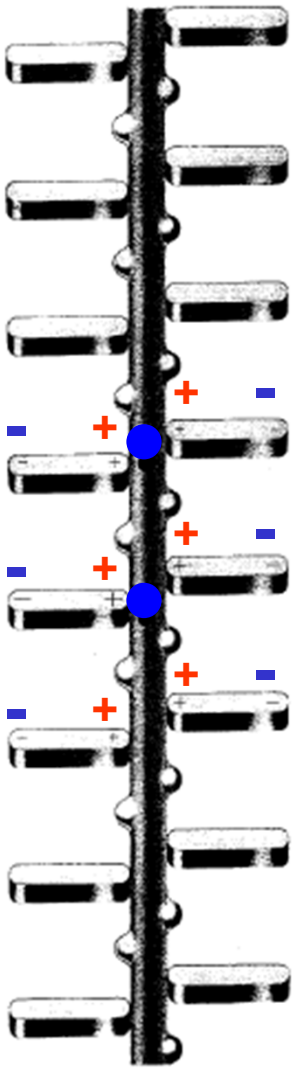
The Road to Room Temperature Superconductivity

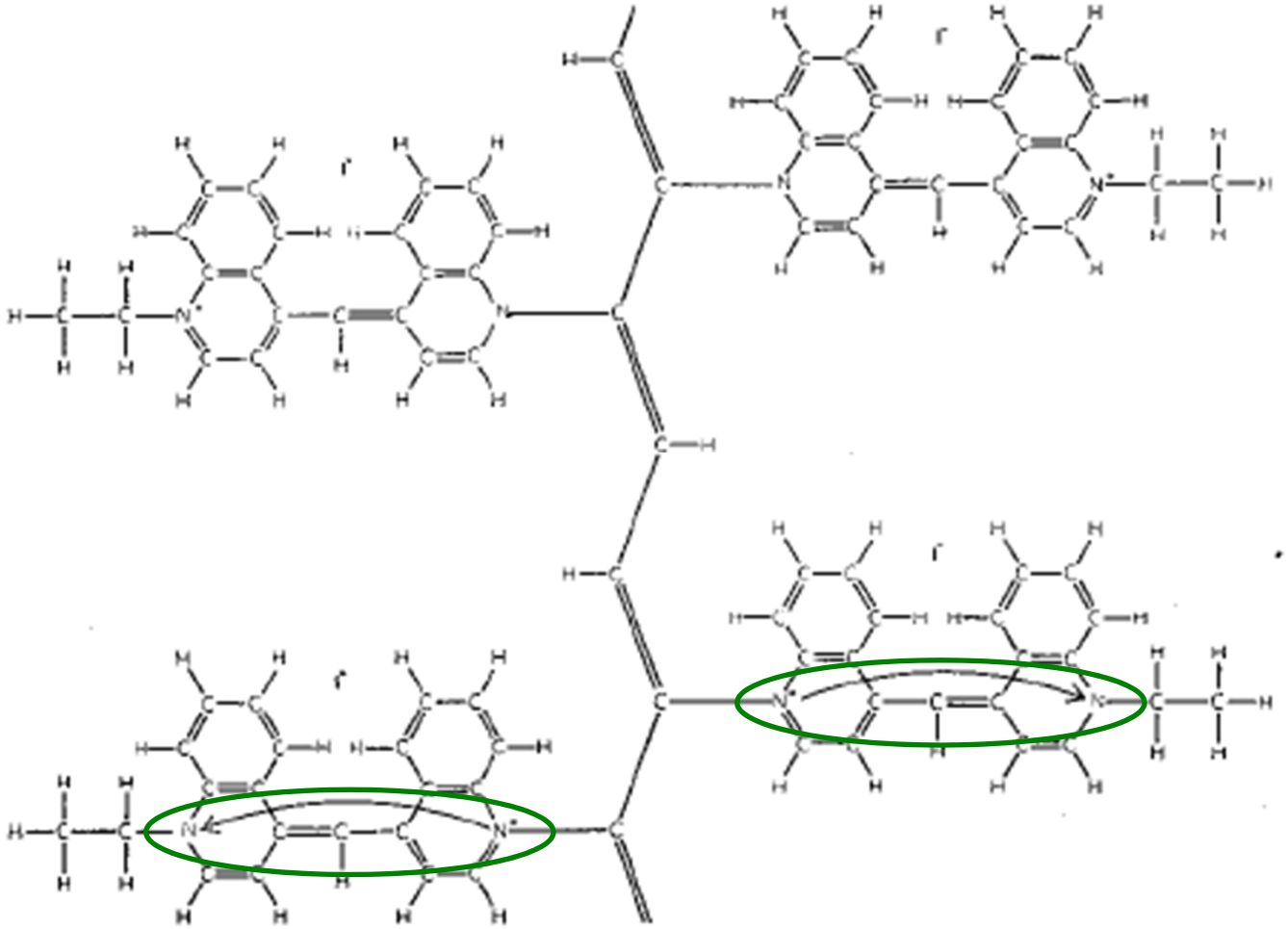
Loen, Norway

Road2RTS

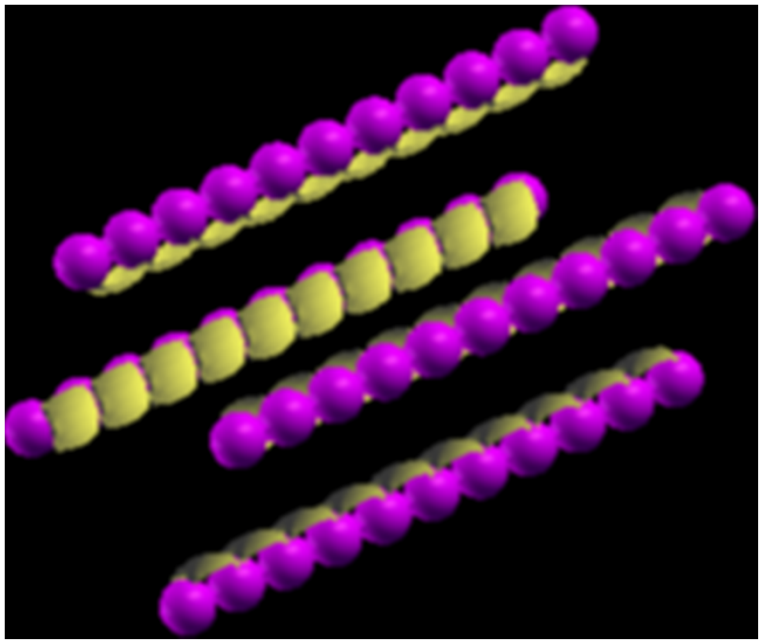
http .htm

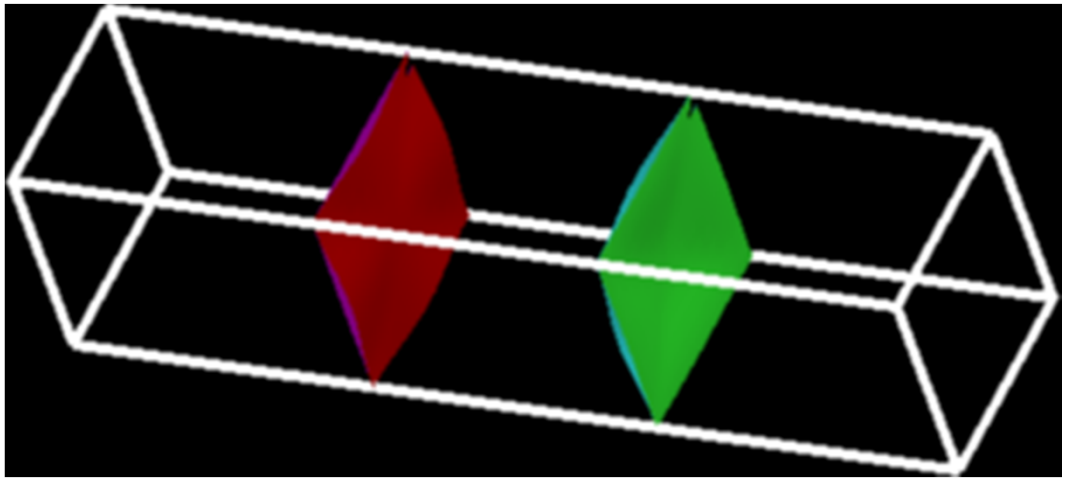
Little, 1963





Diethyl-cyanine iodide





“Not So Famous Danish Kid Brother”

Harald Bohr

Silver Medal, Danish Football Team, 1908 Olympic Games

Fibonacci Chains

"Monte-Carlo Simulation of Fermions on Quasiperiodic Chains,"

P. M. Grant, **BAPS March Meeting** (1992, Indianapolis)

$$G_n \equiv G_{n-1} \,|\, G_{n-2}, \quad n = 3, 4, 5, \ldots, \infty$$

Where $G_1 = a, \; G_2 = ab$

And $\lim_{n\to\infty} N_a(G_n) / N_b(G_n) \equiv \tau = (1+\sqrt{5})/2 \simeq 1.618\ldots$

Example: $G_6 = abaababaab \;\; (N = 13)$

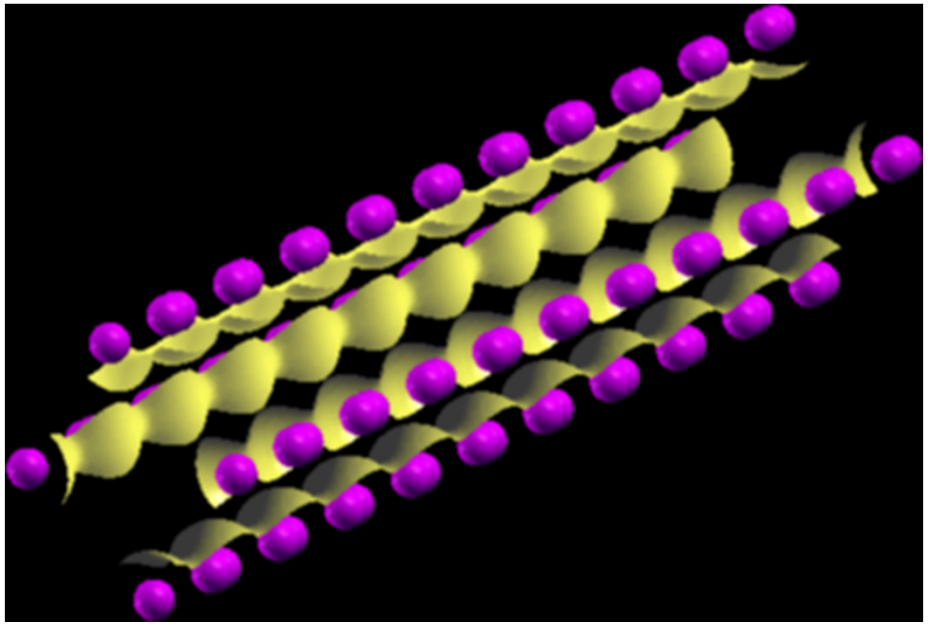
Let $a = c\tau b,$ subject to $\langle a, b \rangle$ invariant,

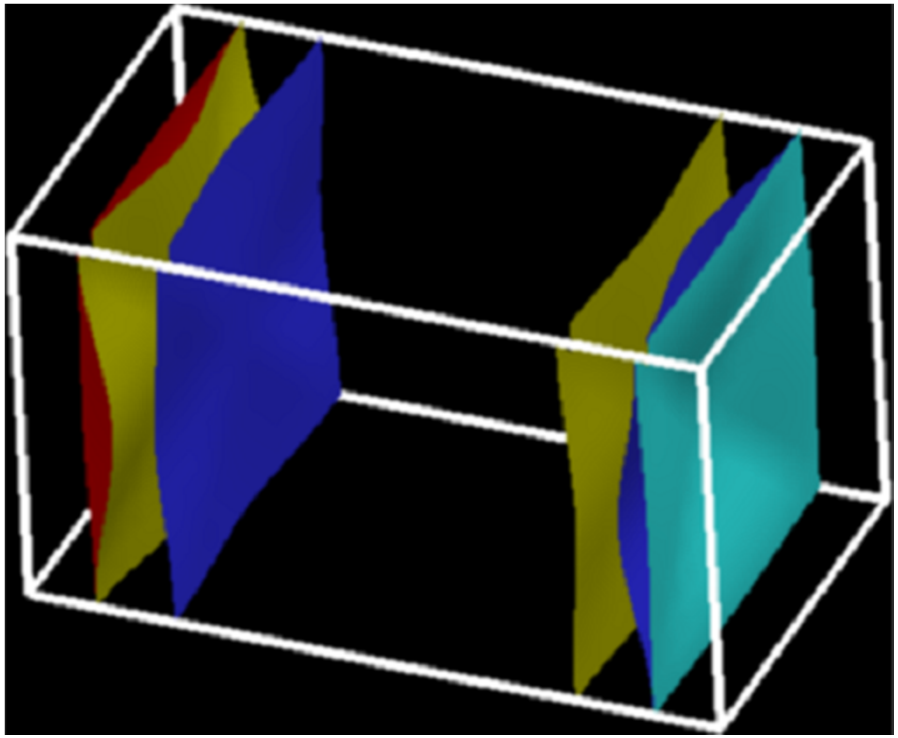
And take a and b

to be "inter-atomic n-n distances,"

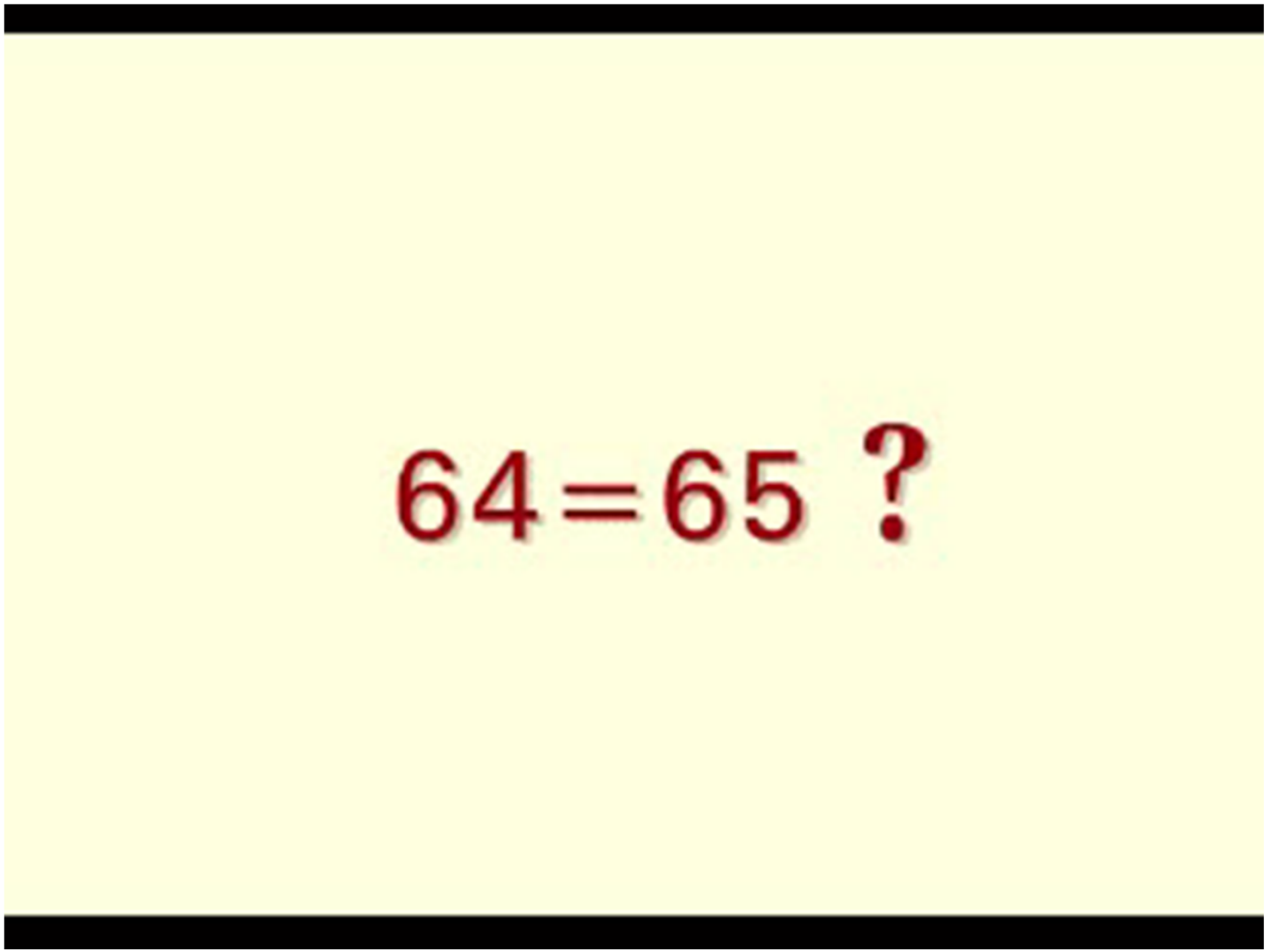
Then $b = \tau \langle a, b \rangle / \left[(1+c)\tau - 1 \right].$

Where c is a "scaling" parameter.





64 = 65



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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 >~ 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 funtion.
- Look for anharmicities a la Newns & Tsuei
- Calculate optical & transport properties as f(c/a).

Supashi-bo !