DUBNA NANO conference 2008

International Conference on Theoretical Physics

Dubna - Nano2008

July 7 - 11, 2008

Bogoliubov Laboratory of Theoretical Physics, Dubna, Russia

BLTP Bogoliubov Laboratory of Theoretical Physics

Павел Джоунс

John Paul Jones

Nature, 18 June 2008

SUPERCONDUCTIVITY

Prospecting for an iron age

Paul M. Grant

Different material options for high-temperature superconductivity — conduction of electricity with little or no resistance at 'practical' temperatures — have arrived. Iron compounds are the latest thing.

High-temperature superconductivity is back in the public eye, and with a bang. But as ever with this topic, we must first journey back to 1986 and 1987, and to Georg Bednorz and Alex Müller[1], and Paul Chu and his colleagues[2]. To start with, there was the headline news[1] of the onset of superconductivity in a previously unexplored class of compounds, the copper oxide perovskites, or layered cuprates, at the then record-setting temperature of 35 kelvin. Shortly afterwards[2], this transition temperature (T_c) was pushed up to 90 K — beyond the temperature of liquid nitrogen.

The initial announcement prompted practically every superconductivity centre on the planet, including my own home lab at IBM Almaden, to ransack the periodic table hoping to strike pay dirt again. So frantic became the search that Tom Lehrer's 1950s classic *The Elements* was chosen as the theme song for a 1988 BBC Horizon documentary, *Superconductor — Race for the Prize*. Special attention was paid to oxides of the first-row transition metals, running from scandium to

Electronic Structure of Rocksalt Copper Monoxide

Paul M. Grant

Visiting Scholar, Stanford University
IBM Research Staff Member, Emeritus
EPRI Science Fellow (retired)
Principal, W2AGZ Technologies

Stanford Collaborators:
- Ted Geballe
- Bob Hammond
- Mac Beasley
- Gert Koster
- Wolter Siemons

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!

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

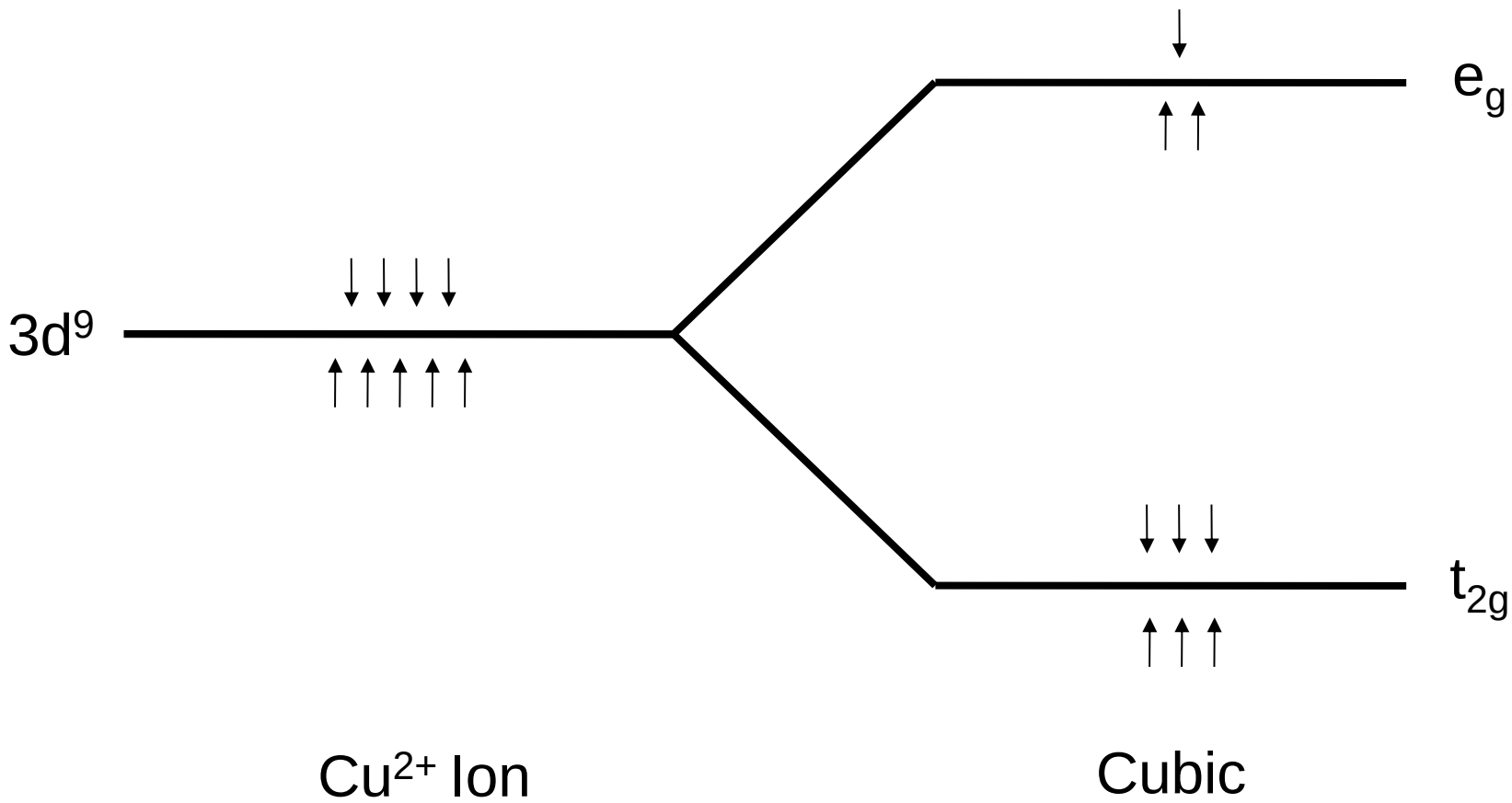
...

Where's spin, Pauli and Darwin? Ya screwed up, Bob…should'a used the many body Dirac equation! Oh yeah, and maybe Maxwell, Boltzman and Gibbs, too…and Newton's Apple.

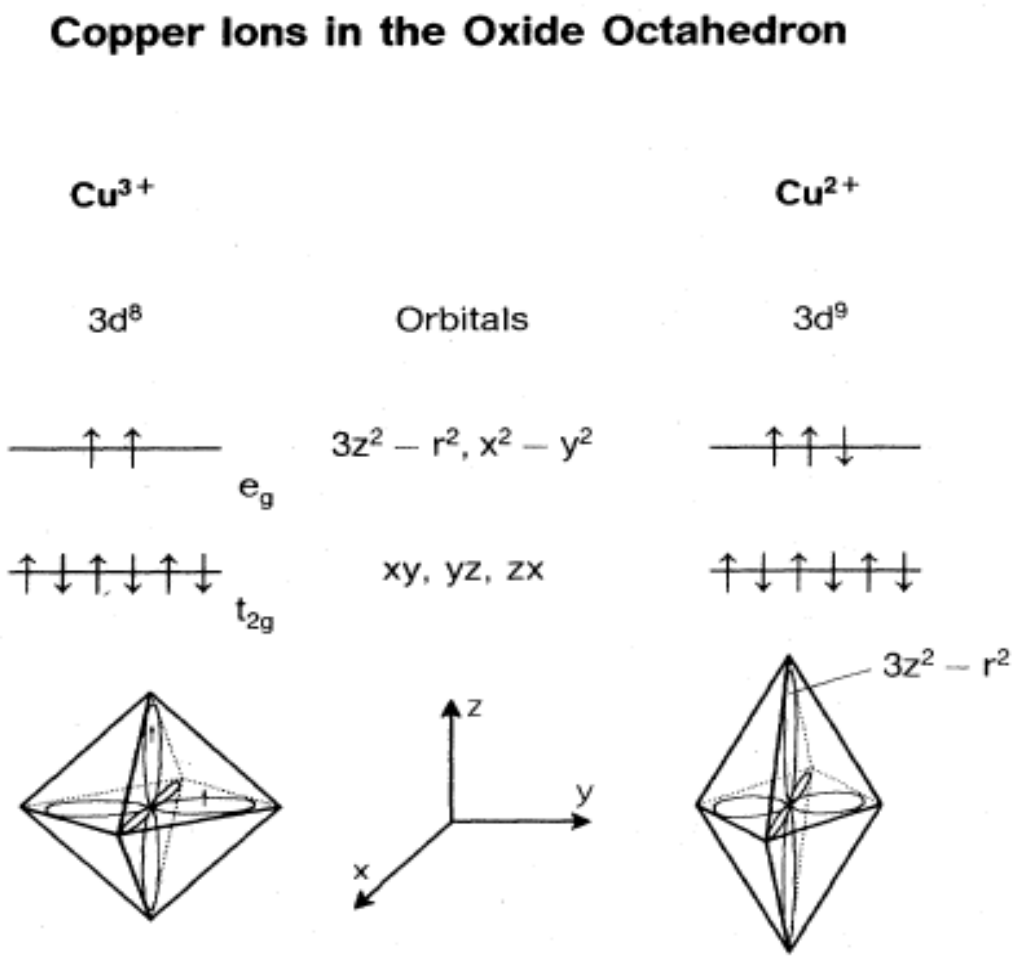
The crunch comes when Σ_i with i >= 3 -> "thermodynamic limit."

"Size Matters !"

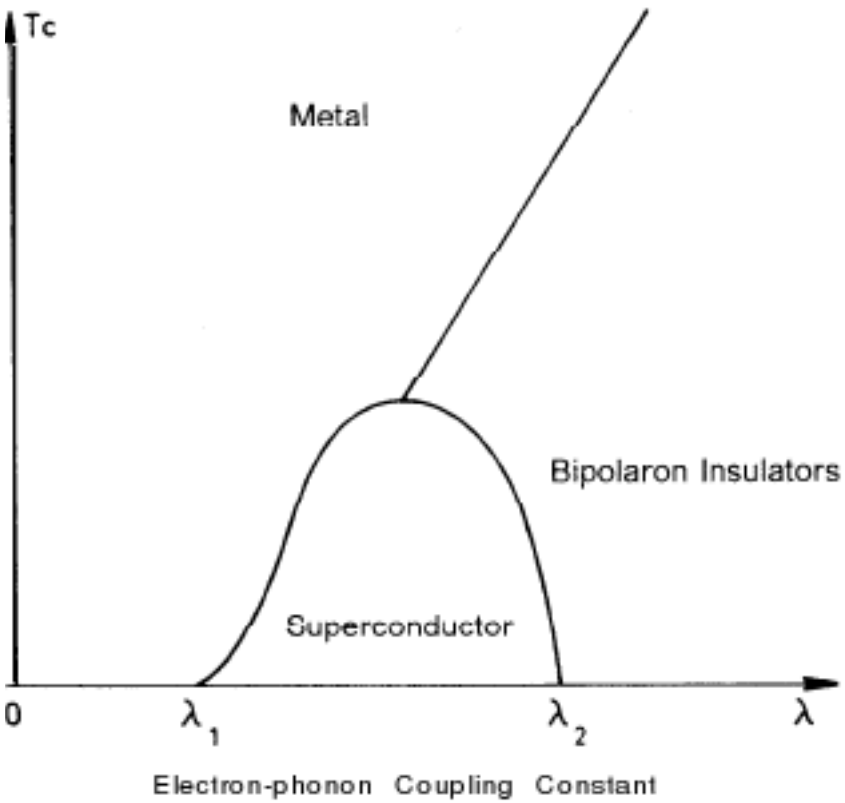
Cu^{2+} 3d Multiplet Splitting (Cubic)



Bednorz-Mueller Nobel Lecture



Jahn-Teller Effect: Elongation of the Octahedron



After Chakravarty, (1979)

Hubbard Theory

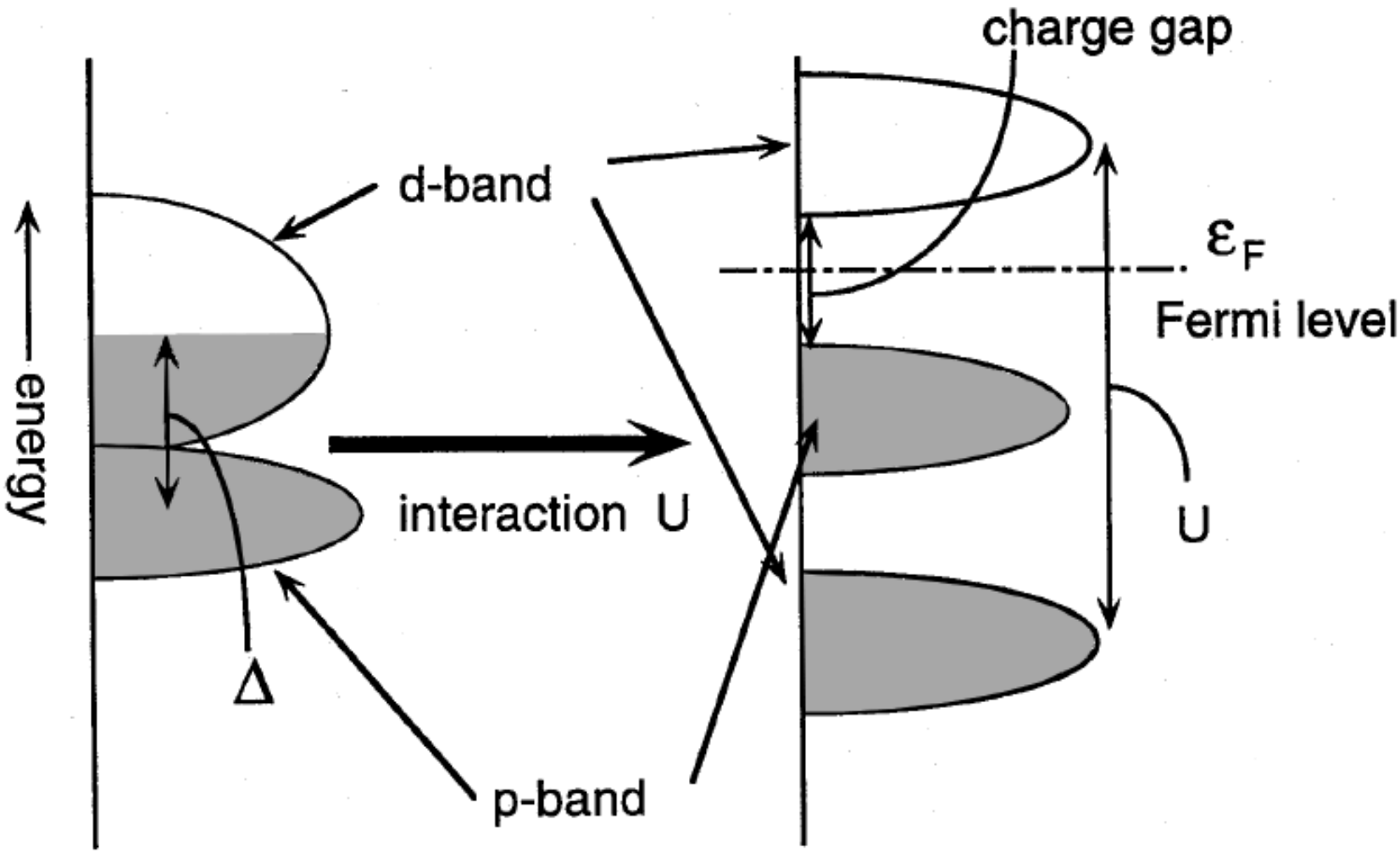
$$H = \sum_{\langle ij \rangle, \sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} n_{i\downarrow} n_{i\uparrow} + \frac{V}{2} \sum_{\langle ij \rangle, \sigma, s} n_{i\sigma} n_{js}$$

One-electron "band" term

On-site "Hubbard" double occupation coulomb repulsion

Off-site repulsion

Charge Transfer Insulator



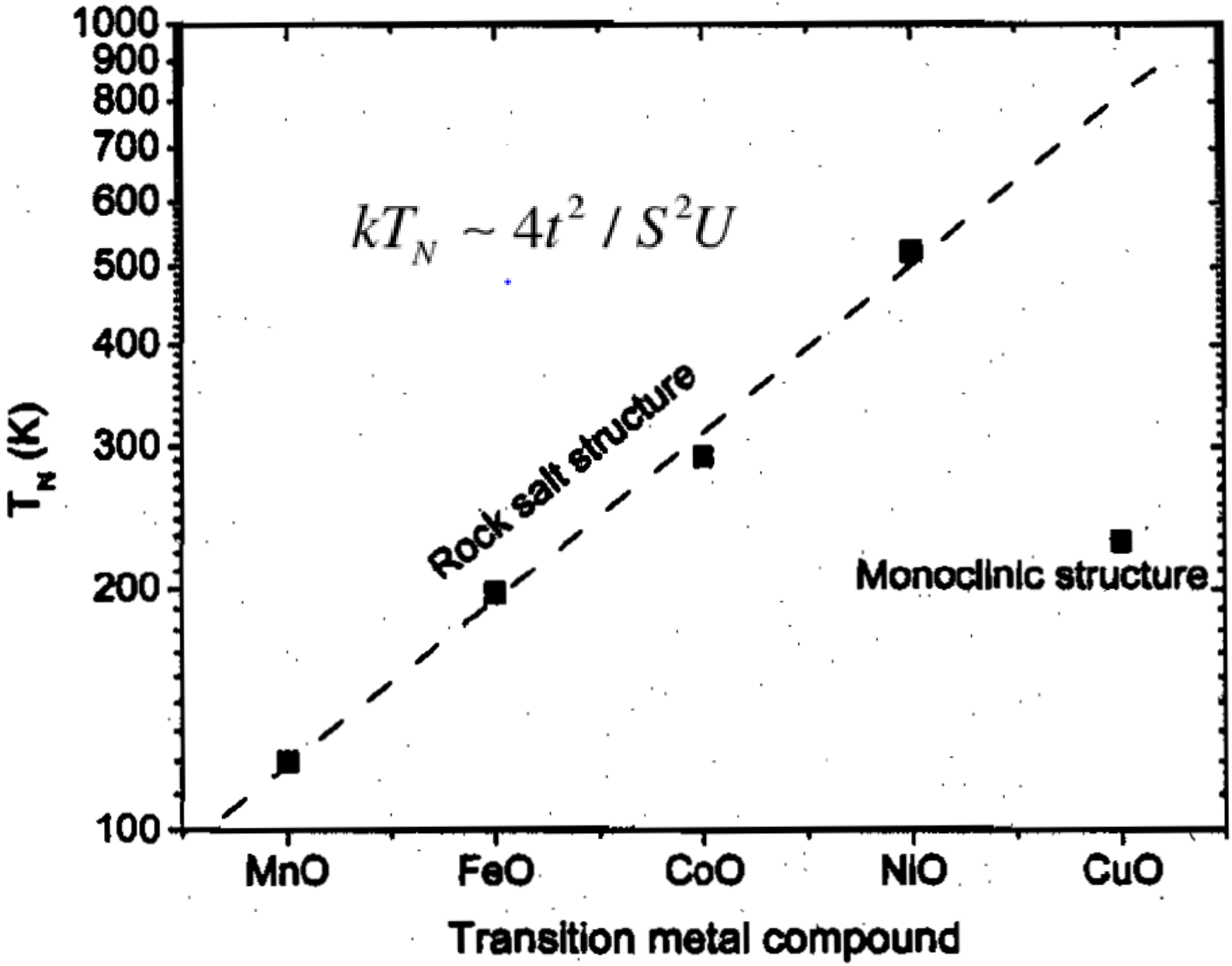
After Imada, et al, RMP 70, 1039 (1998)

Cubic Rocksalt Divalent TMOs

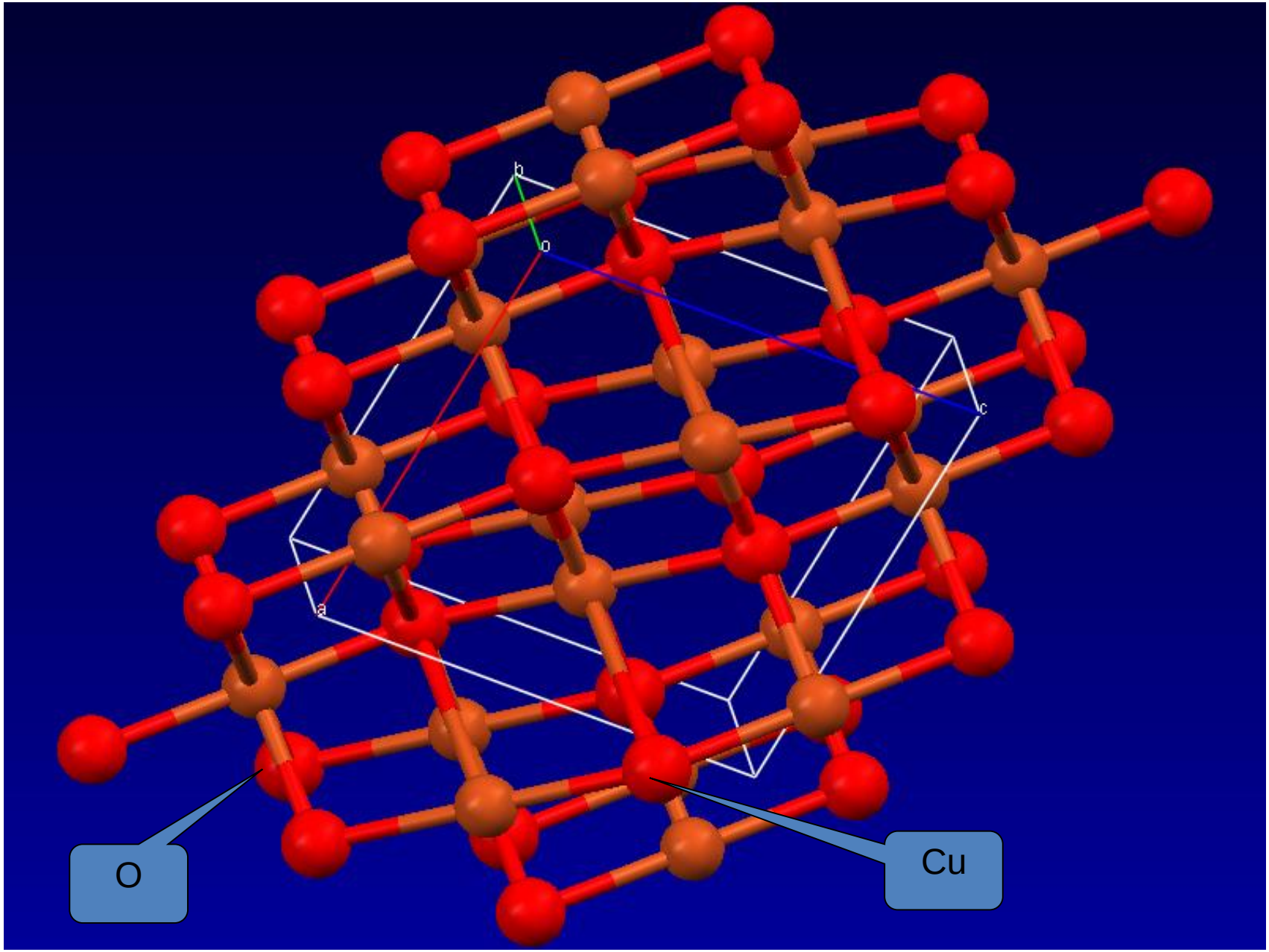
TMO	3d Config	Properties
MnO	5	MH-CTI (5.6)
FeO	6	MH-CTI (5.9)
CoO	7	MH-CTI (6.3)
NiO	8	MH-CTI (6.5)
CuO	9	***XX Doesn't Exist!***

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

Néel Temperature vs. TMO Atomic Number



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

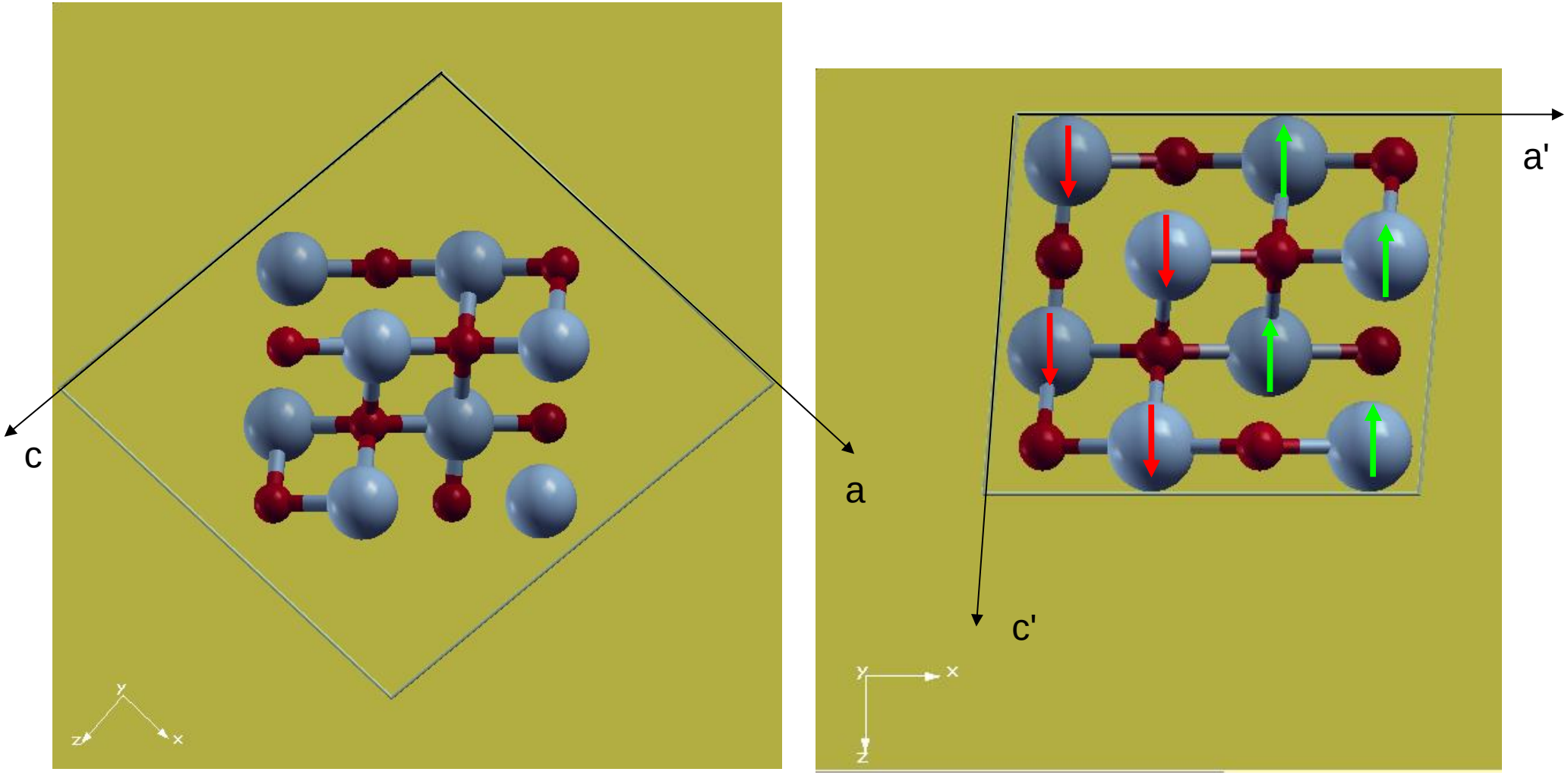
Experimental Equipment (Software)

- 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 $\rho = 320$ Ry
  - Convergence $\leq 10^{-6}$ Ry
  - "Smearing" = Methfessel-Paxton
  - Psuedopotentials: Ultrasoft, XC = Perdew-Zunger
    Cu: $3d^9 4s^2$ O: $2s^2 2p^4$

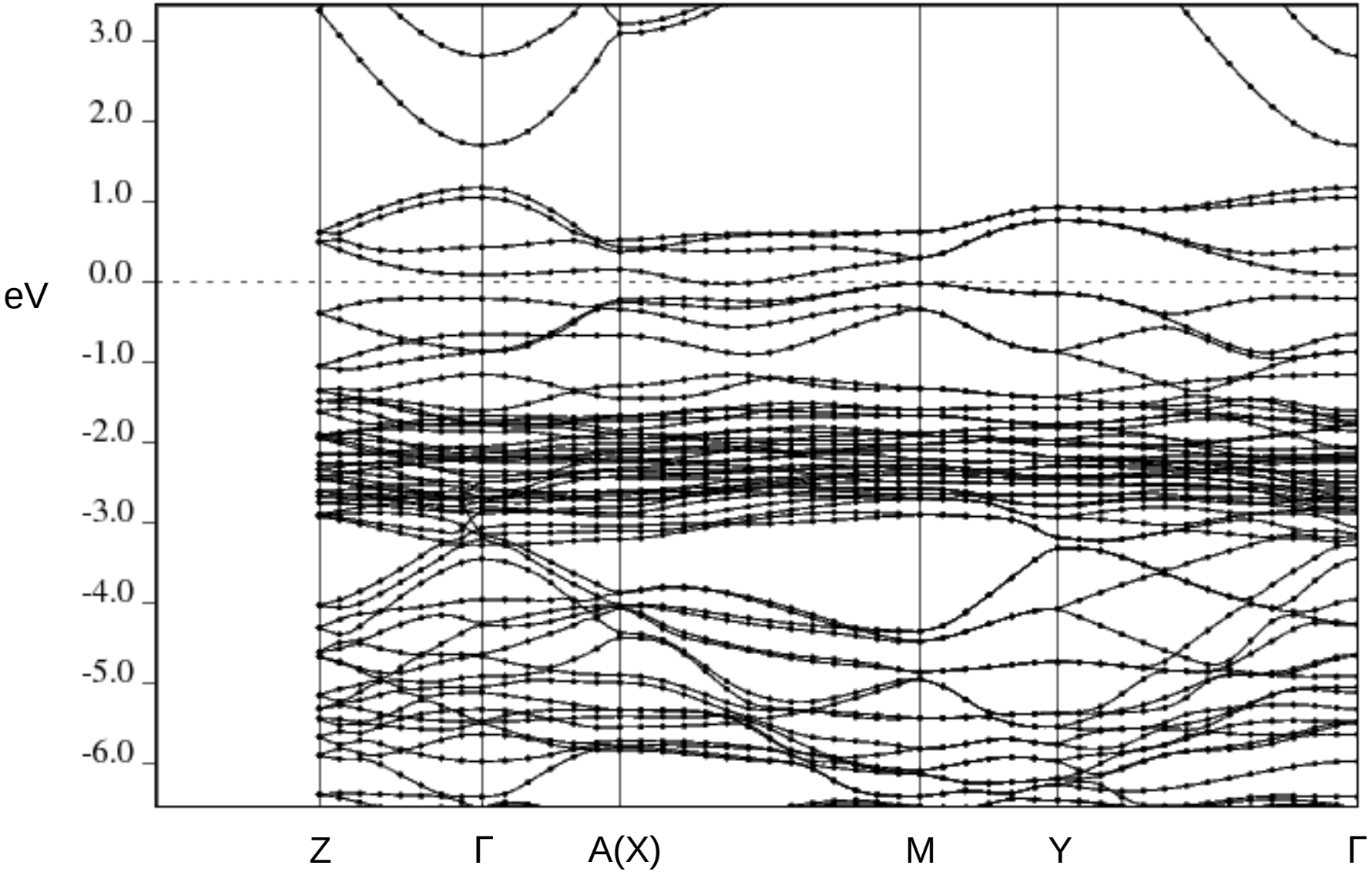
Experimental Equipment (Hardware)

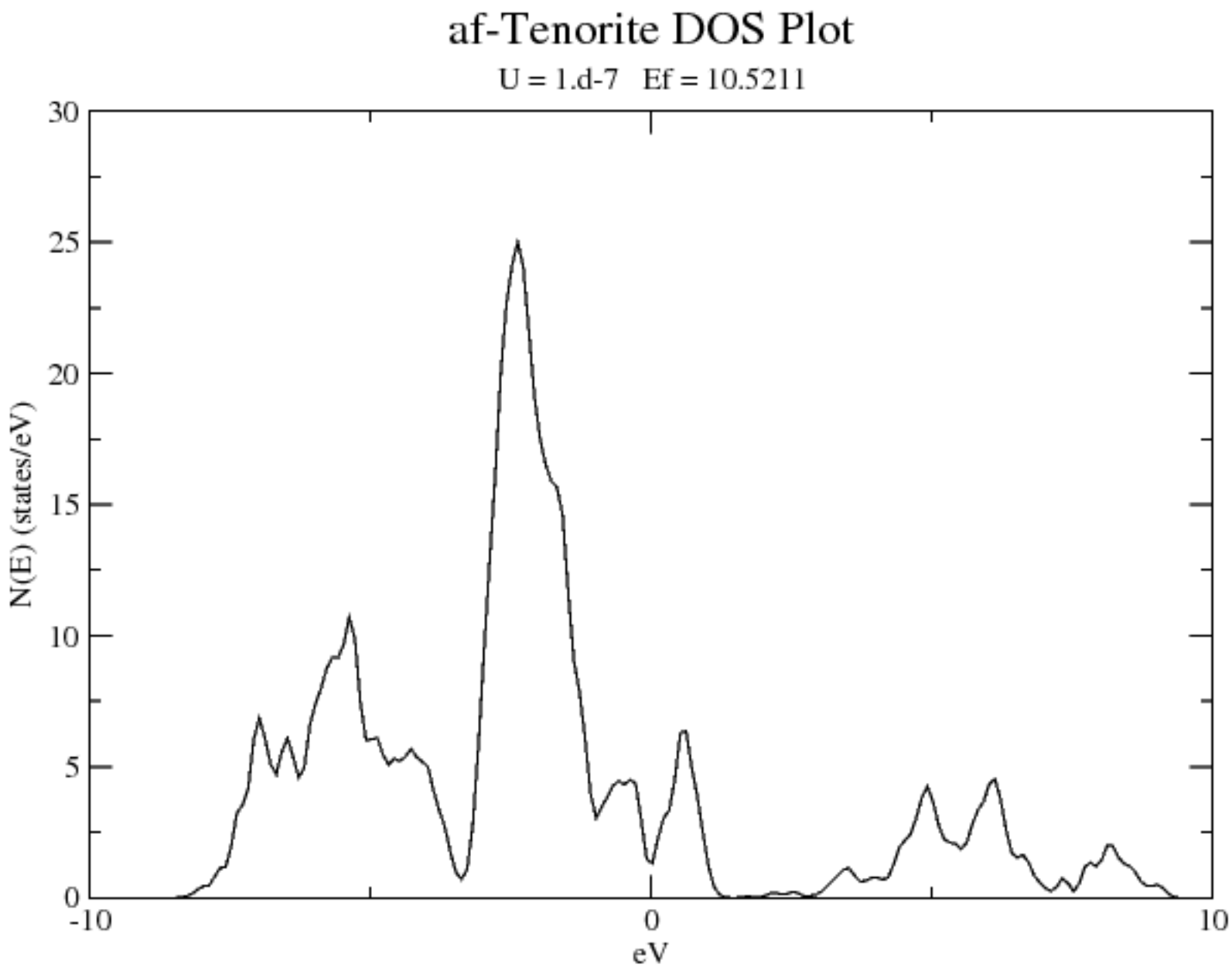
3-Cluster Home Network: AMD64 dual 3.5 GHz, 12 GB + IBM-X41 +…

nm & af Unit Cells

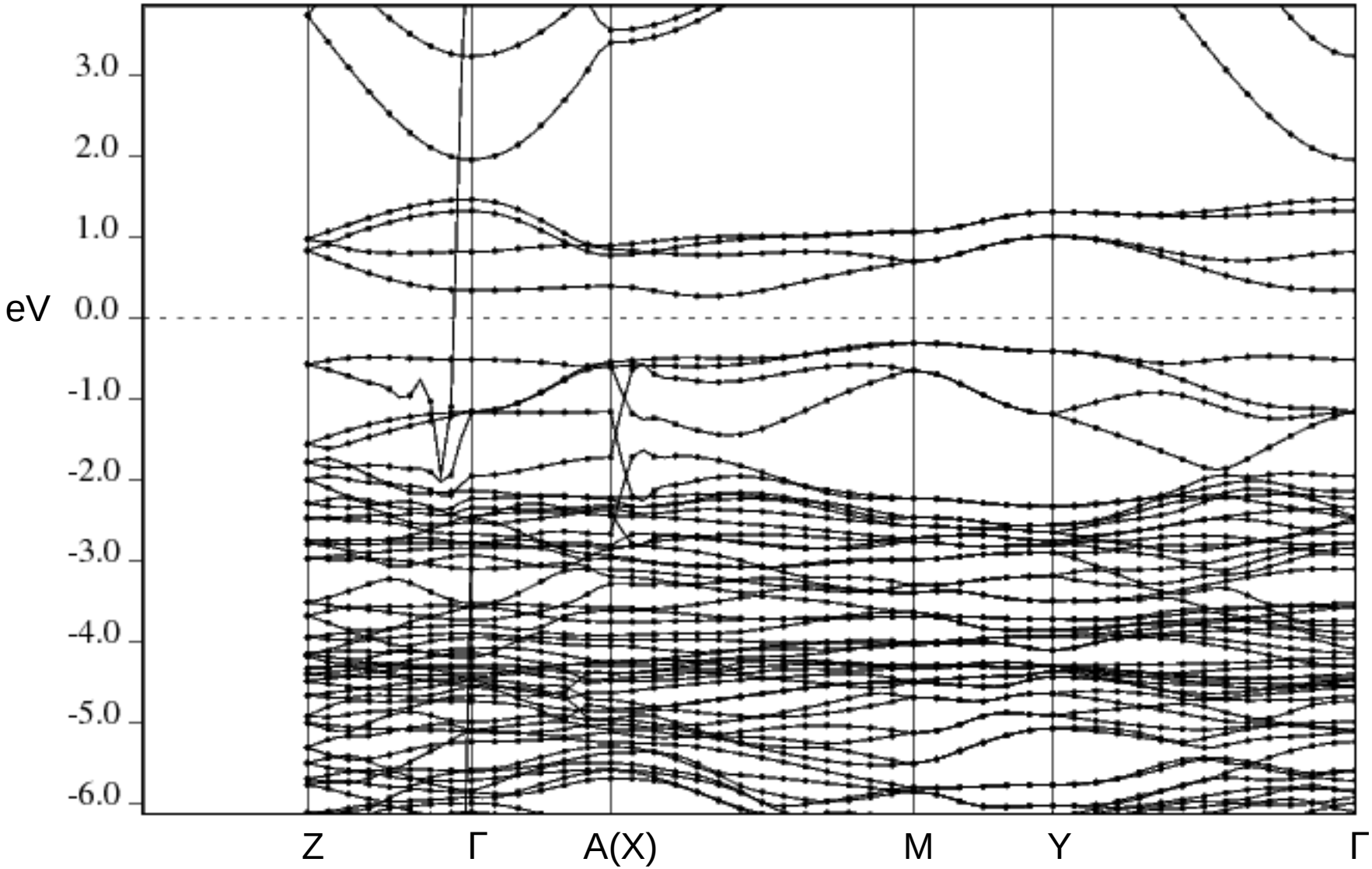


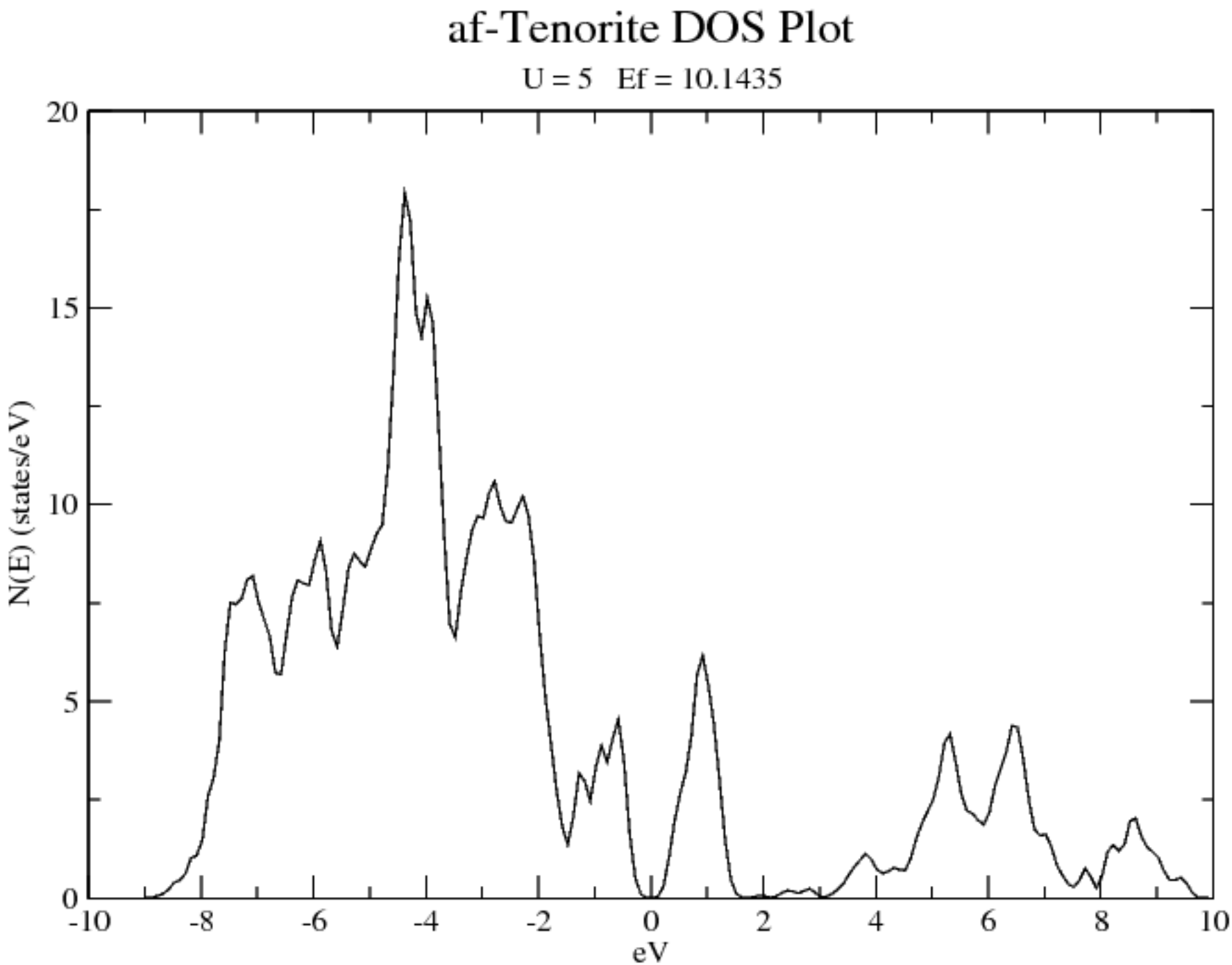
af_0_pmg (U = 0)



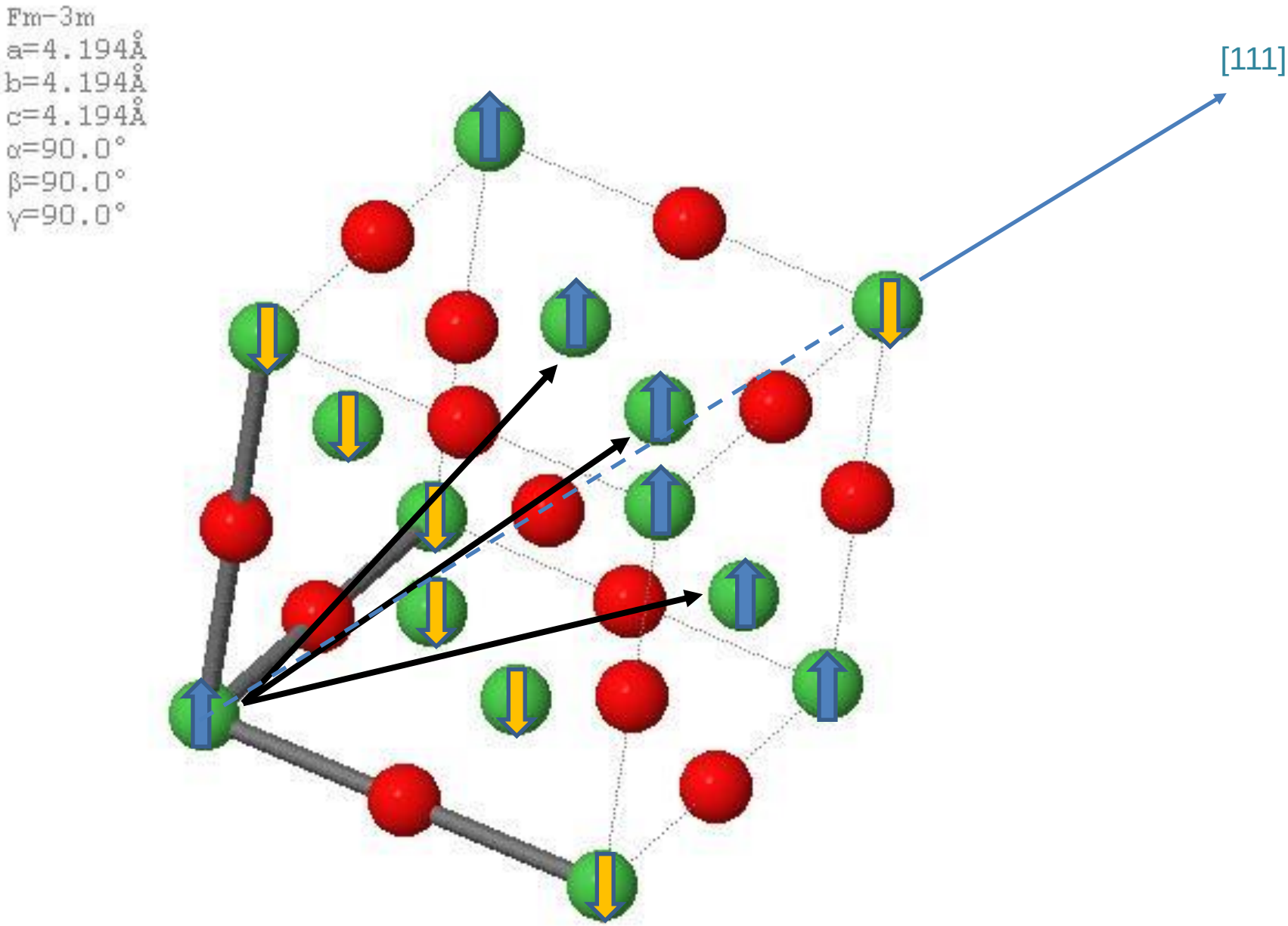

af-Tenorite DOS Plot
U = 1.d-7 Ef = 10.5211
N(E) (states/eV)
eV
30
25
20
15
10
5
0
-10
0
10

af_5_pmg (U = 5)

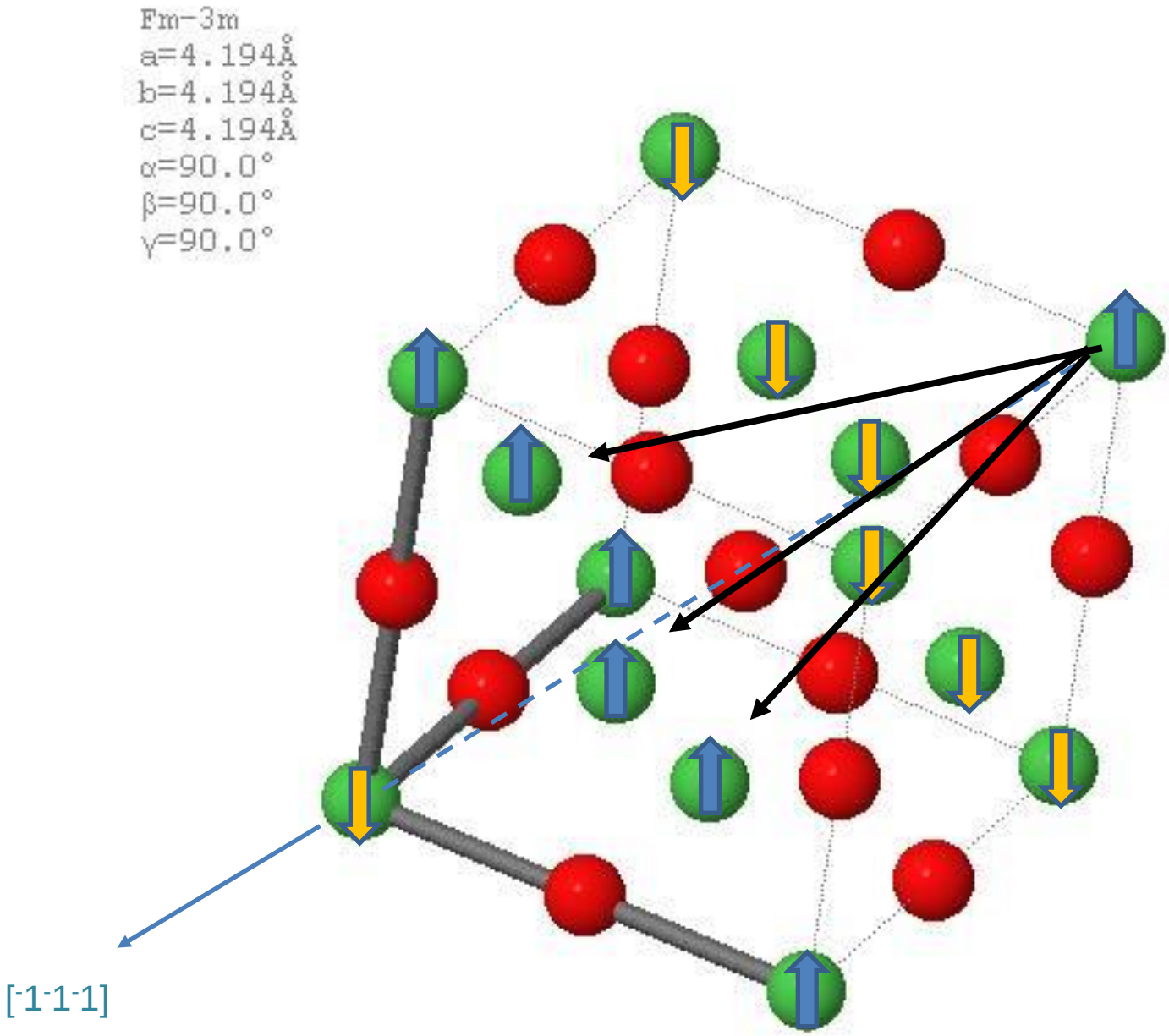



af-Tenorite DOS Plot
U = 5 Ef = 10.1435
N(E) (states/eV)
eV
20
15
10
5
0
-10
-8
-6
-4
-2
0
2
4
6
8
10

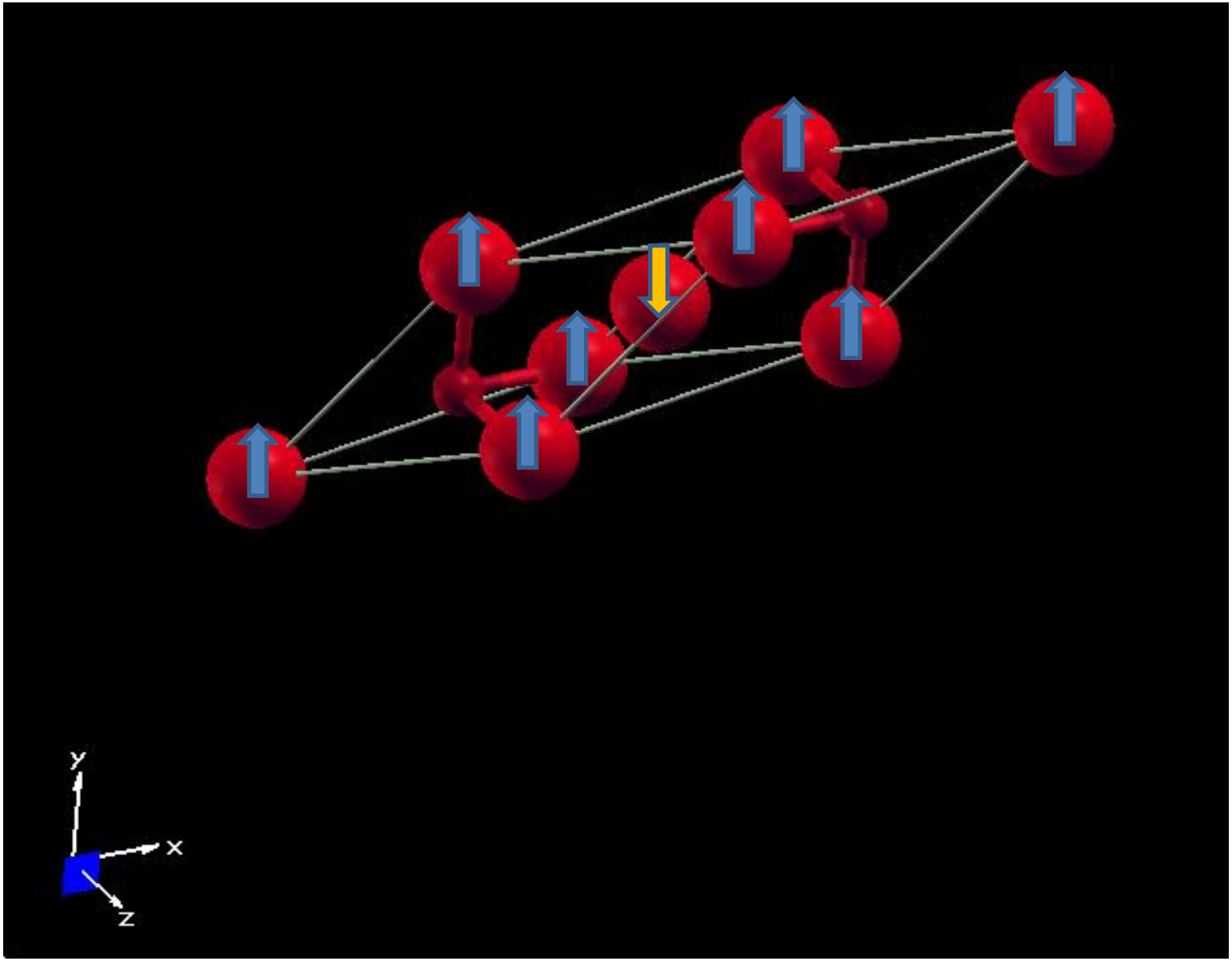
Proto-TMO AF Rock Salt



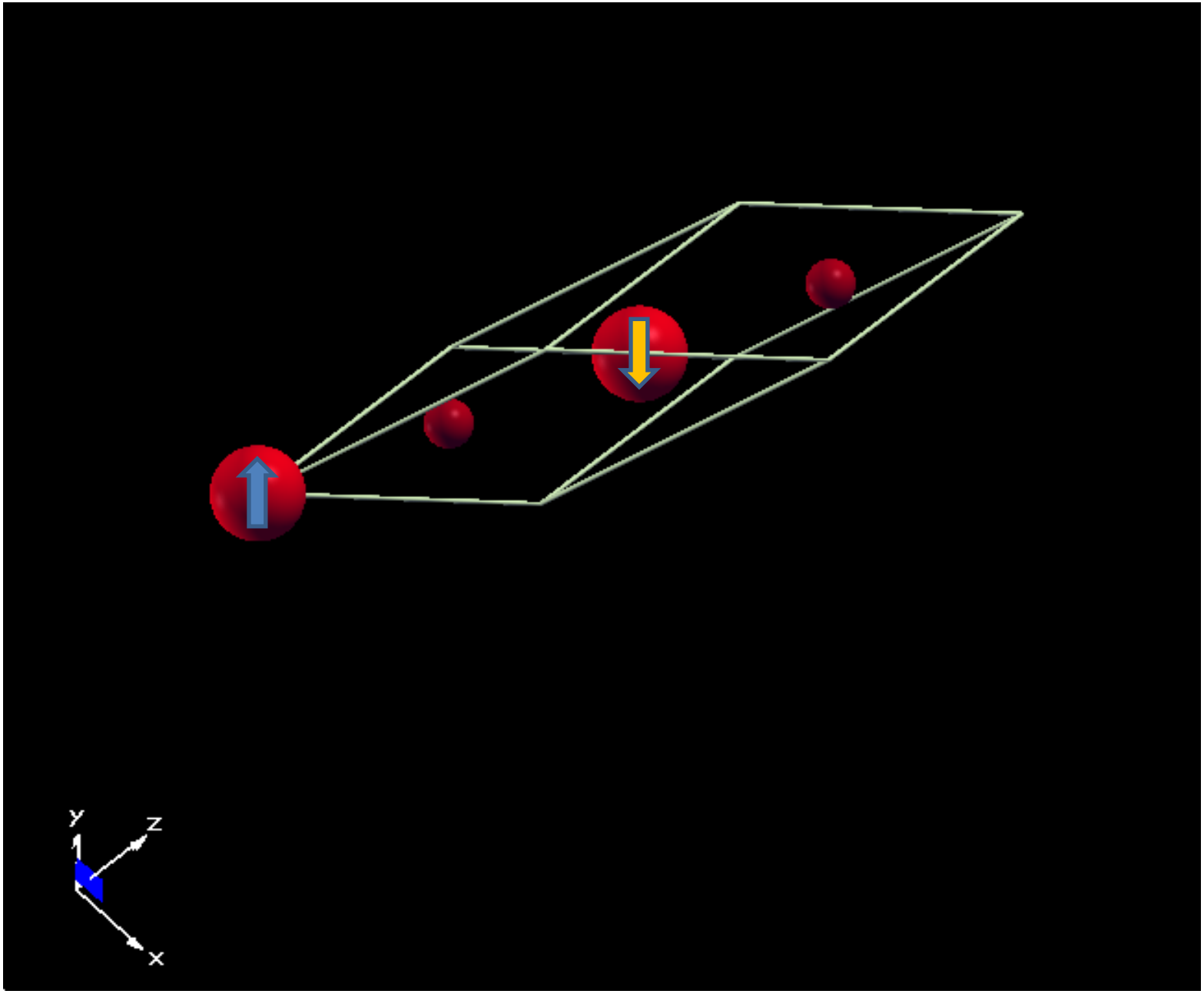
Proto-TMO AF Rock Salt

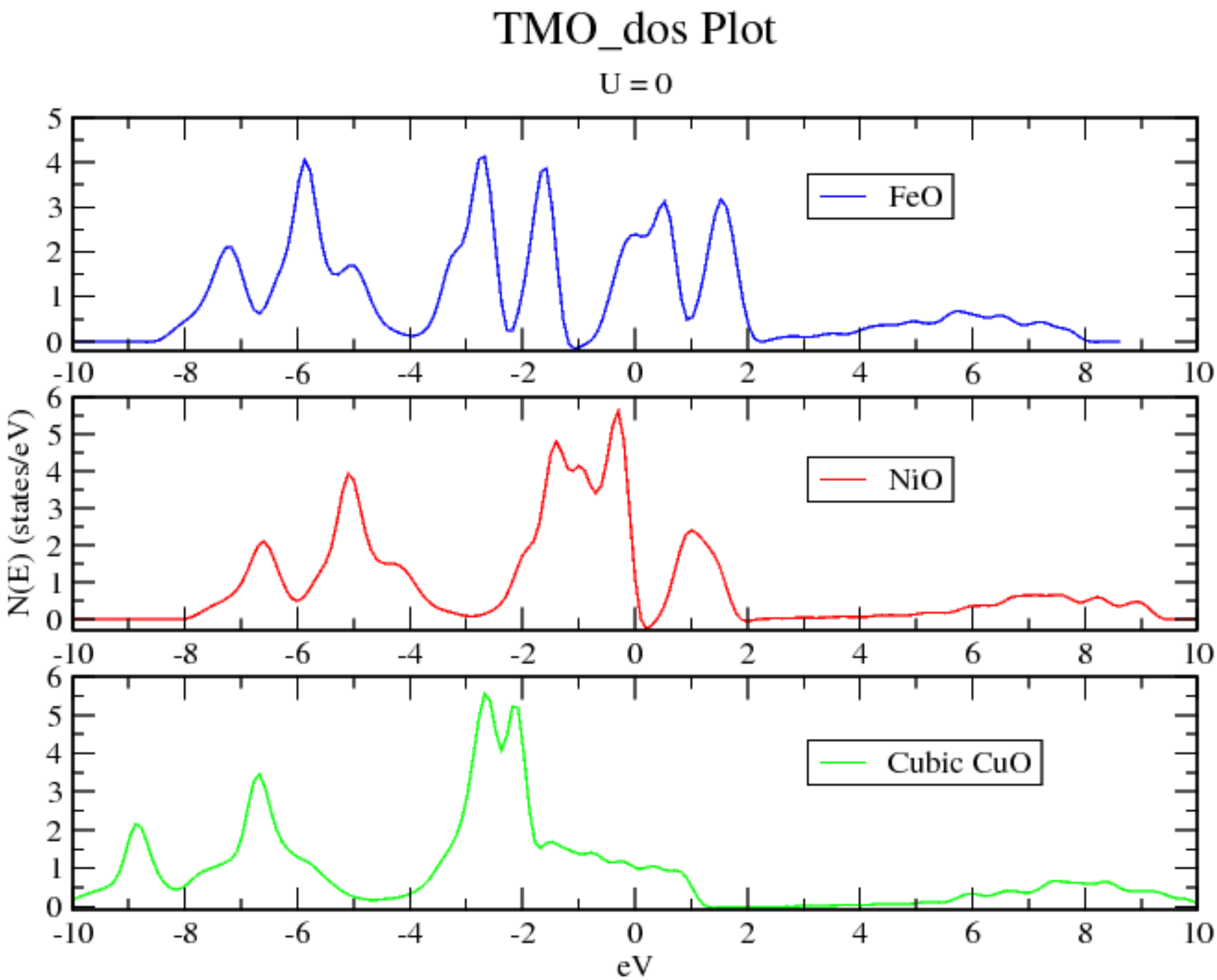


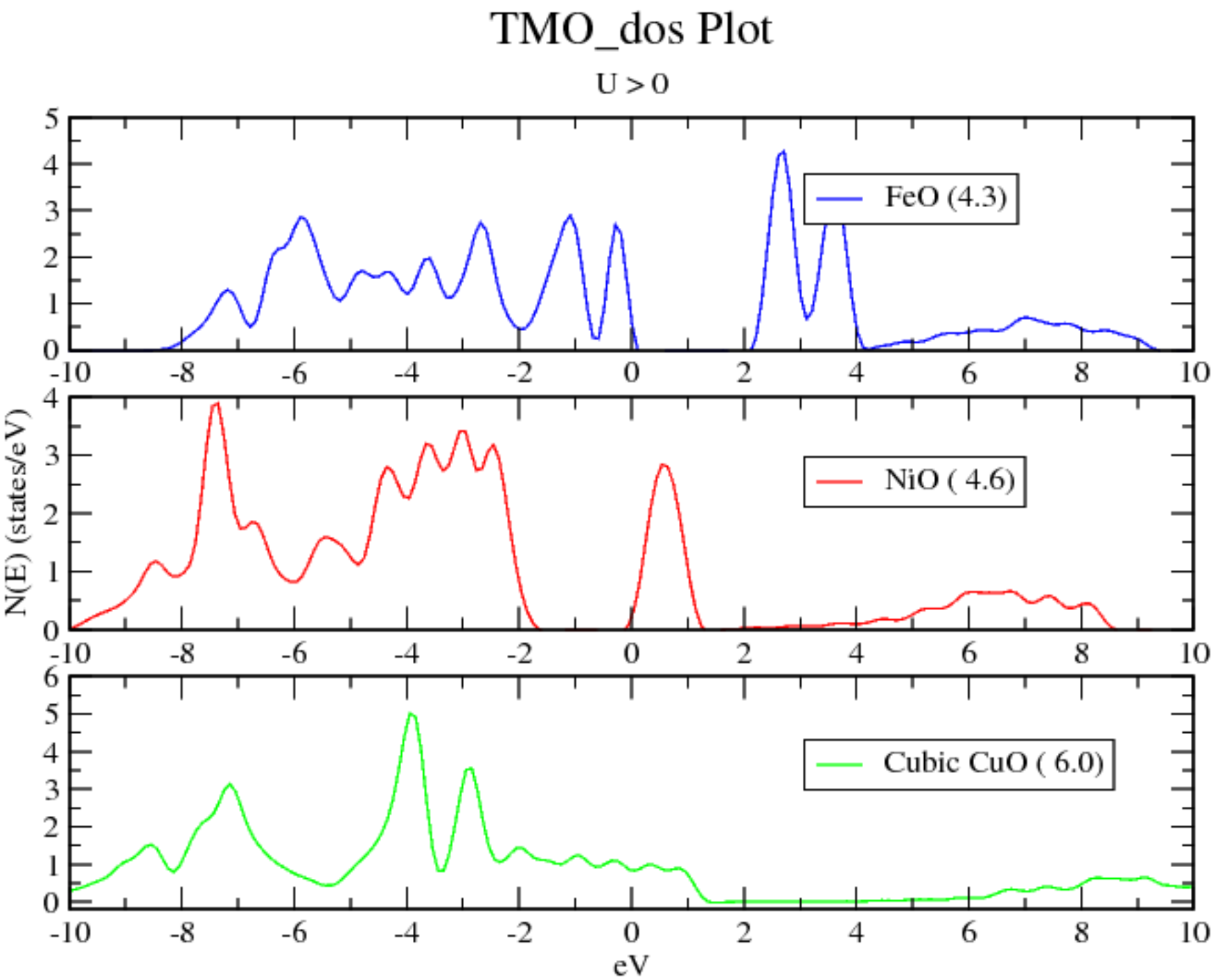
AF Type II Primitive Cell



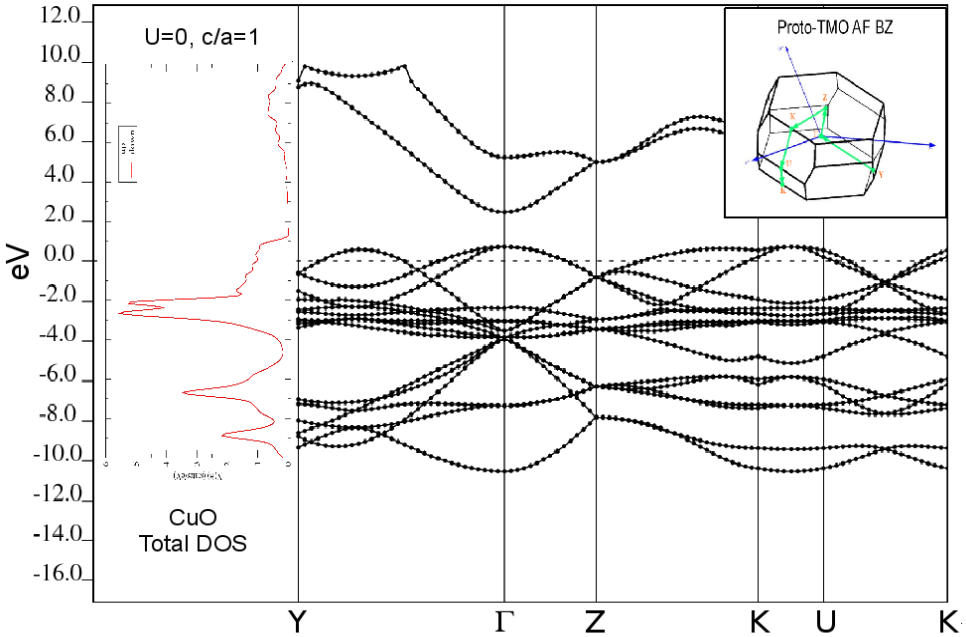
Basic Asymmetric AF Cell

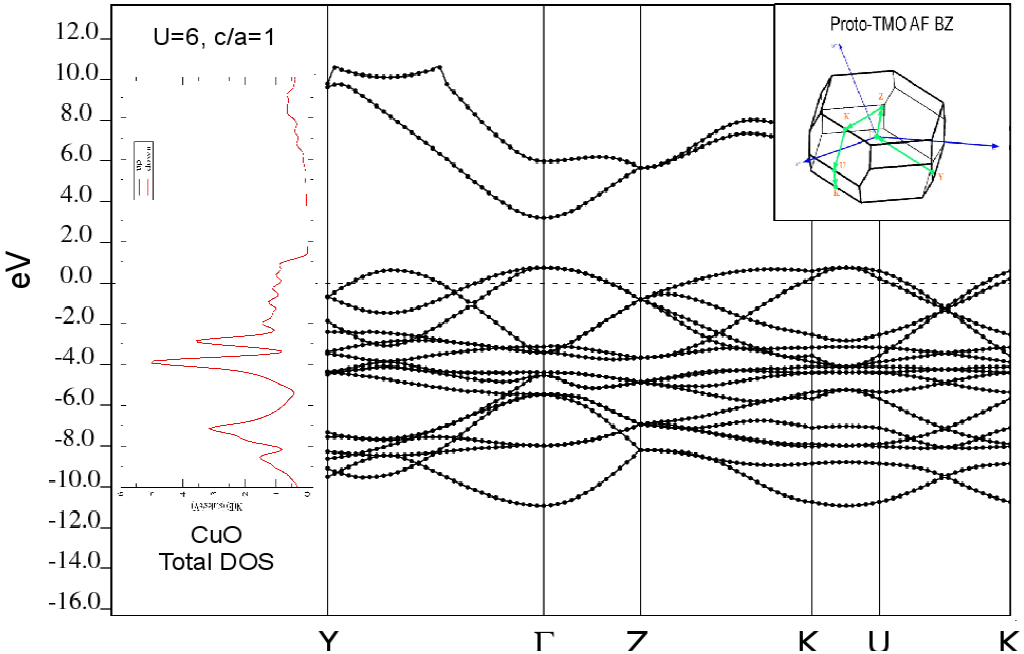


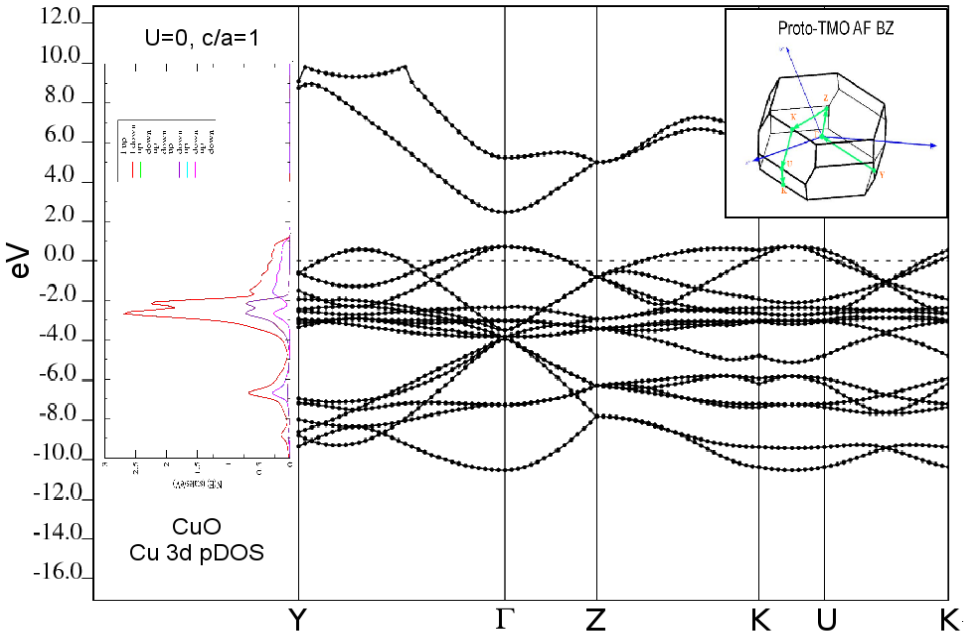

TMO_dos Plot
U = 0
FeO
NiO
Cubic CuO
N(E) (states/eV)
eV

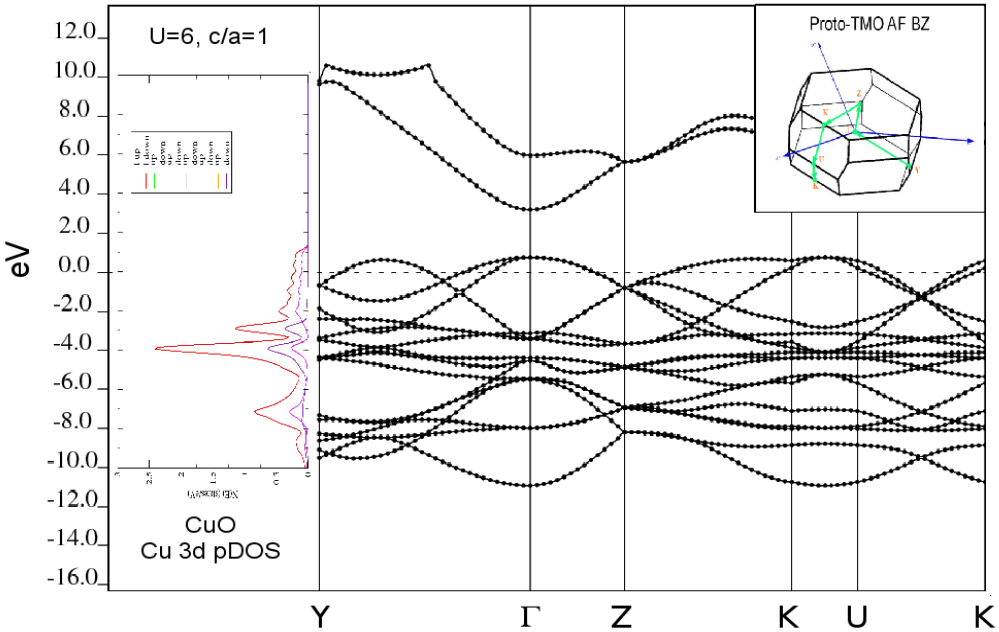

TMO_dos Plot
U > 0
FeO (4.3)
NiO (4.6)
Cubic CuO (6.0)
N(E) (states/eV)
eV

Cubic Rocksalt CuO

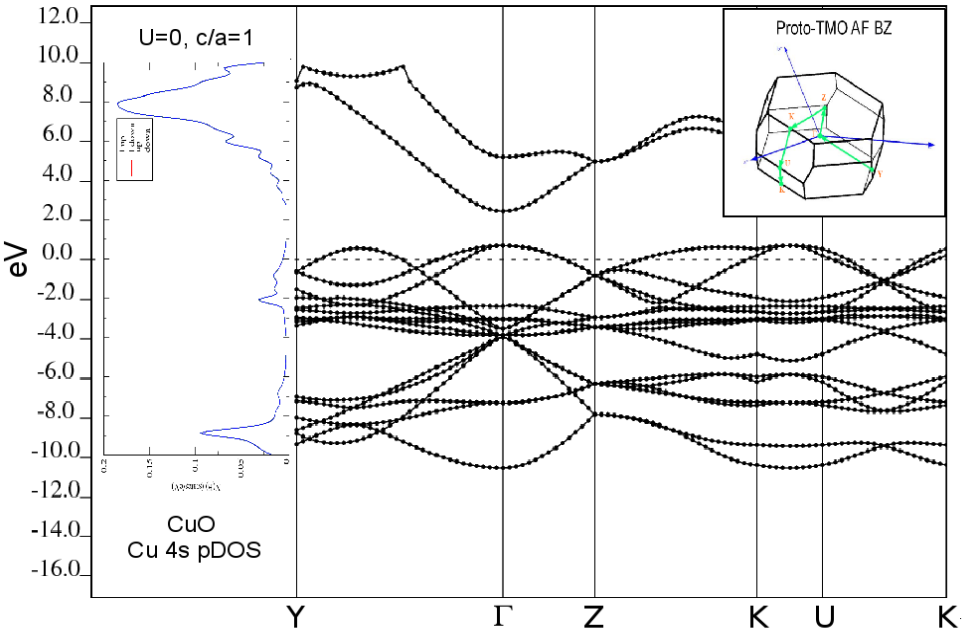


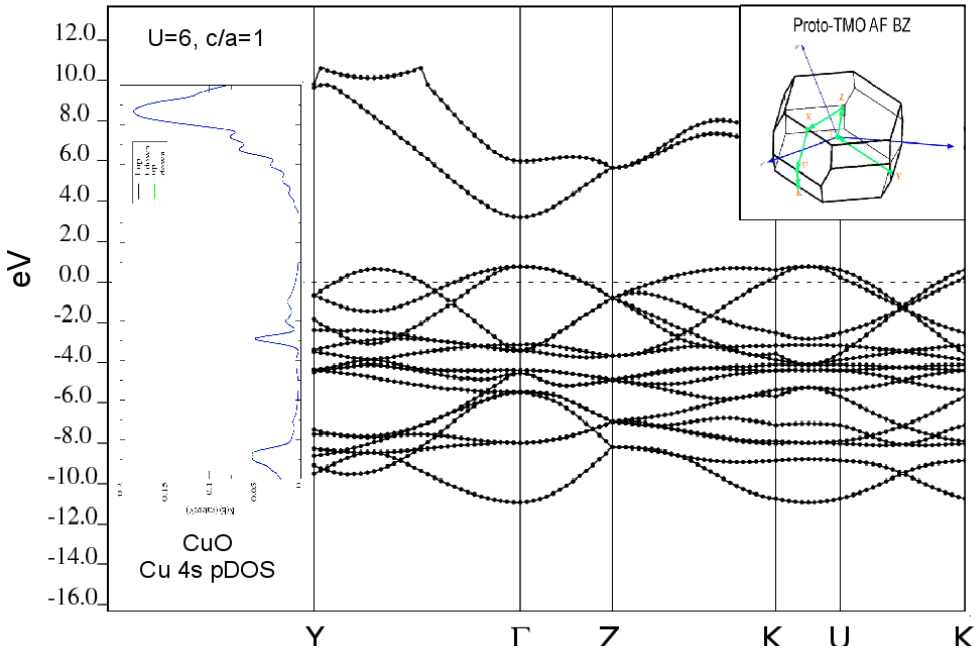


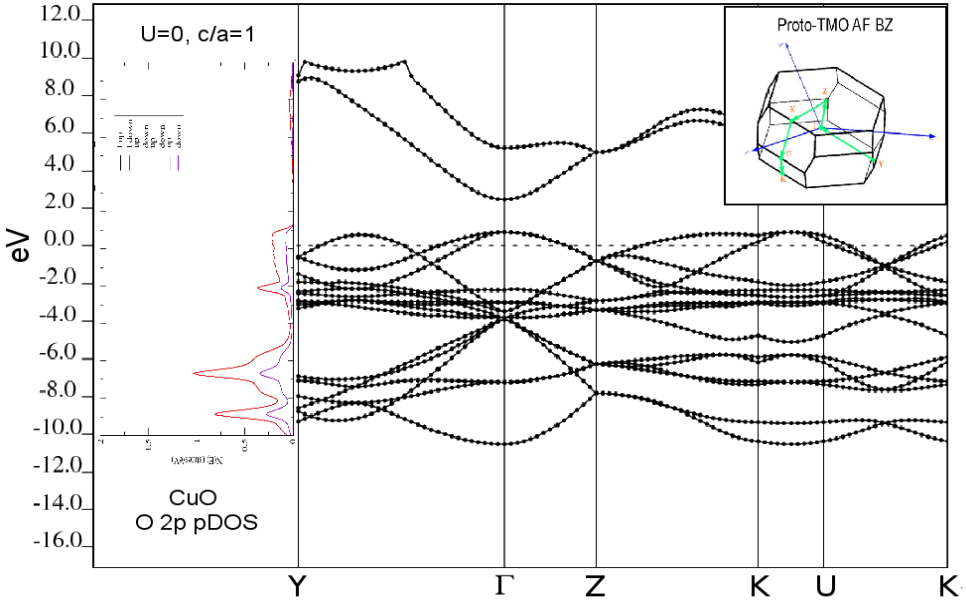


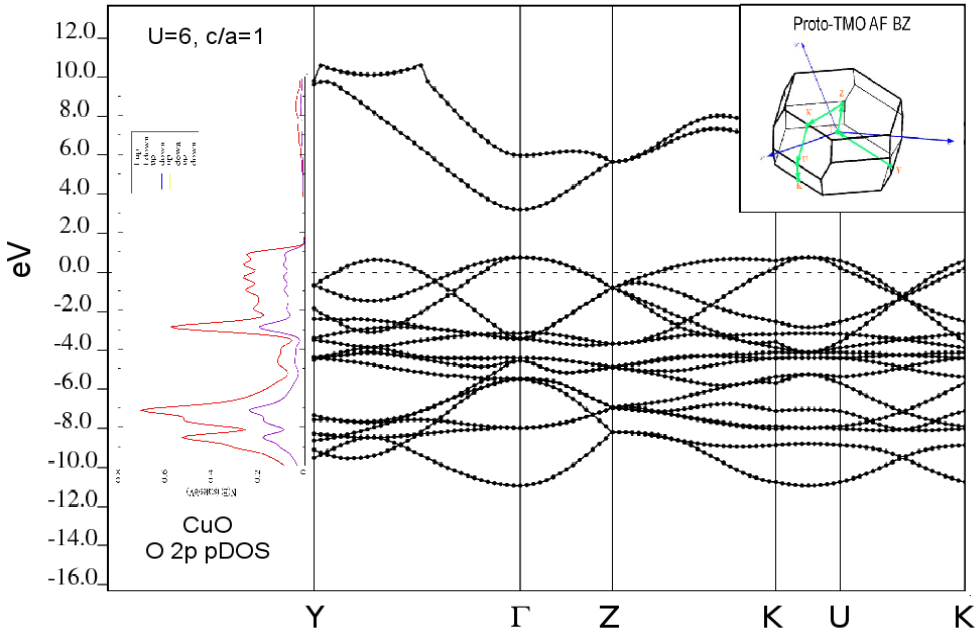


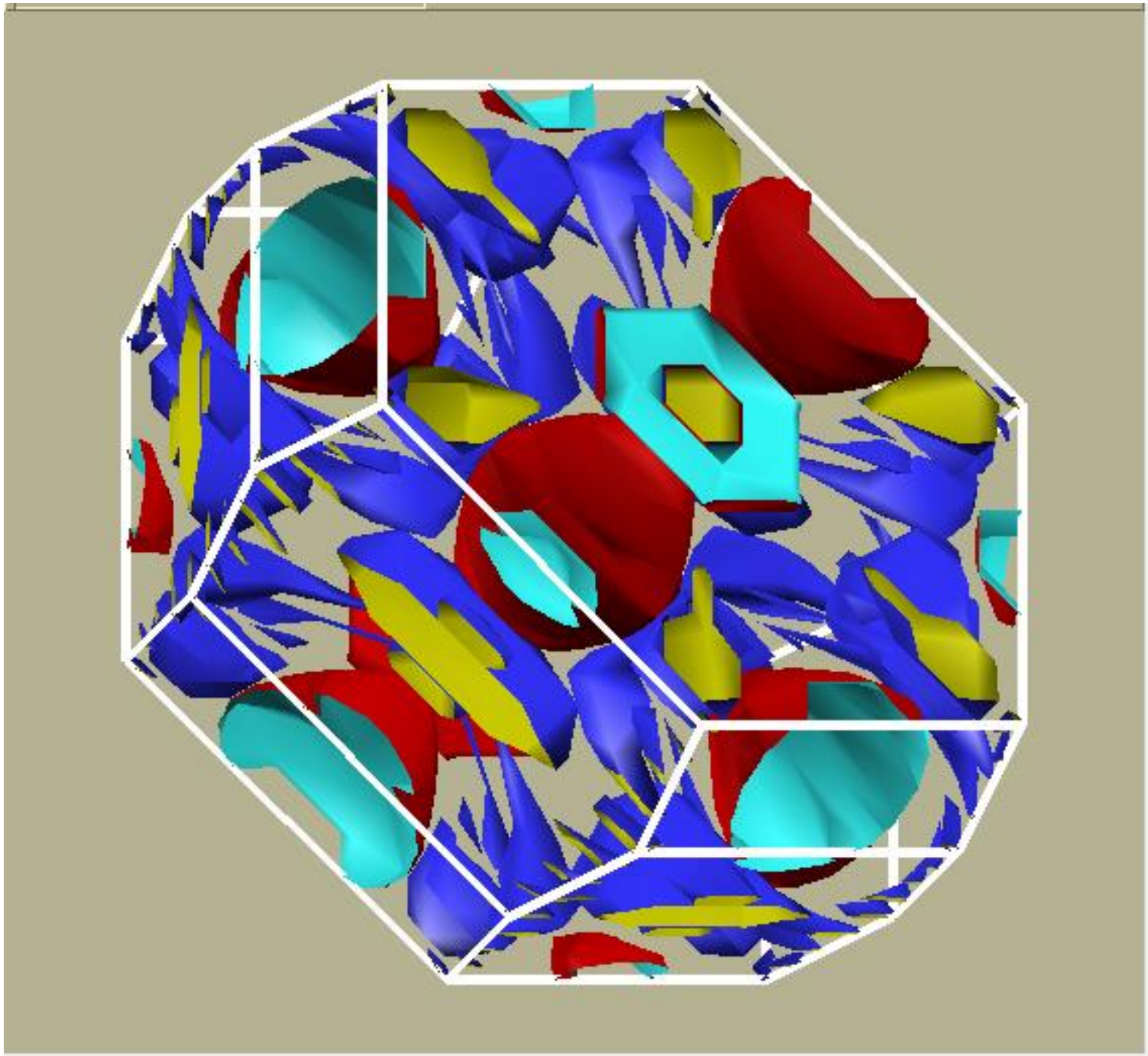
Cubic Rocksalt CuO (Cu 4s & O2p)

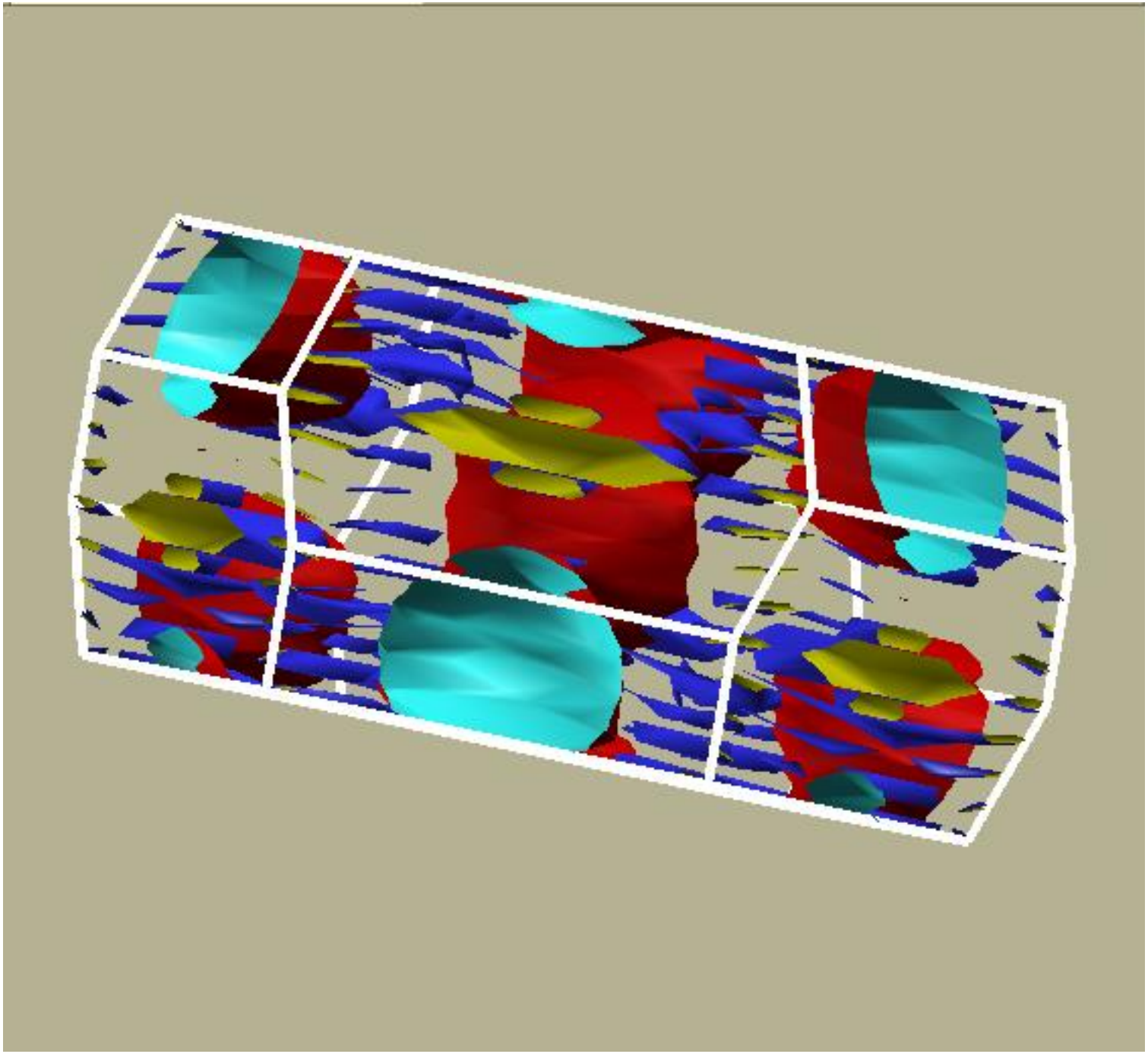






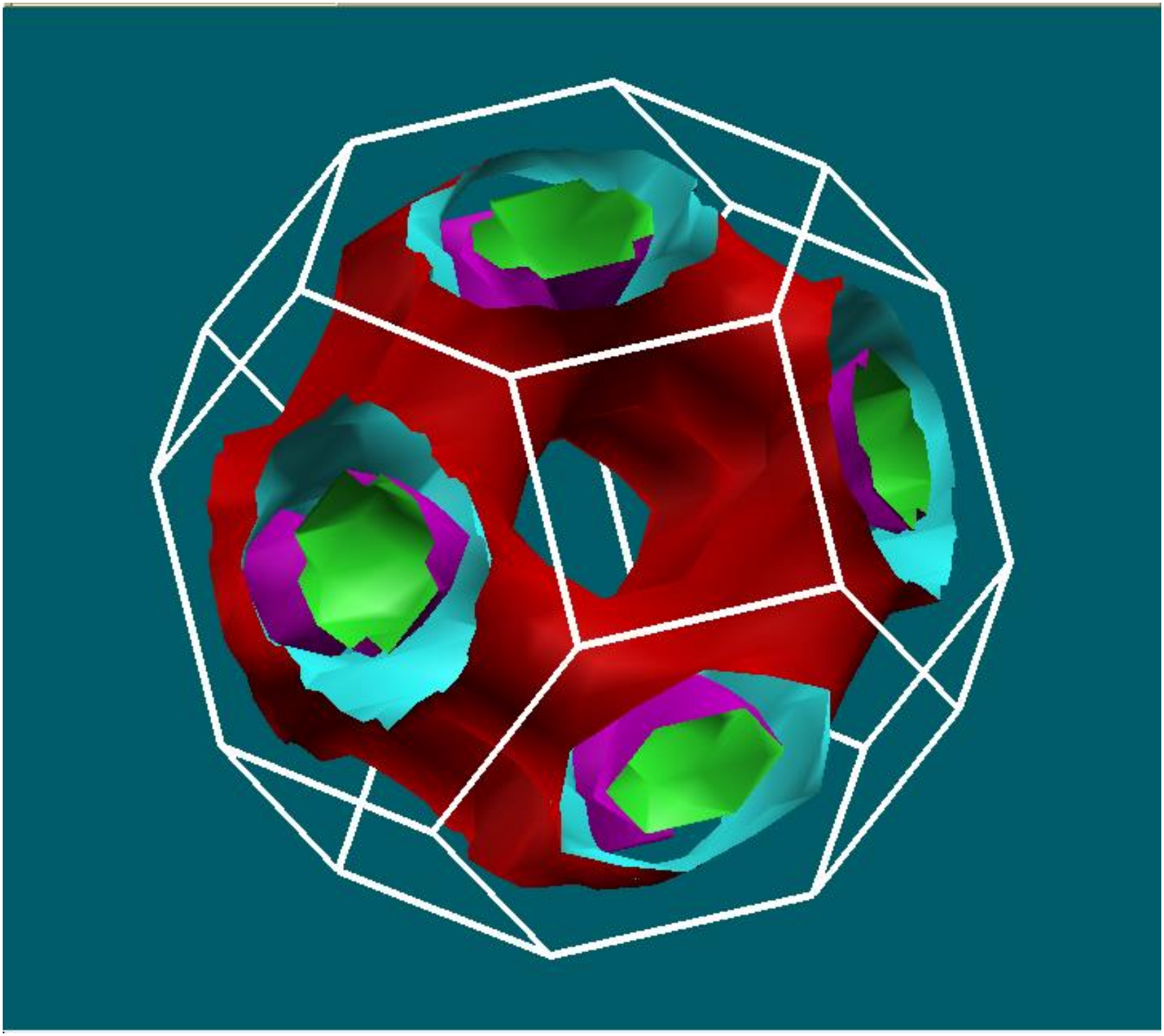






Electron-Phonon Coupling - Superconductivity -

- 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)

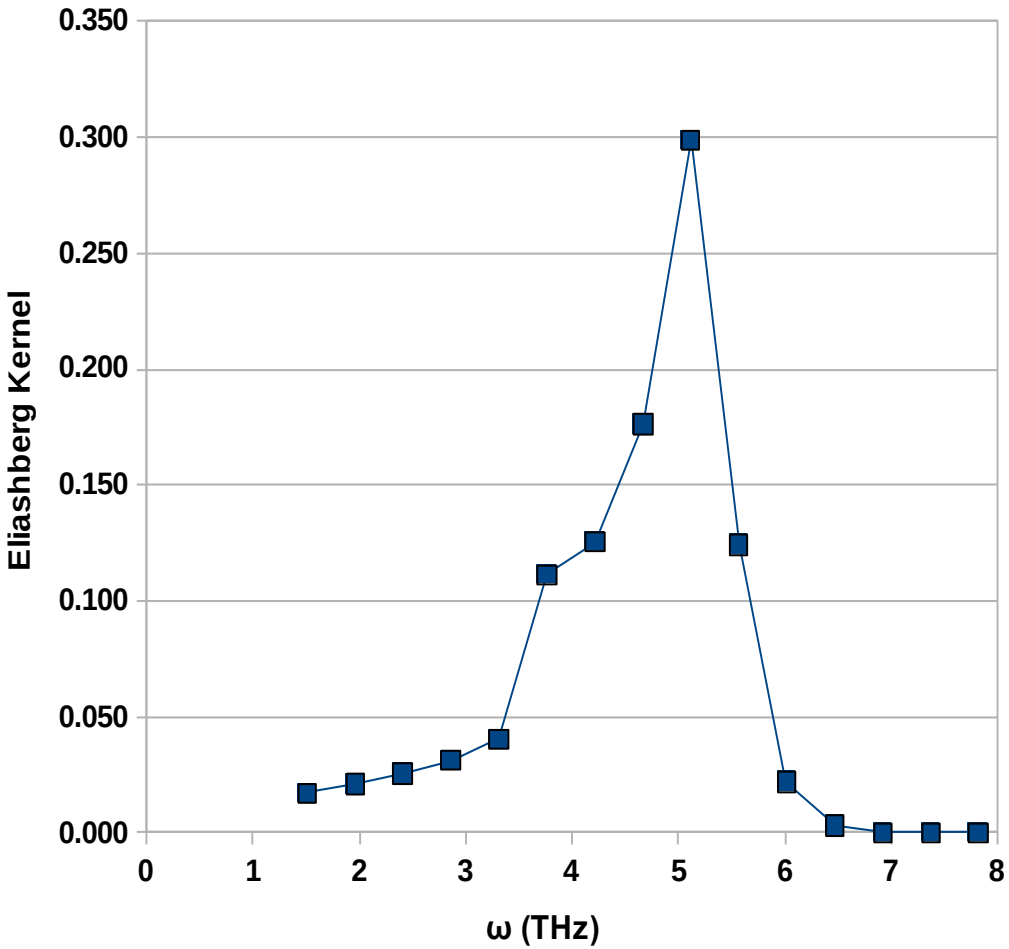
$$H_{el-ph} = \sum_{\mathbf{k}\mathbf{q}\nu} g^{\mathbf{q}\nu,mn}_{\mathbf{k}+\mathbf{q},\mathbf{k}}\, c^{\dagger m}_{\mathbf{k}+\mathbf{q}} c^{n}_{\mathbf{k}}\, (b^{\dagger}_{-\mathbf{q}\nu} + b_{\mathbf{q}\nu}) \qquad (1)$$

$$\begin{aligned} \alpha^2 F(\omega) &= \frac{1}{N(\varepsilon_F)} \sum_{mn} \sum_{\mathbf{q}\nu} \delta(\omega - \omega_{\mathbf{q}\nu}) \sum_{\mathbf{k}} |g^{\mathbf{q}\nu,mn}_{\mathbf{k}+\mathbf{q},\mathbf{k}}|^2 \\ &\quad \times \delta(\varepsilon_{\mathbf{k}+\mathbf{q},m} - \varepsilon_F)\delta(\varepsilon_{\mathbf{k},n} - \varepsilon_F), \qquad (2) \\ \lambda &= 2\int \frac{\alpha^2 F(\omega)}{\omega} d\omega = \sum_{\mathbf{q}\nu} \lambda_{\mathbf{q}\nu}, \qquad (3) \\ \lambda_{\mathbf{q}\nu} &= \frac{2}{N(\varepsilon_F)\omega_{\mathbf{q}\nu}} \sum_{mn} \sum_{\mathbf{k}} |g^{\mathbf{q}\nu,mn}_{\mathbf{k}+\mathbf{q},\mathbf{k}}|^2 \\ &\quad \times \delta(\varepsilon_{\mathbf{k}+\mathbf{q},m} - \varepsilon_F)\delta(\varepsilon_{\mathbf{k},n} - \varepsilon_F). \qquad (4) \end{aligned}$$

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…

$$T_c \propto \frac{1}{\lambda k_B \Theta_D E_F}$$

	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	-

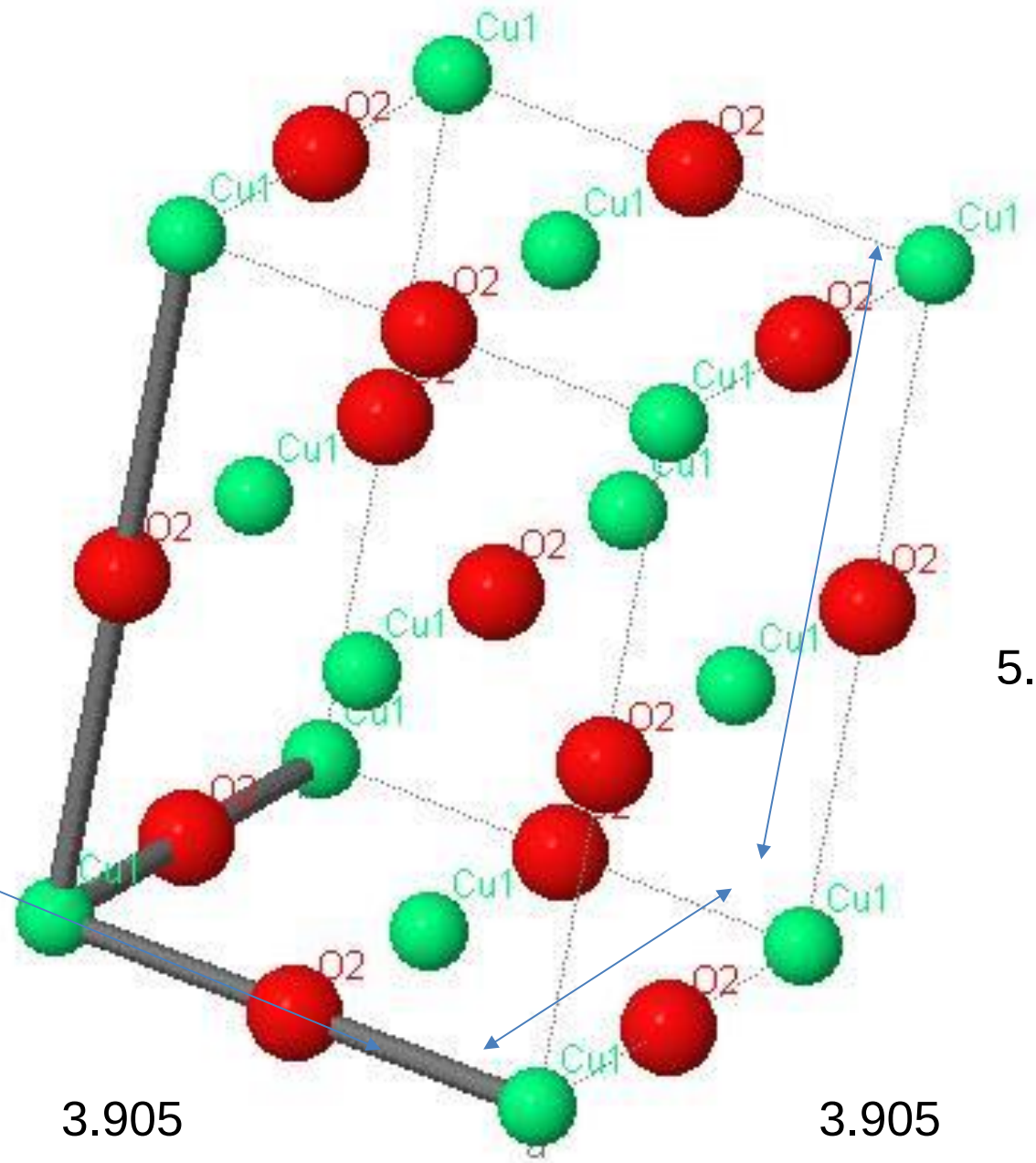
Tetragonal CuO

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)

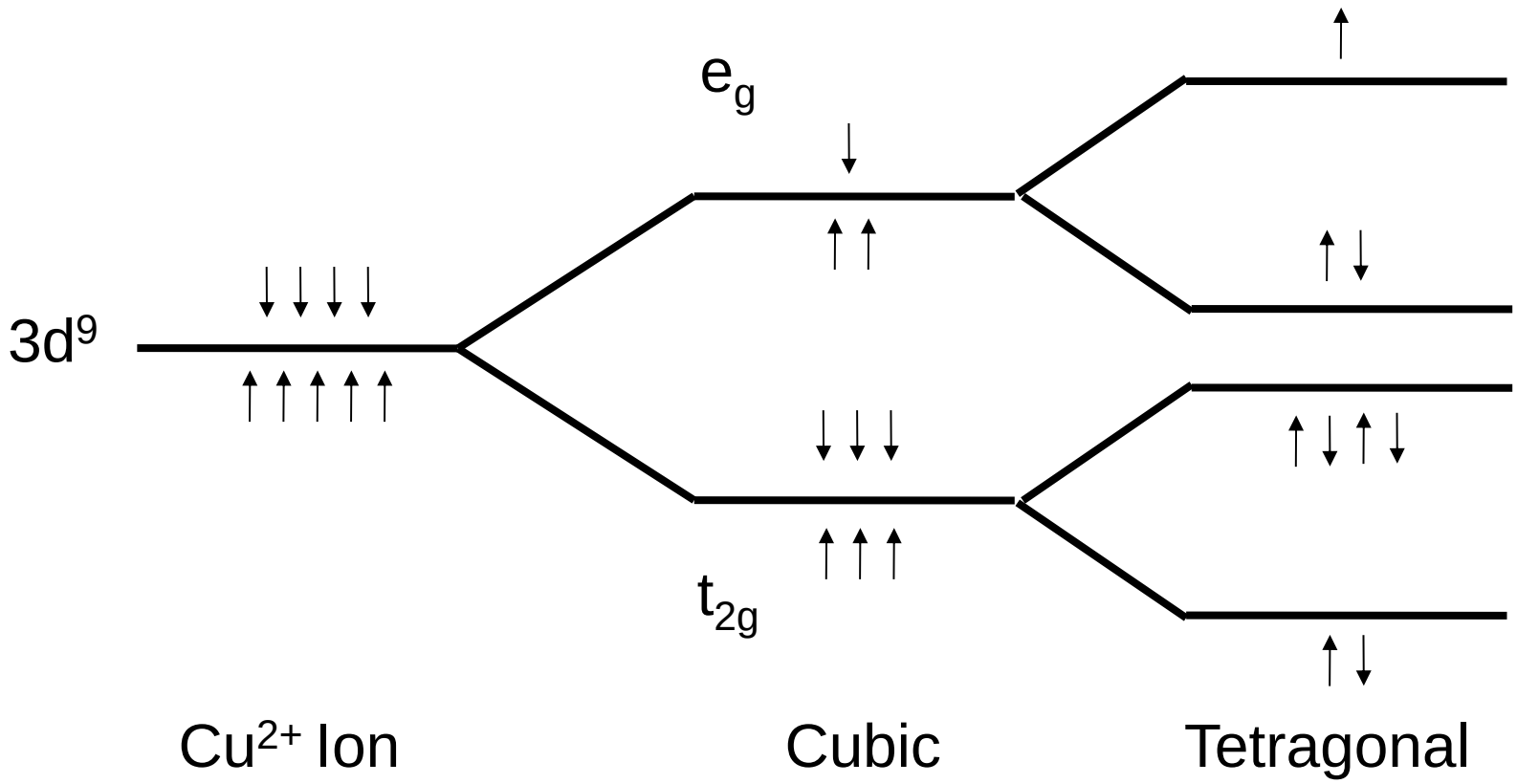


5.320

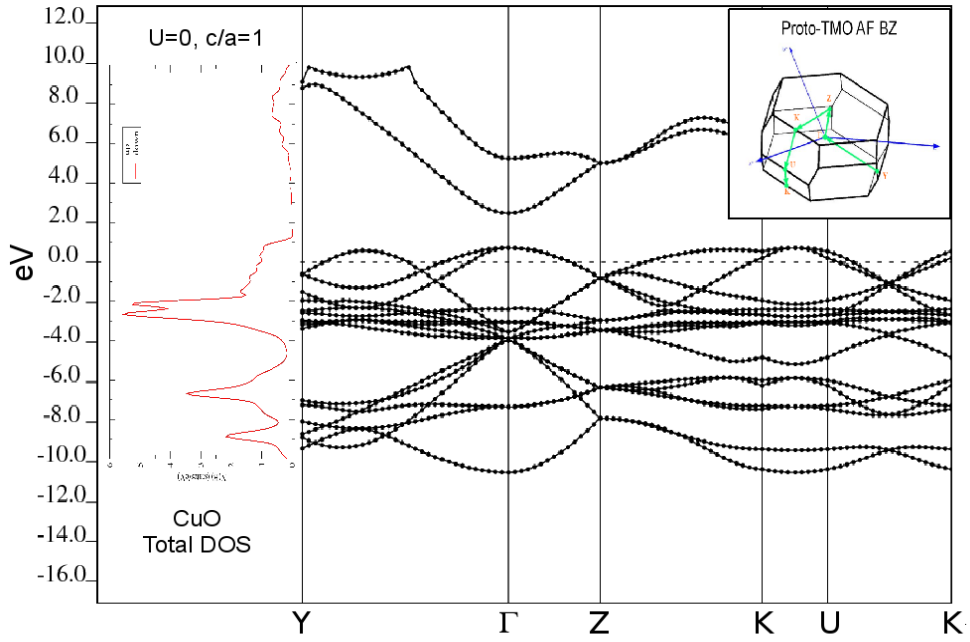
3.905

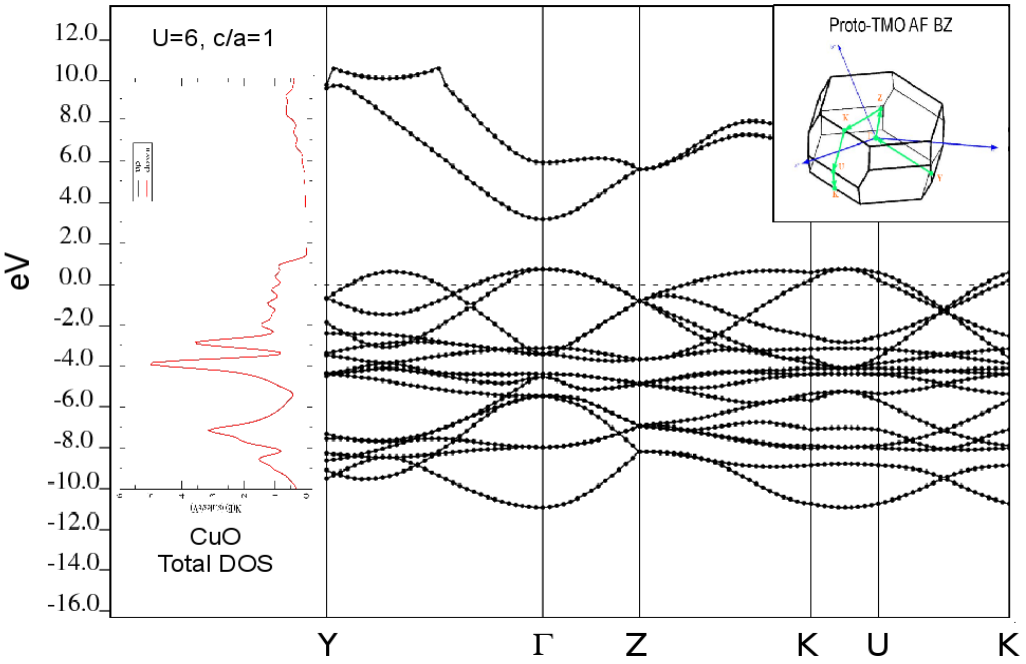
3.905

Cu2+ 3d Multiplet Splitting (Tetra)

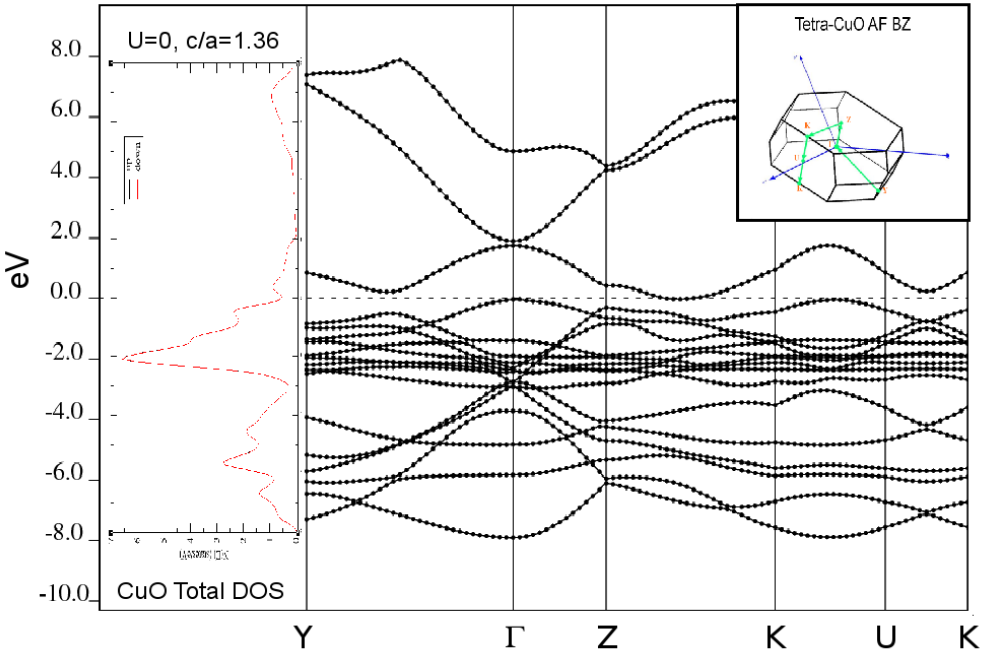


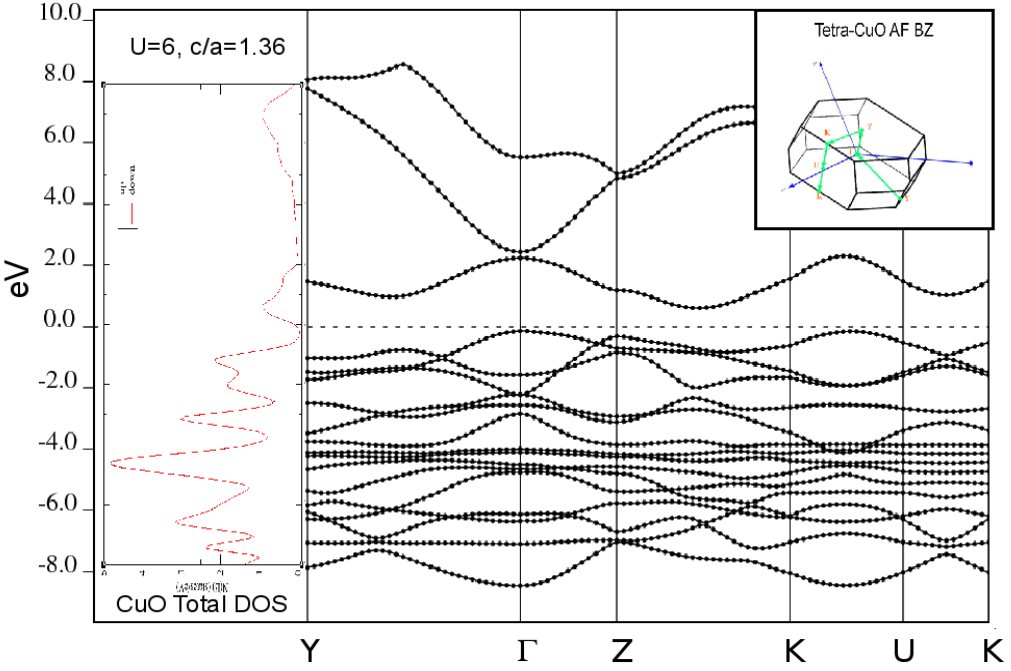
Cubic



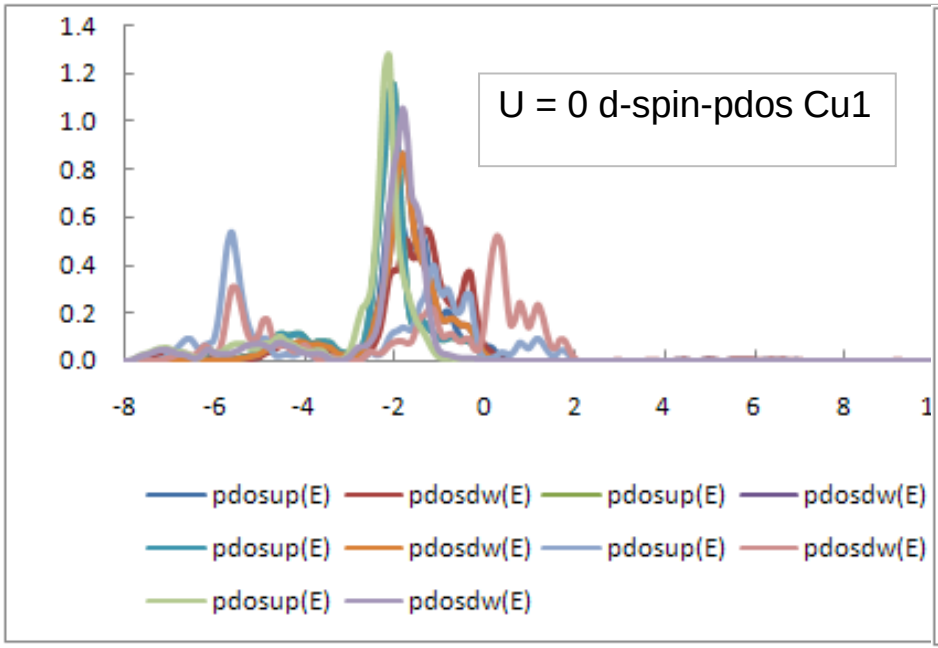


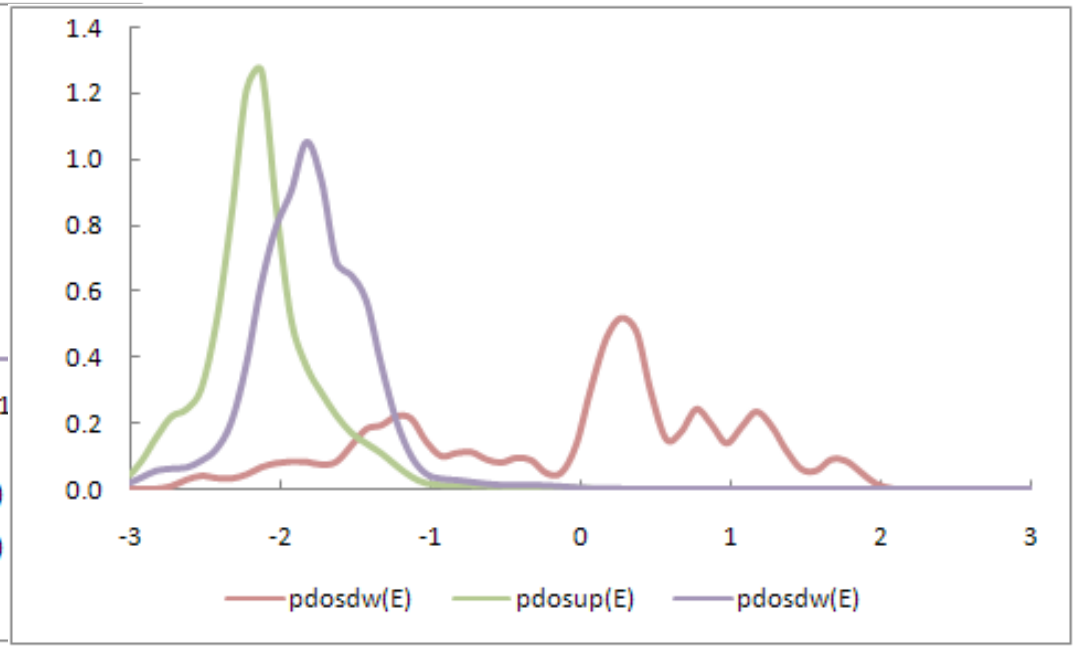
Tetragonal

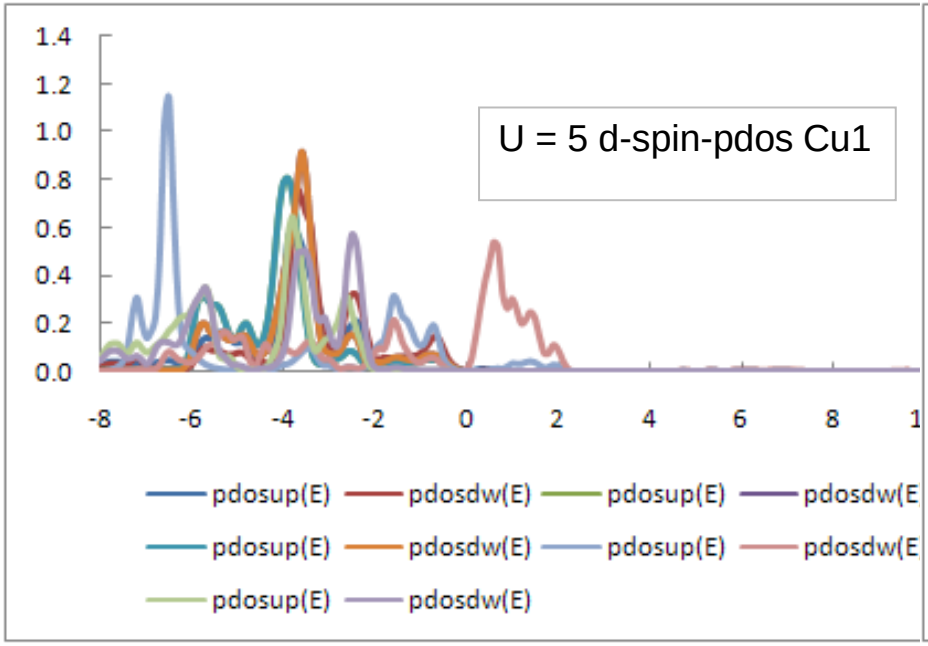


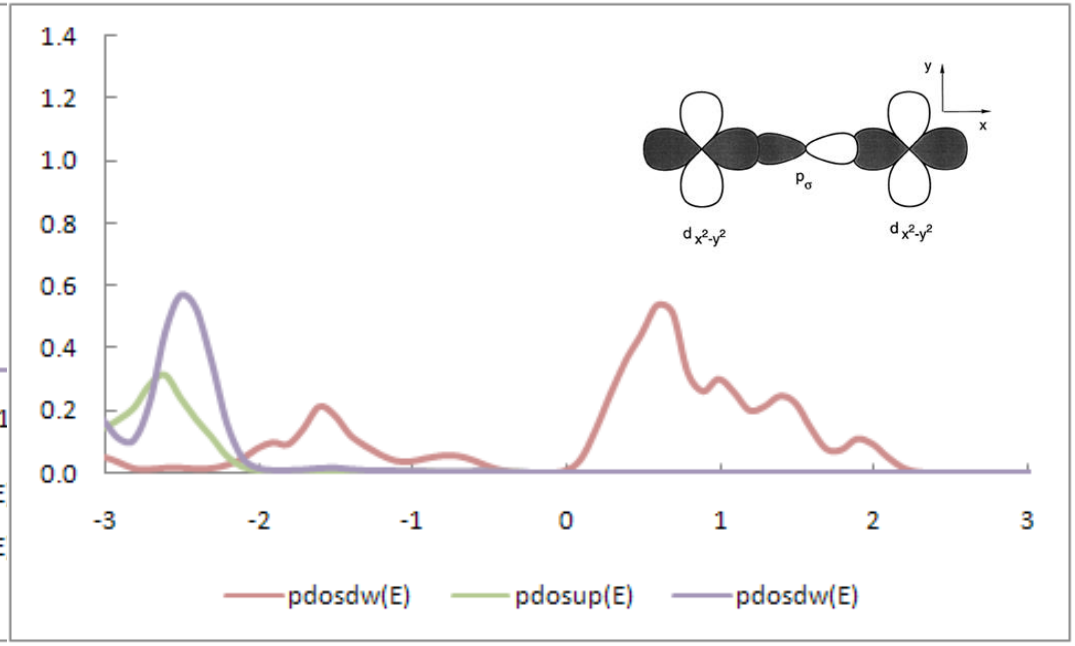


Spin Composition of Cu 3d pDOS as fn(Hubbard)

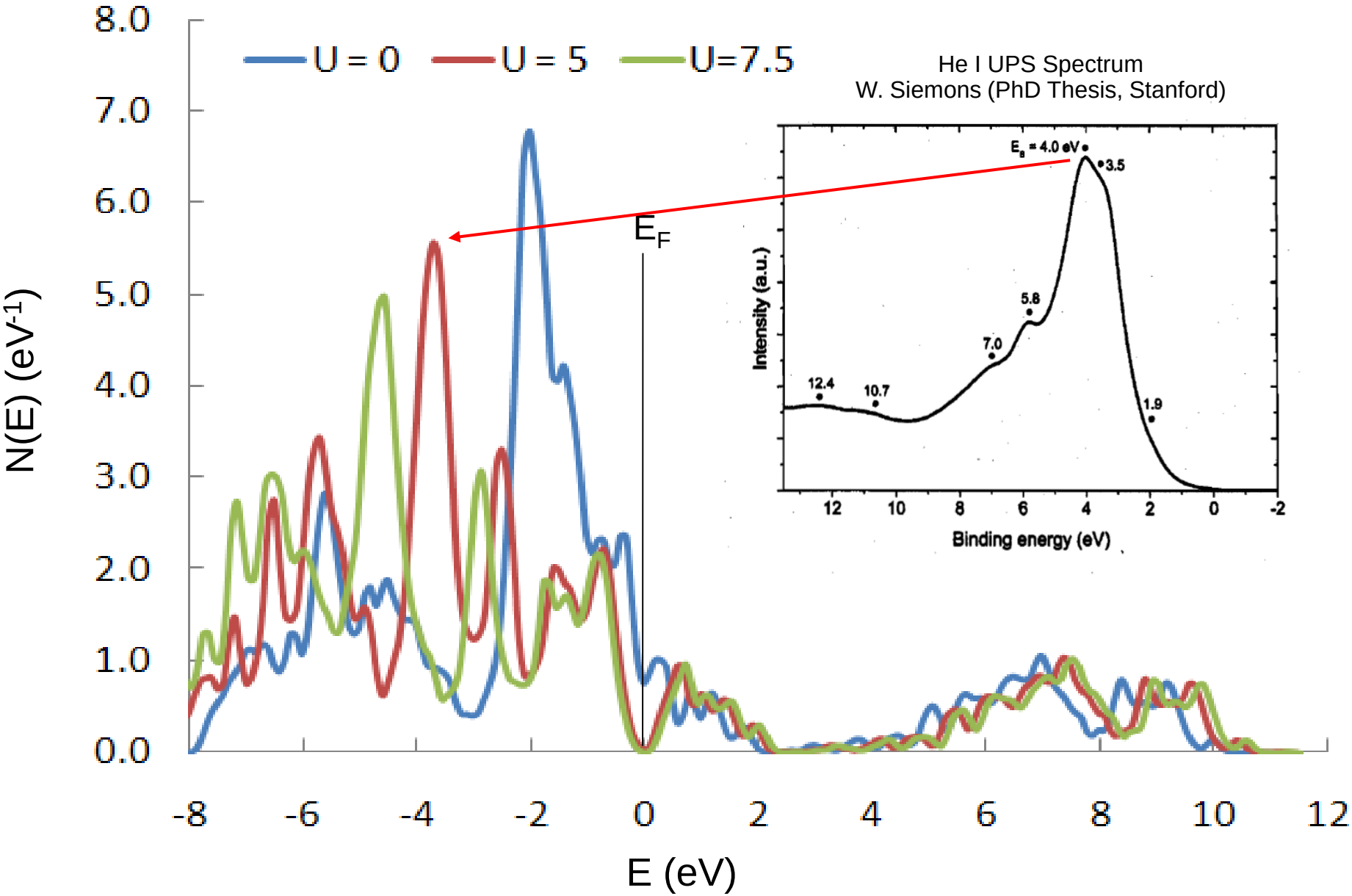








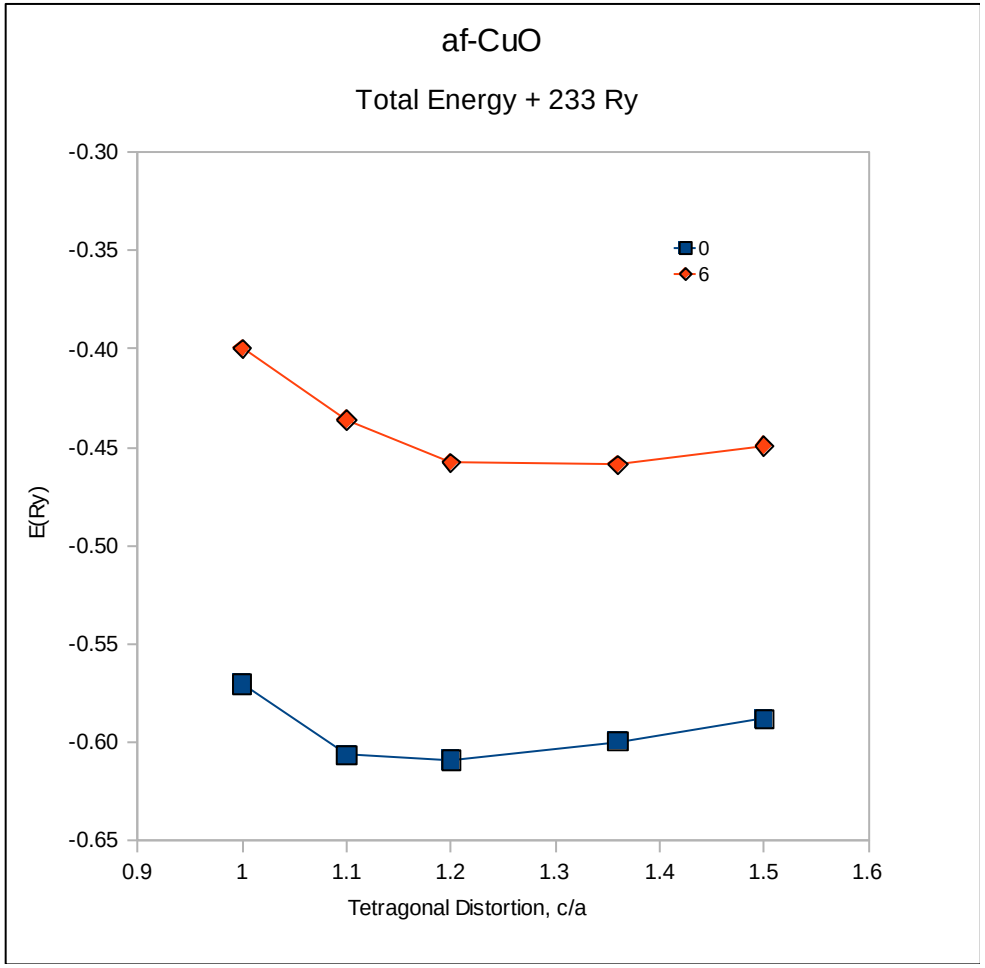
t-CuO Density-of-States



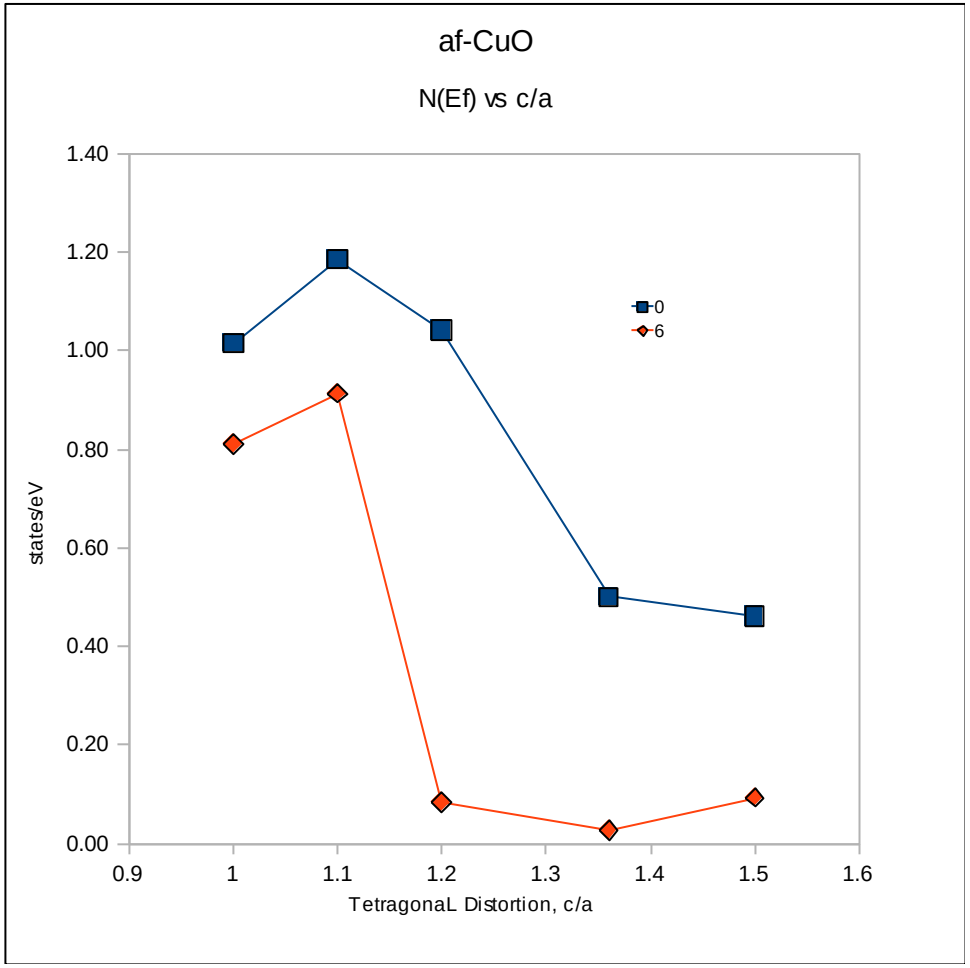
Cubic & Tetragonal CuO

Ground State Properties

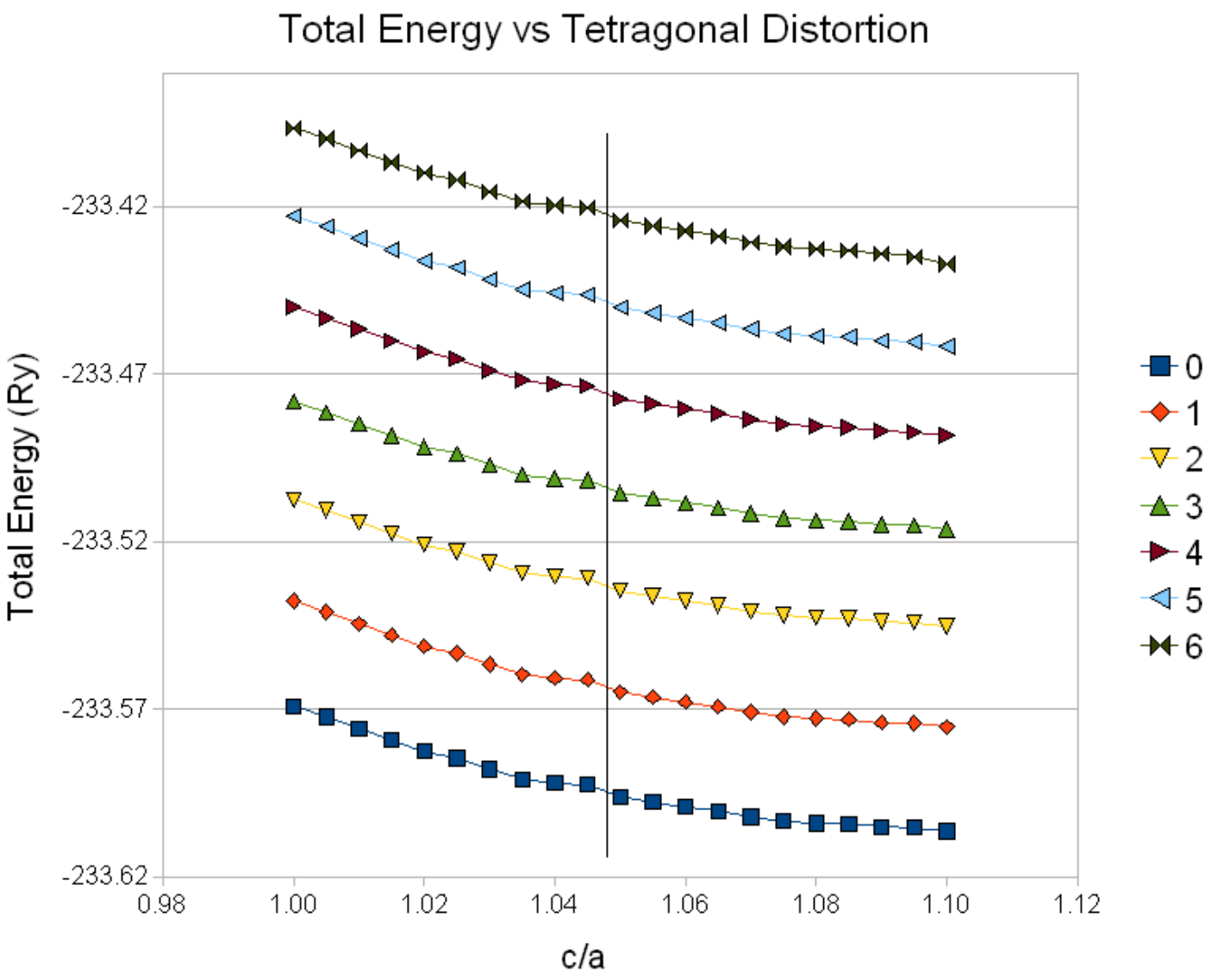
Total GS Energy



DOS at Fermi Energy



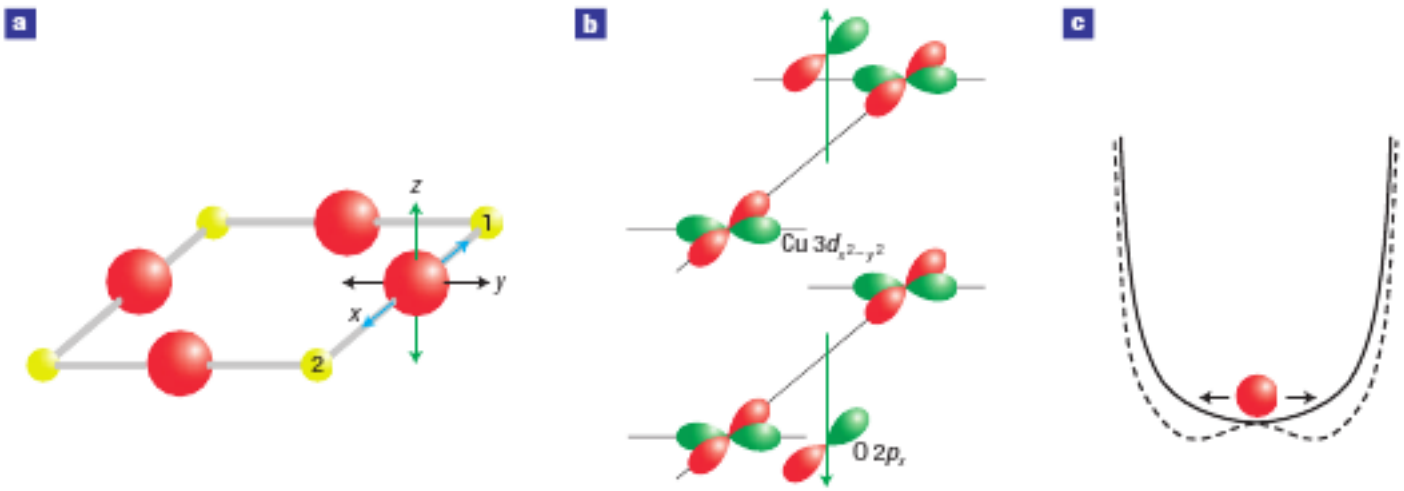
Total Energy vs. c/a



Anharmonic Phonon-Driven HTSC?

"Fluctuating Cu-O-Cu bond model of high-temperature superconductivity,"

D. M. Newns and C. C. Tsuei, Nature Physics 3, 184 (2007)



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).

Спαсибо, Дъна !

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