Nature, 18 June 2008

http://www.w2agz.com

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
Principal, W2AGZ Technologies
http://www.w2agz.com

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 Kokal, Ljubljana

...*e tutto di consorzio “Quantum Espresso,” ICTP*

22 Years Ago...

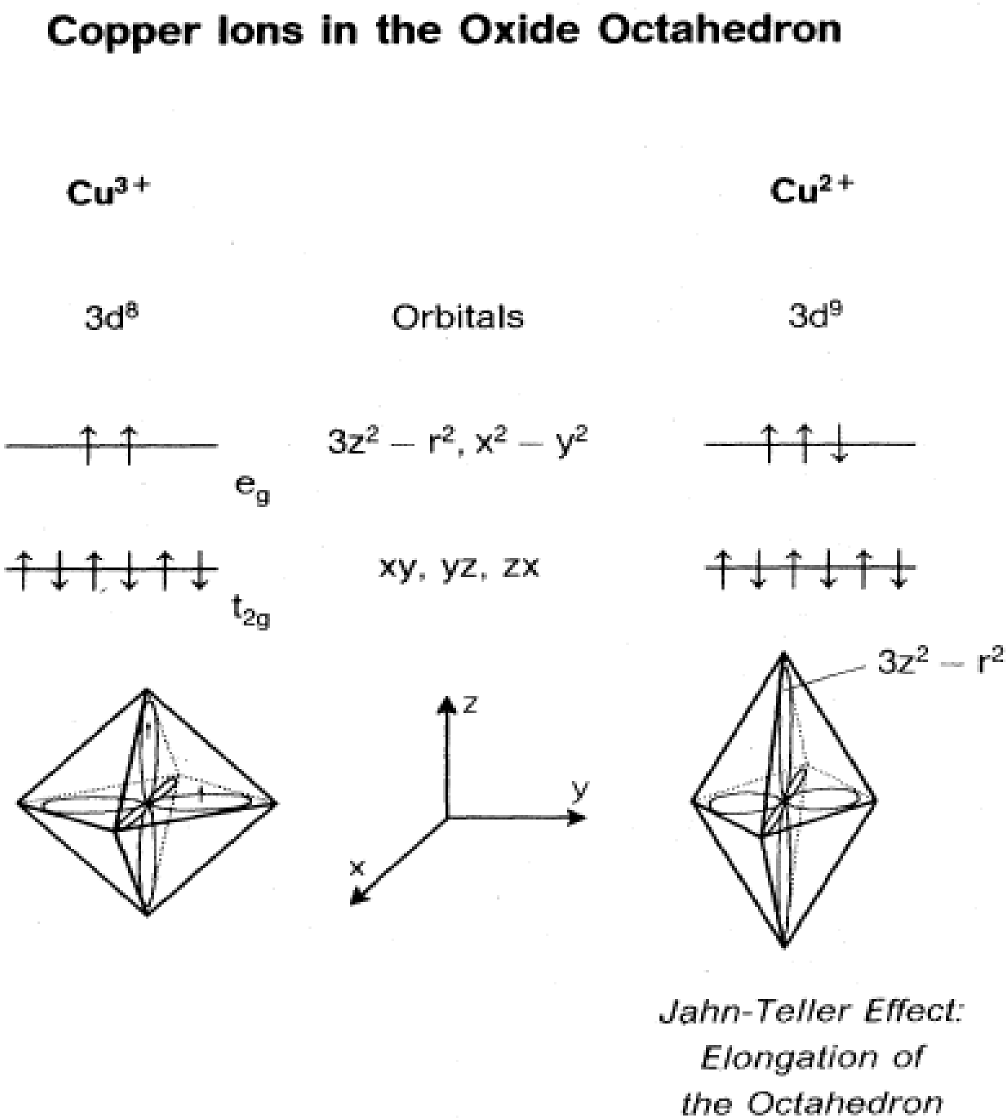
Possible High T_c Superconductivity in the Ba – La – Cu – O System

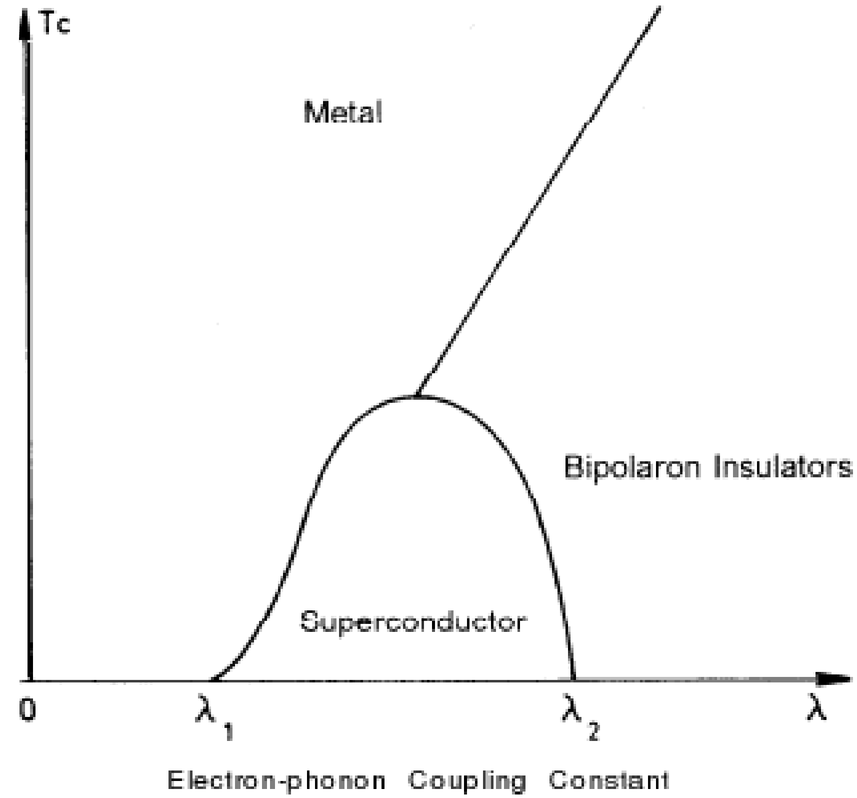
J.G. Bednorz and K.A. Müller
IBM Zürich Research Laboratory, Rüschlikon, Switzerland

Received April 17, 1986

...Still No Theory!

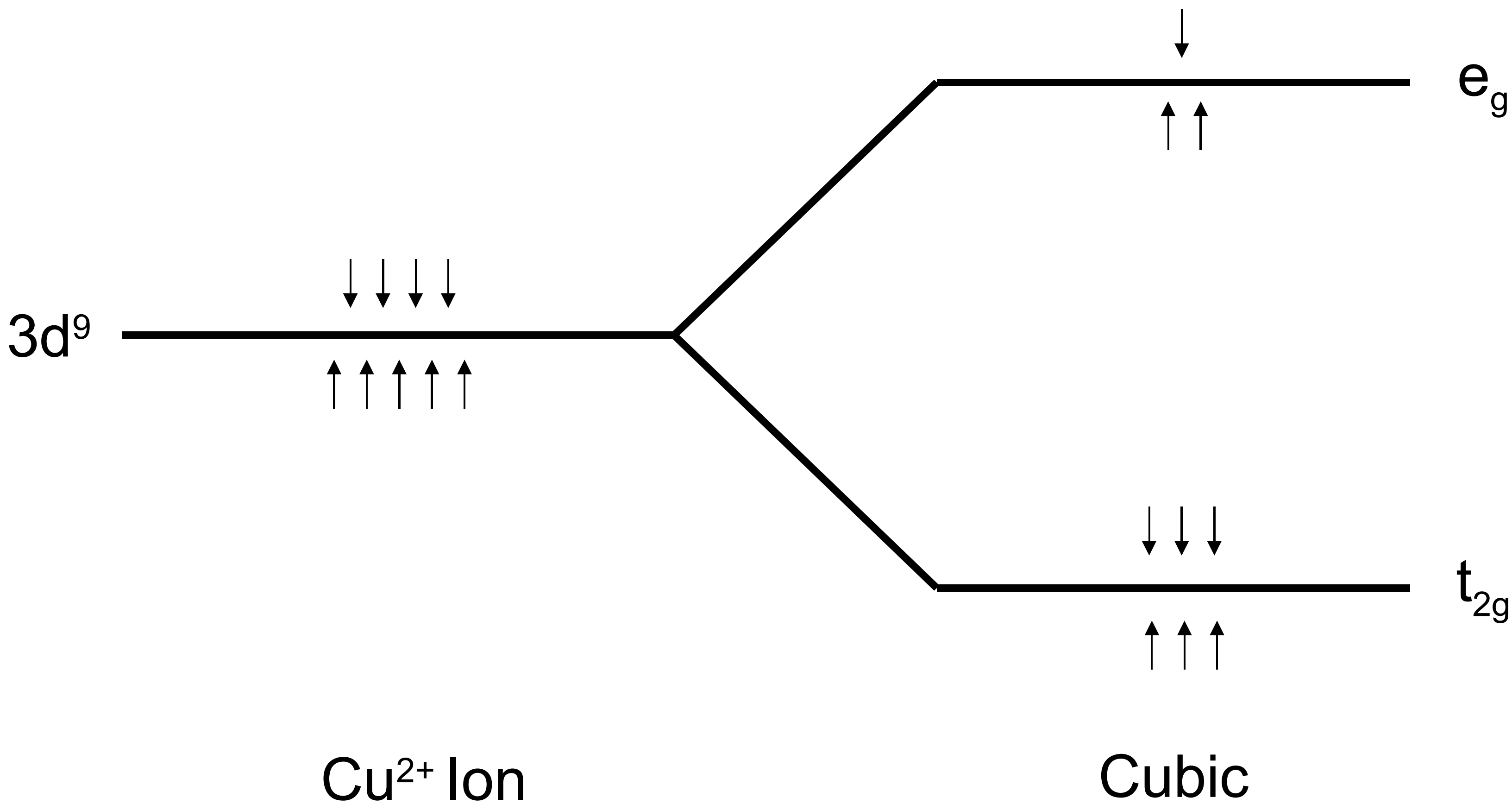
Bednorz-Mueller Nobel Lecture





After Chakravarty, (1979)

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



Hubbard Theory

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

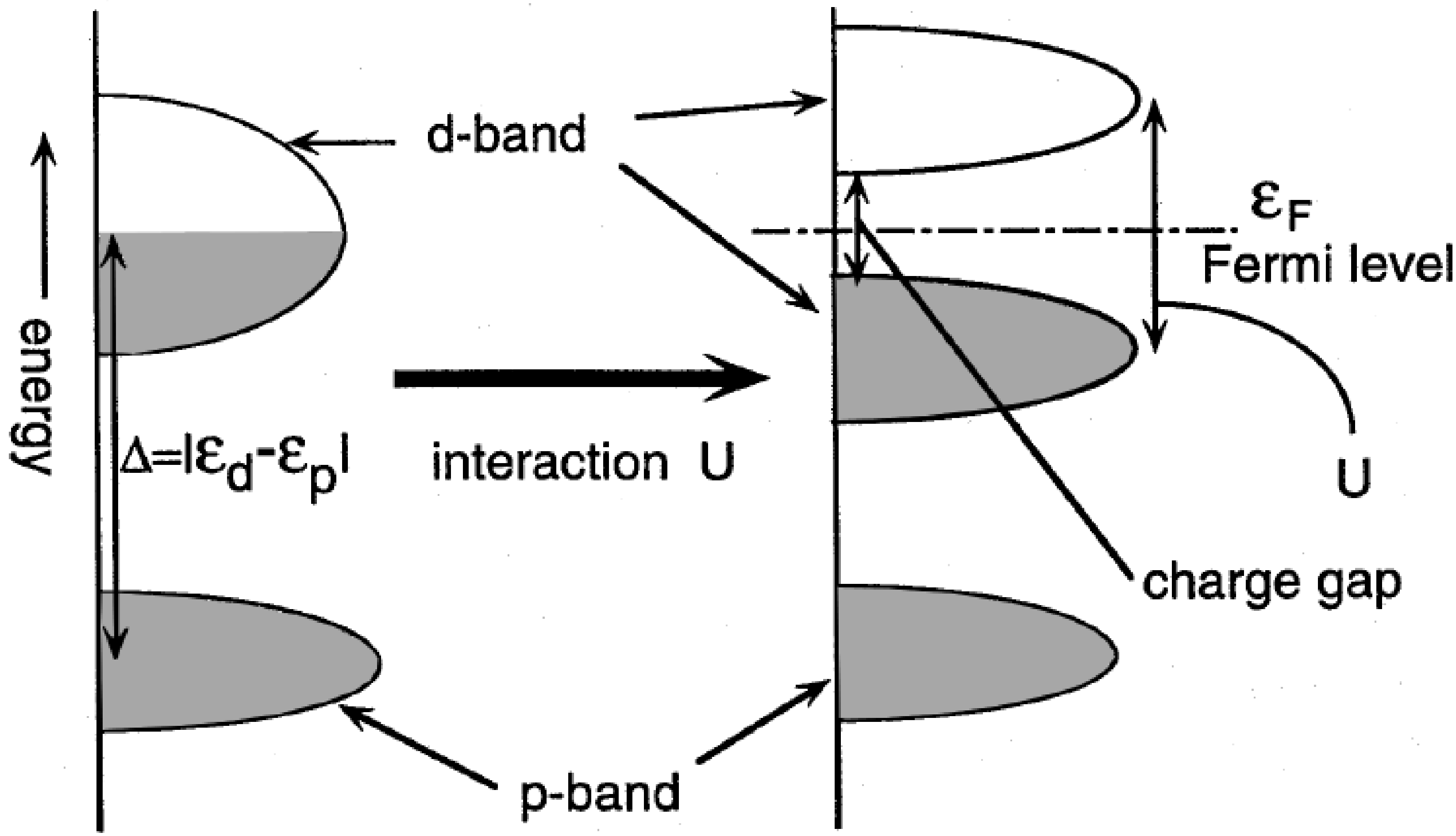
One-electron "band" term

On-site "Hubbard" double occupation coulomb repulsion

Off-site repulsion

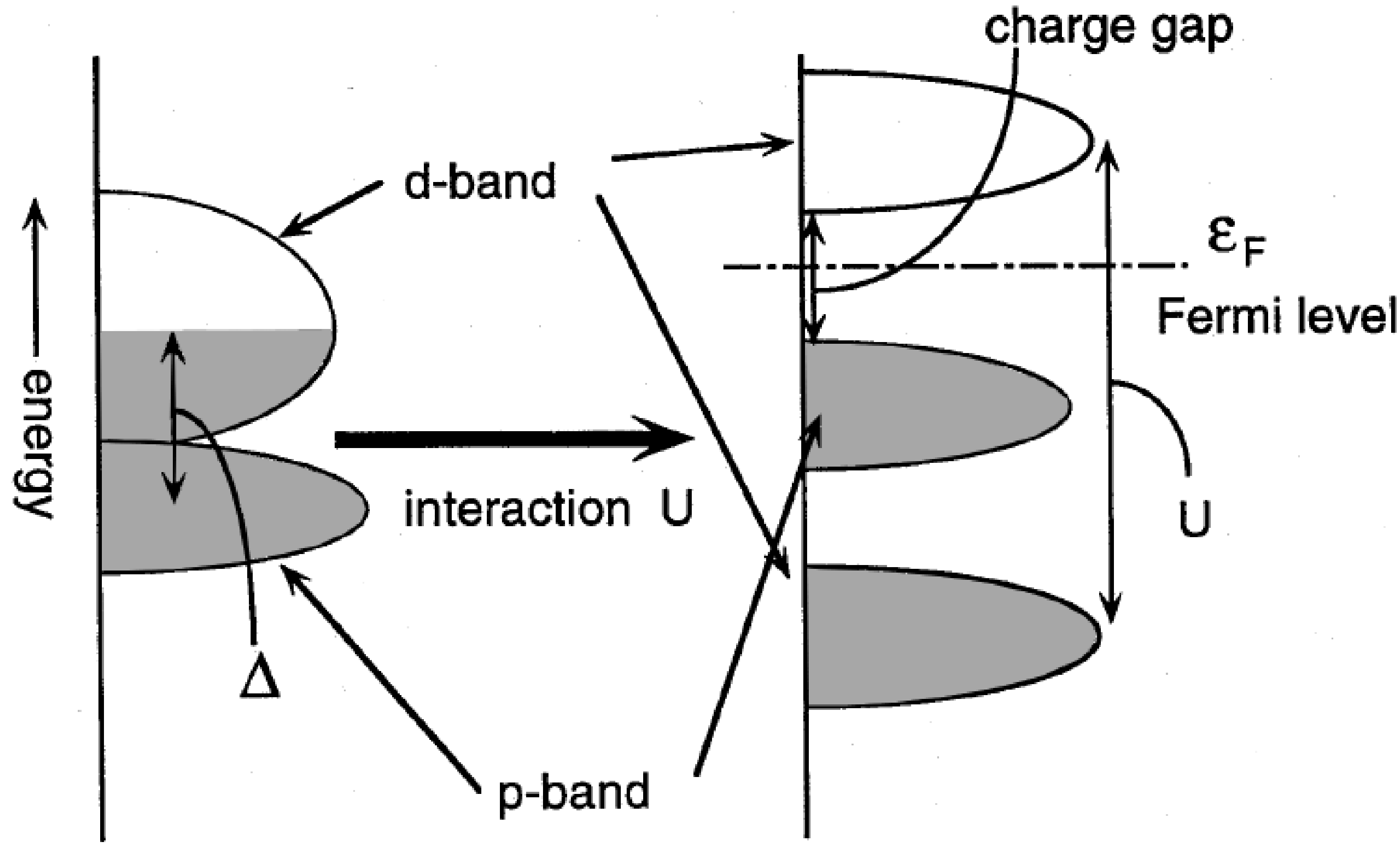
$$kT_N \sim 4t^2 / S^2 U$$

Mott-Hubbard Insulator



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

Charge Transfer Insulator



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

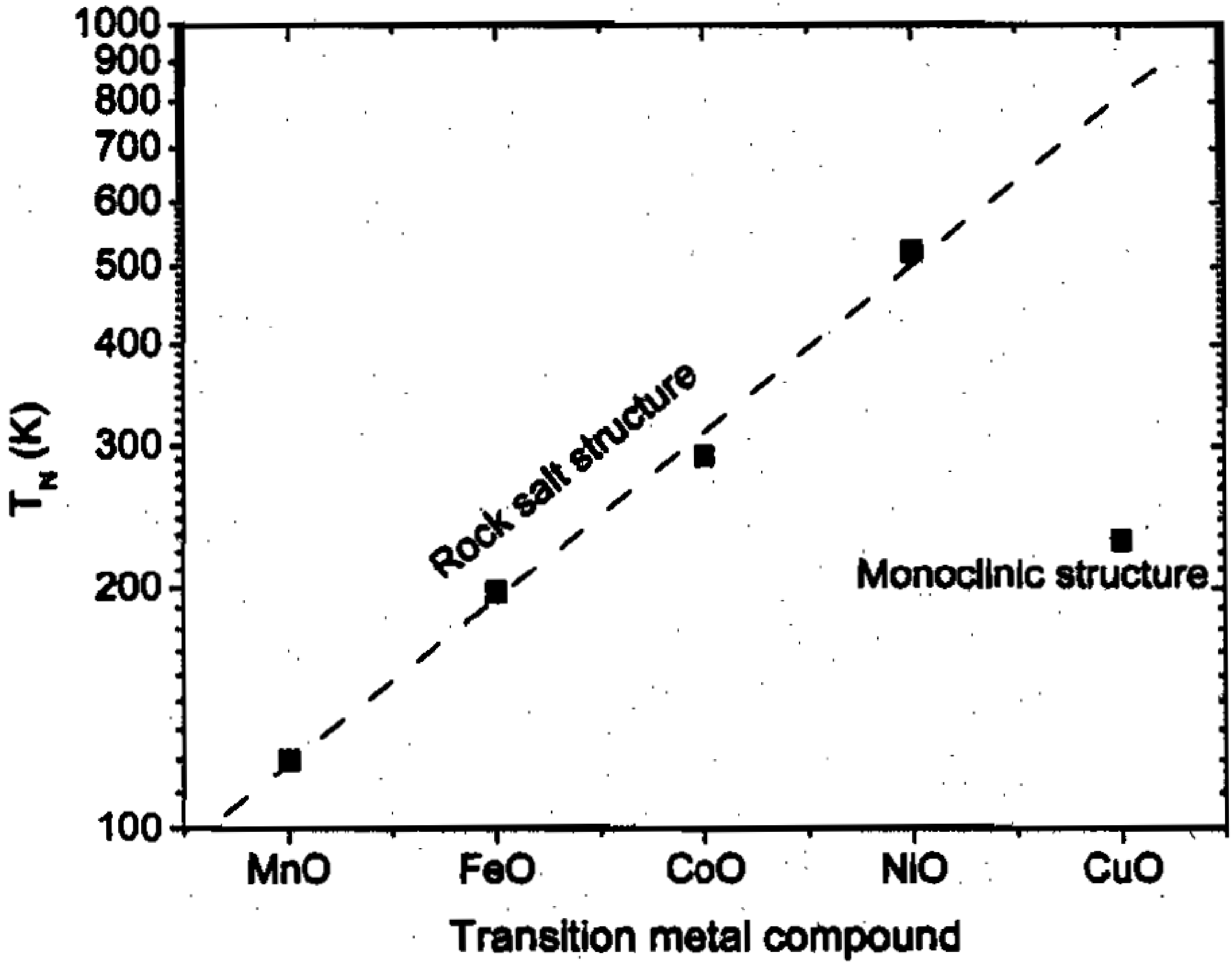
Cubic Rocksalt Divalent TMOs

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	

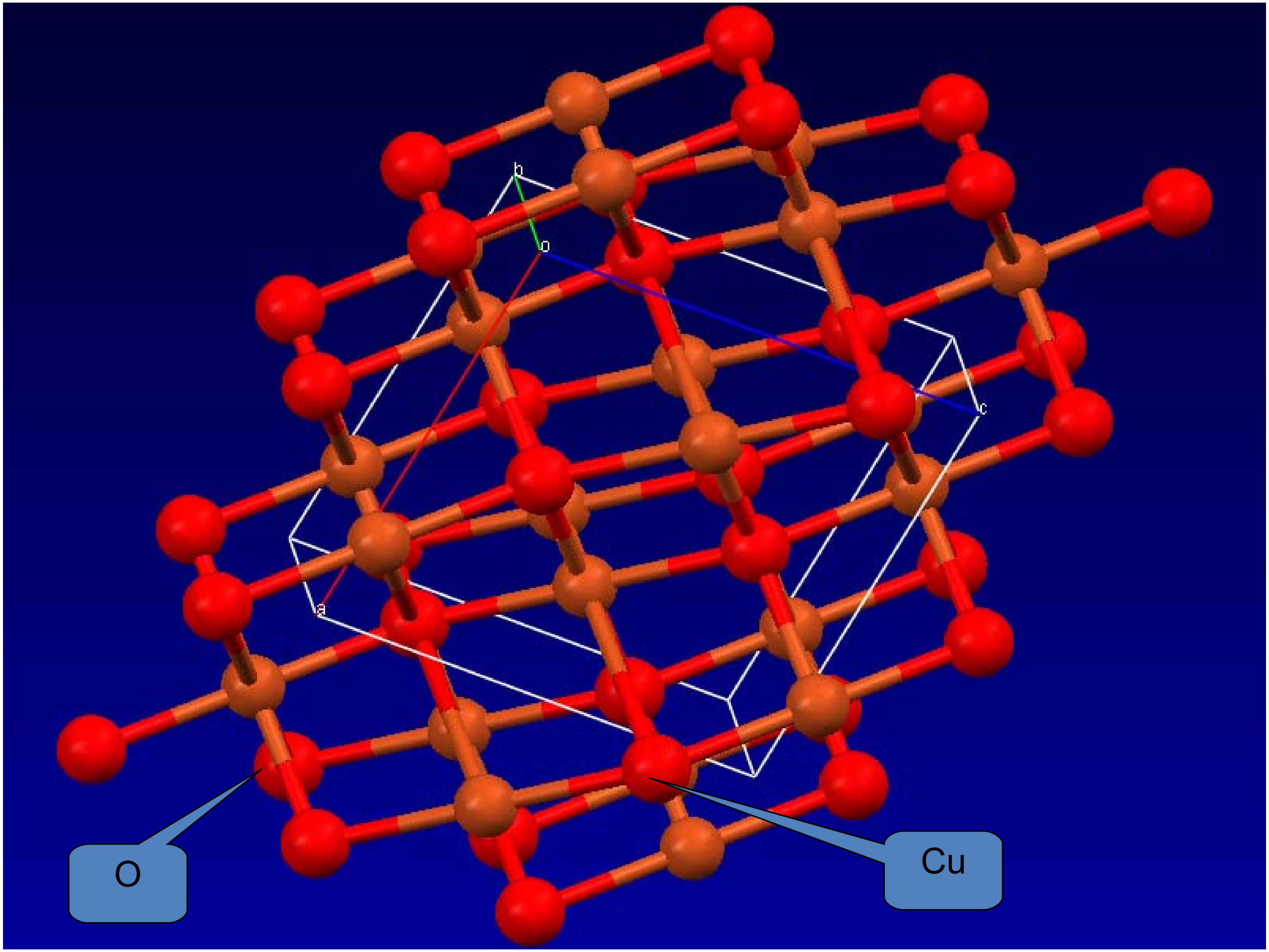
XX *Doesn't Exist!*

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

Néel Temperature vs. TMO Atomic Number



Tenorite (Monoclinic CuO)

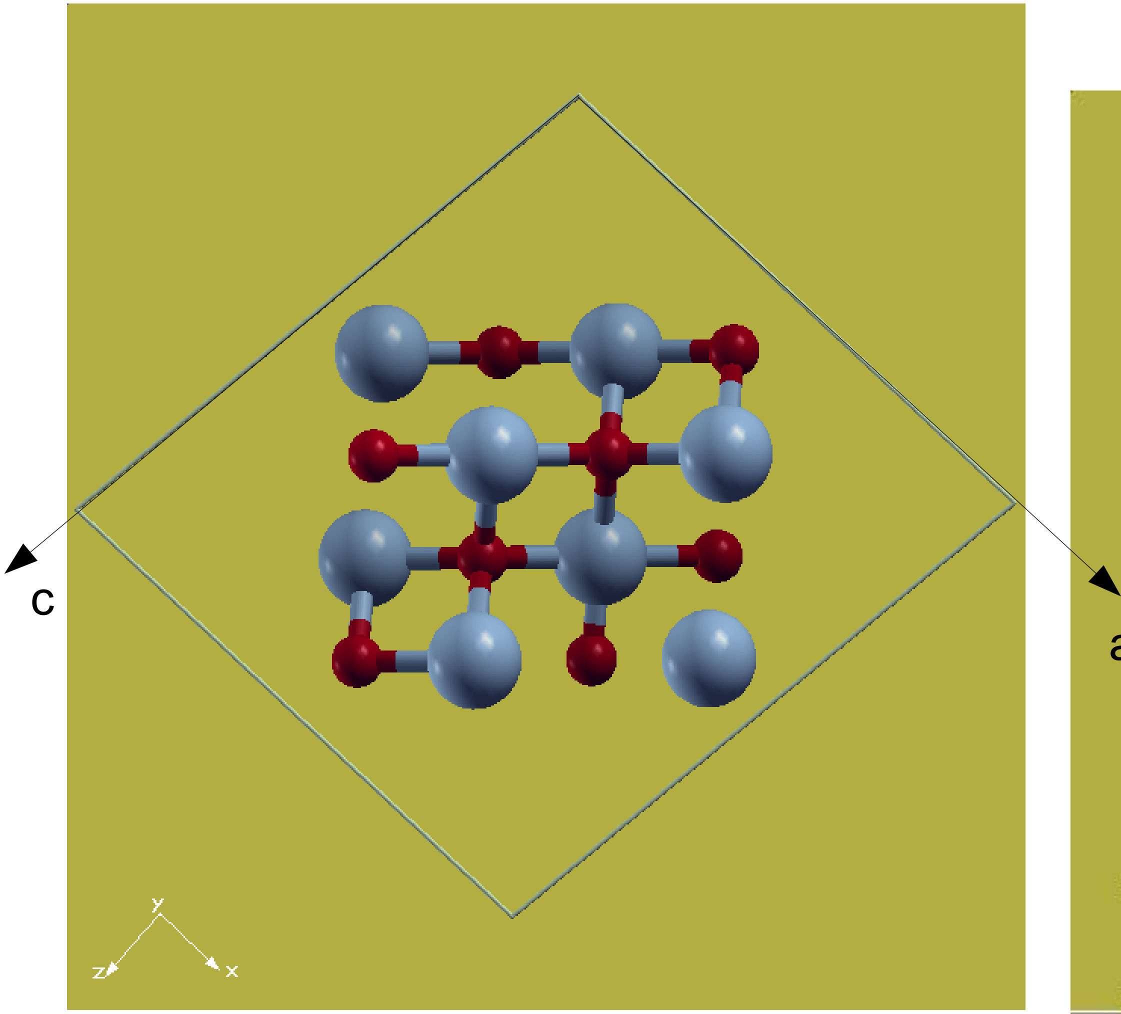


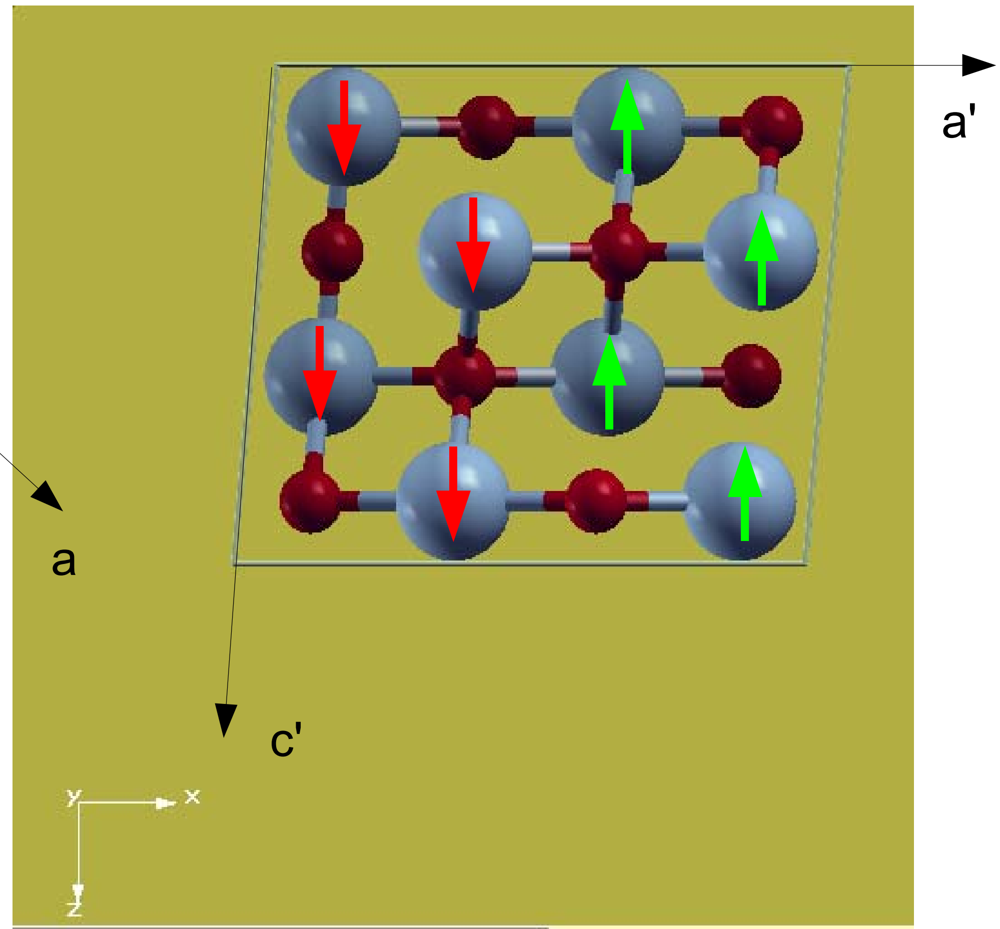
DFT & (LDA + U)

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

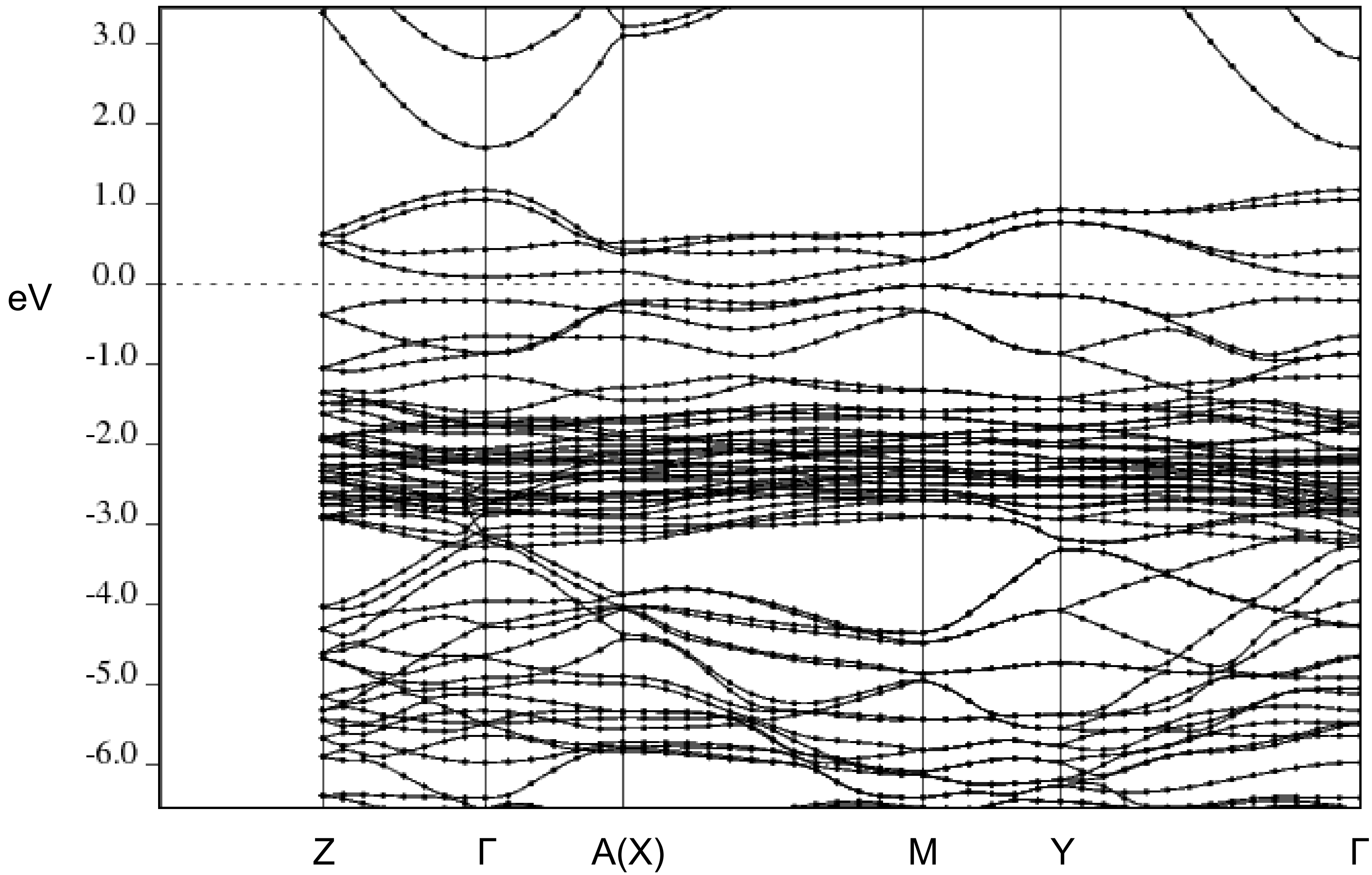
- Implemented in LMTO by Anisimov, et al, JPCM 2, 3973 (1990)
  - Applied to NiO, MnO, FeO, CoO and La_2CuO_4
- Plane-Wave Pseudopotential Implementation by Cococcioni and de Gironcoli, PRB 71, 035105 (2005)
  - Applied to FeO and NiO
  - Download open-source package from http://www.pwscf.org

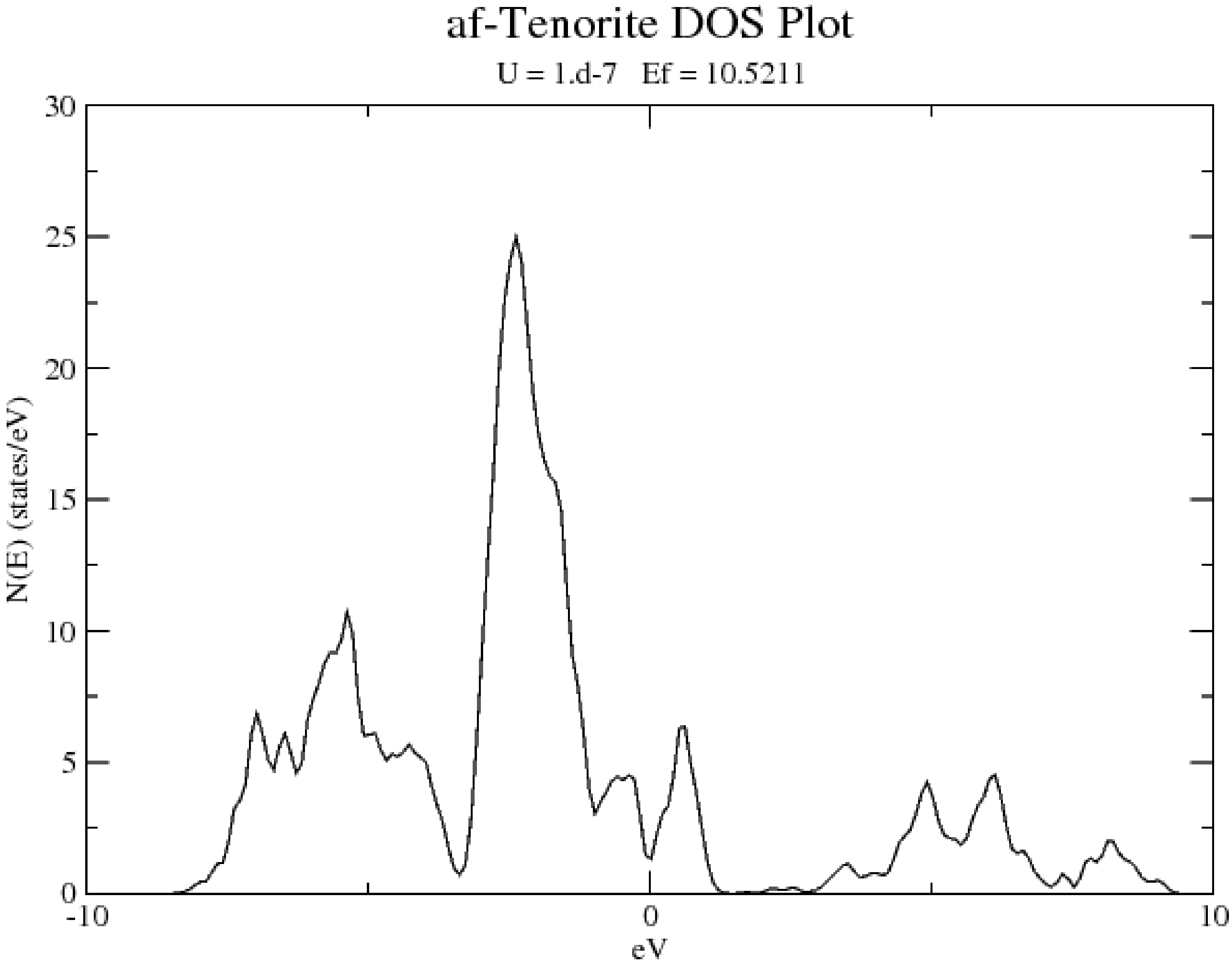
nm & af Unit Cells





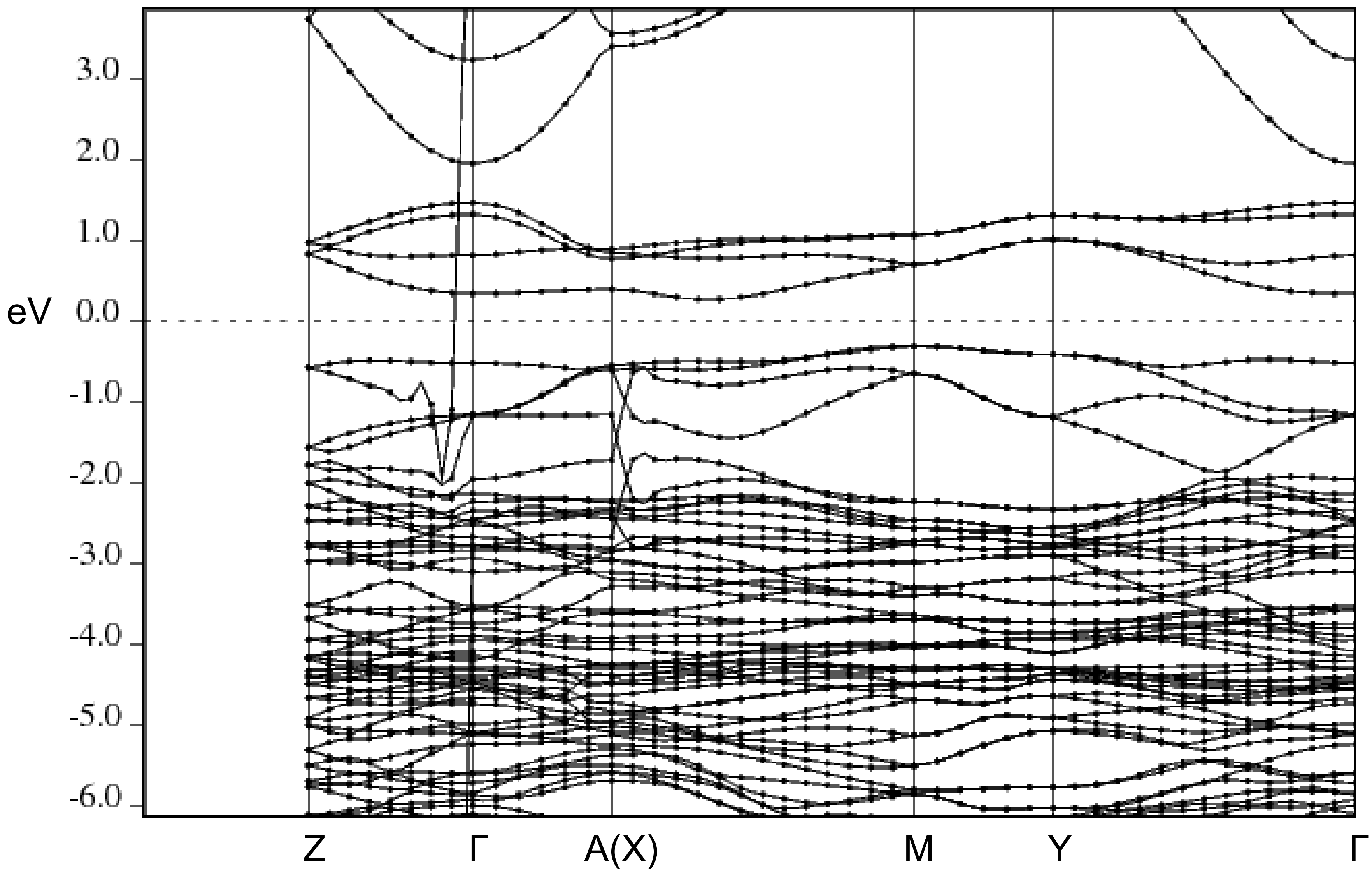
af_0_pmg (U = 0)

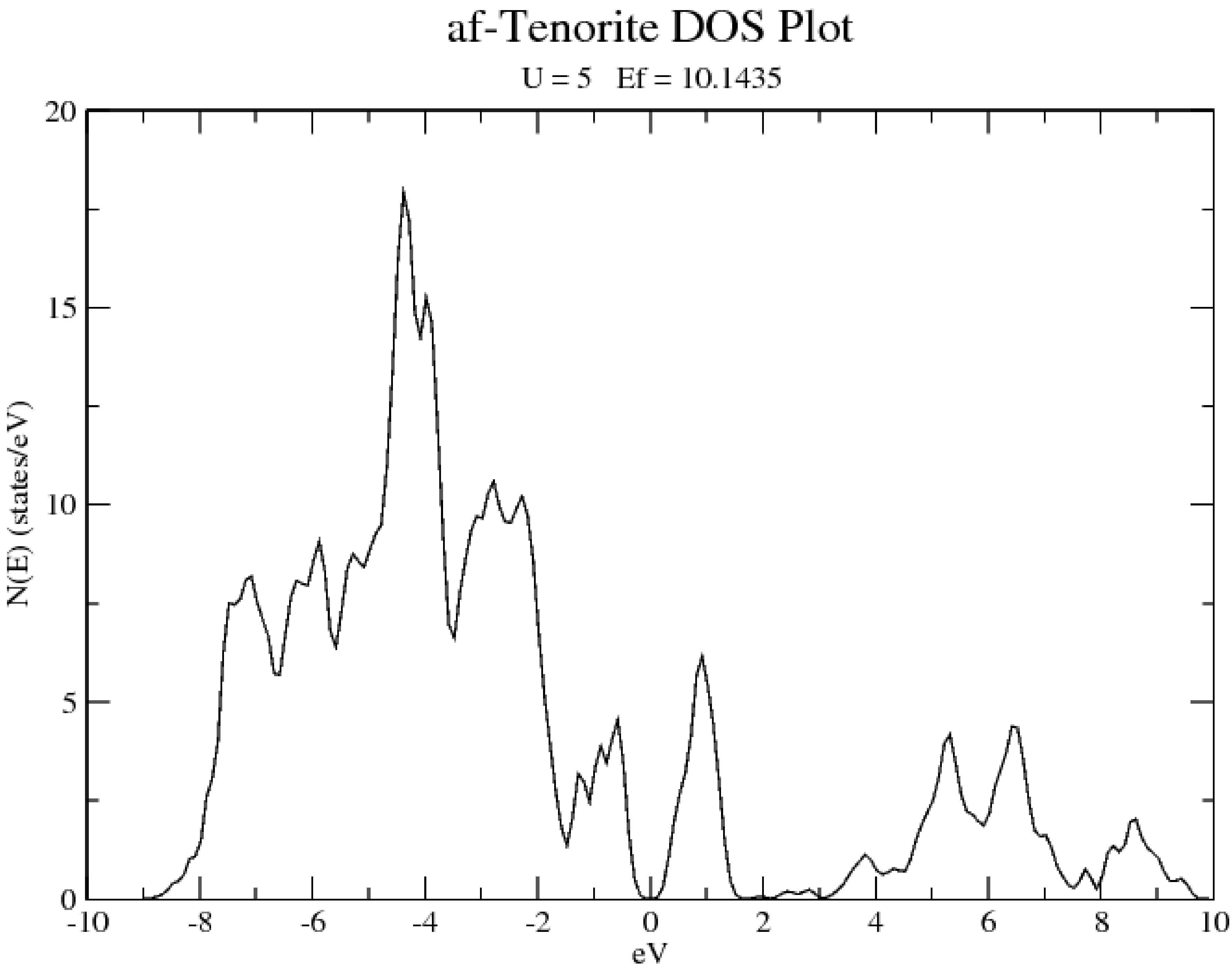




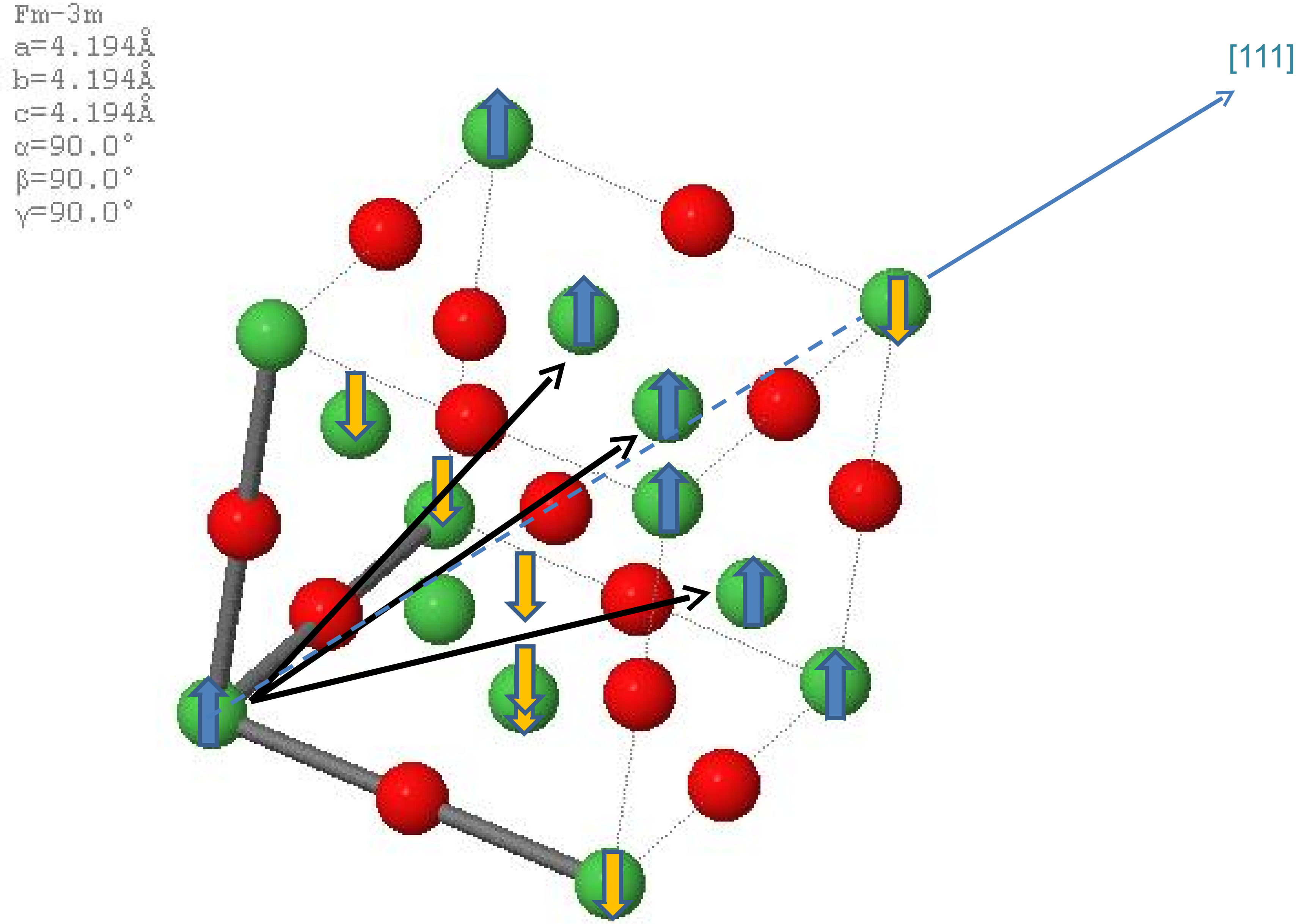
af-Tenorite DOS Plot
U = 1.d-7 Ef = 10.5211
N(E) (states/eV)
eV
0
5
10
15
20
25
30
-10
0
10

af_5_pmg (U = 5)

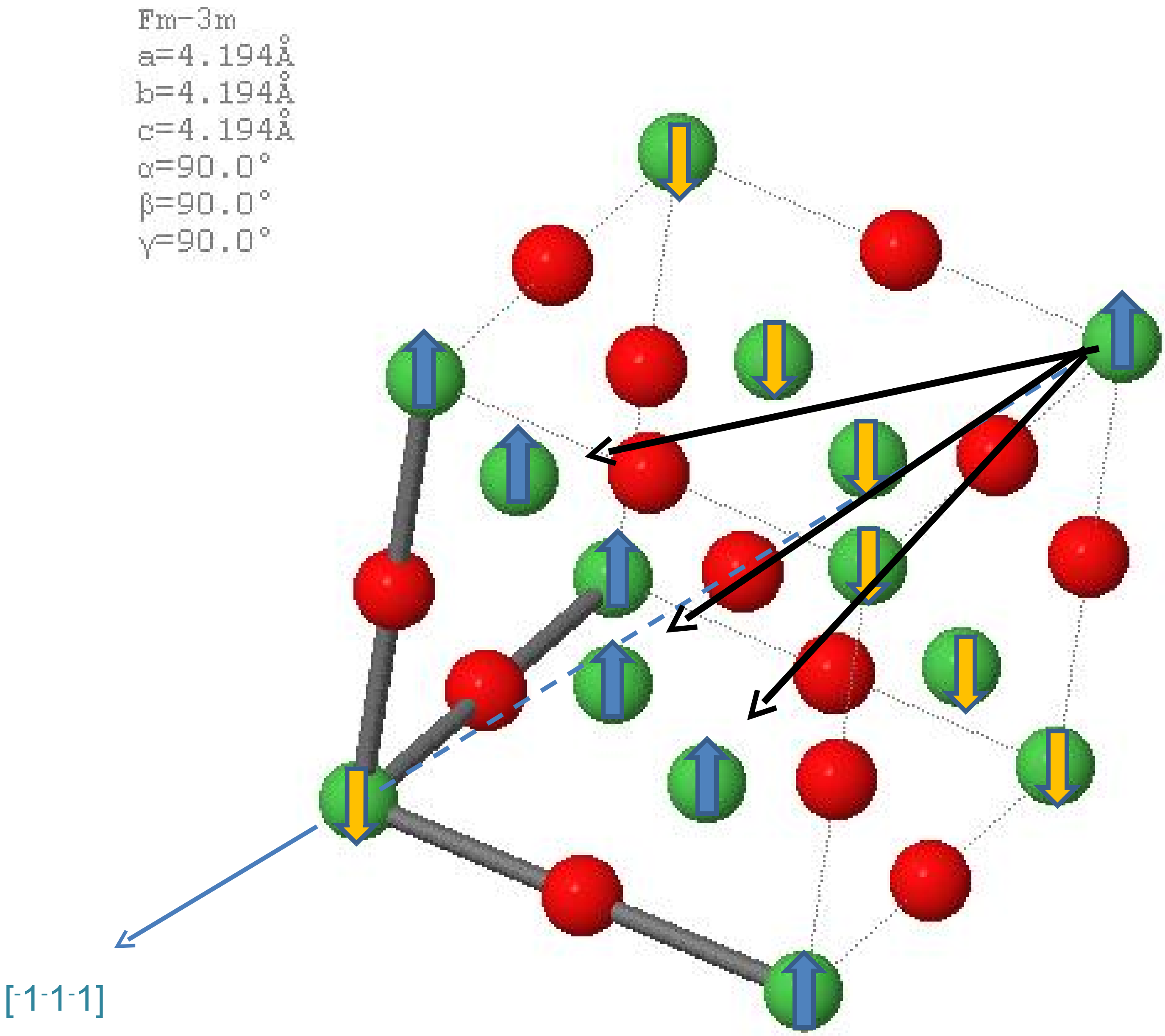


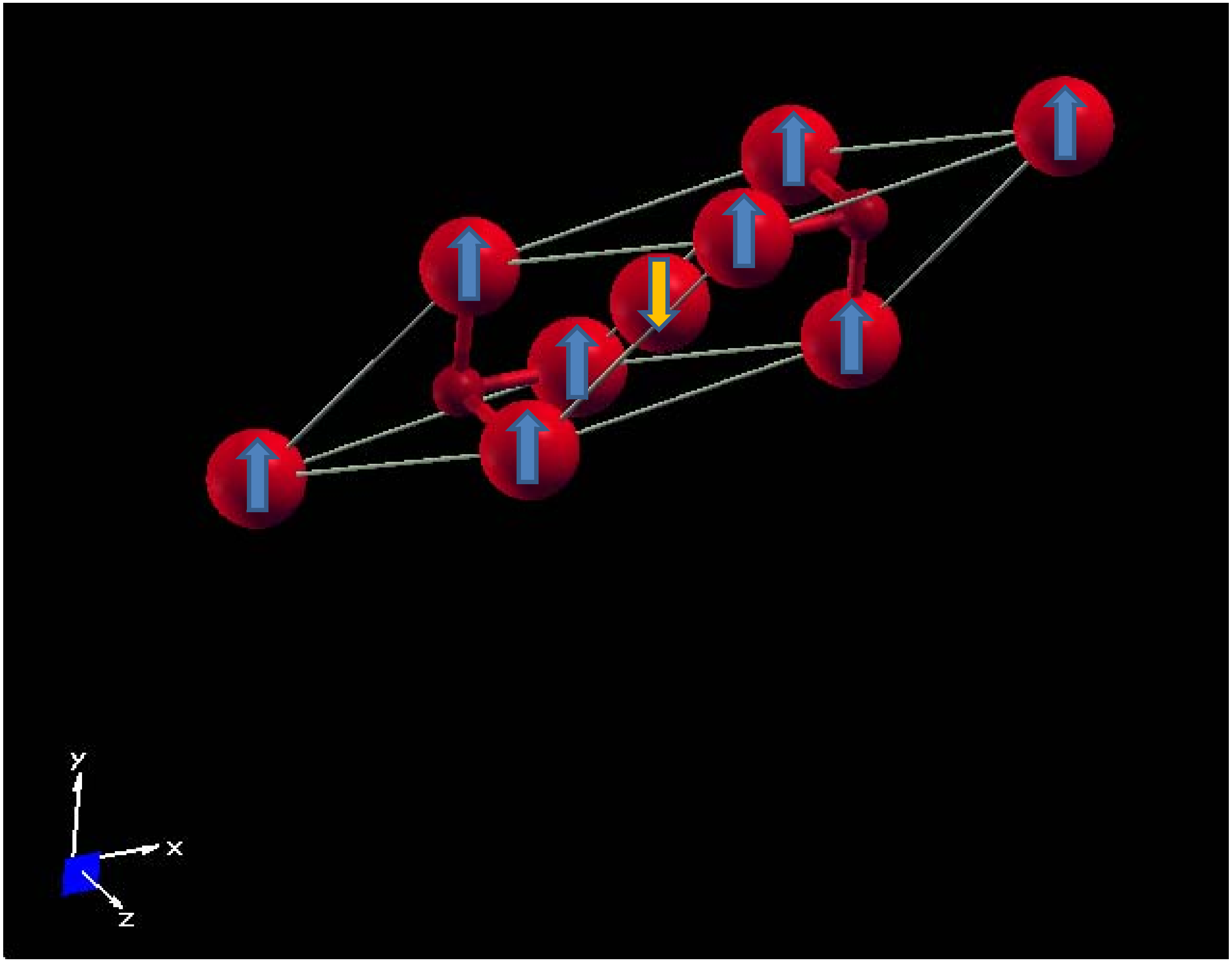

af-Tenorite DOS Plot
U = 5   Ef = 10.1435
N(E) (states/eV)
eV
0
5
10
15
20
-10
-8
-6
-4
-2
0
2
4
6
8
10

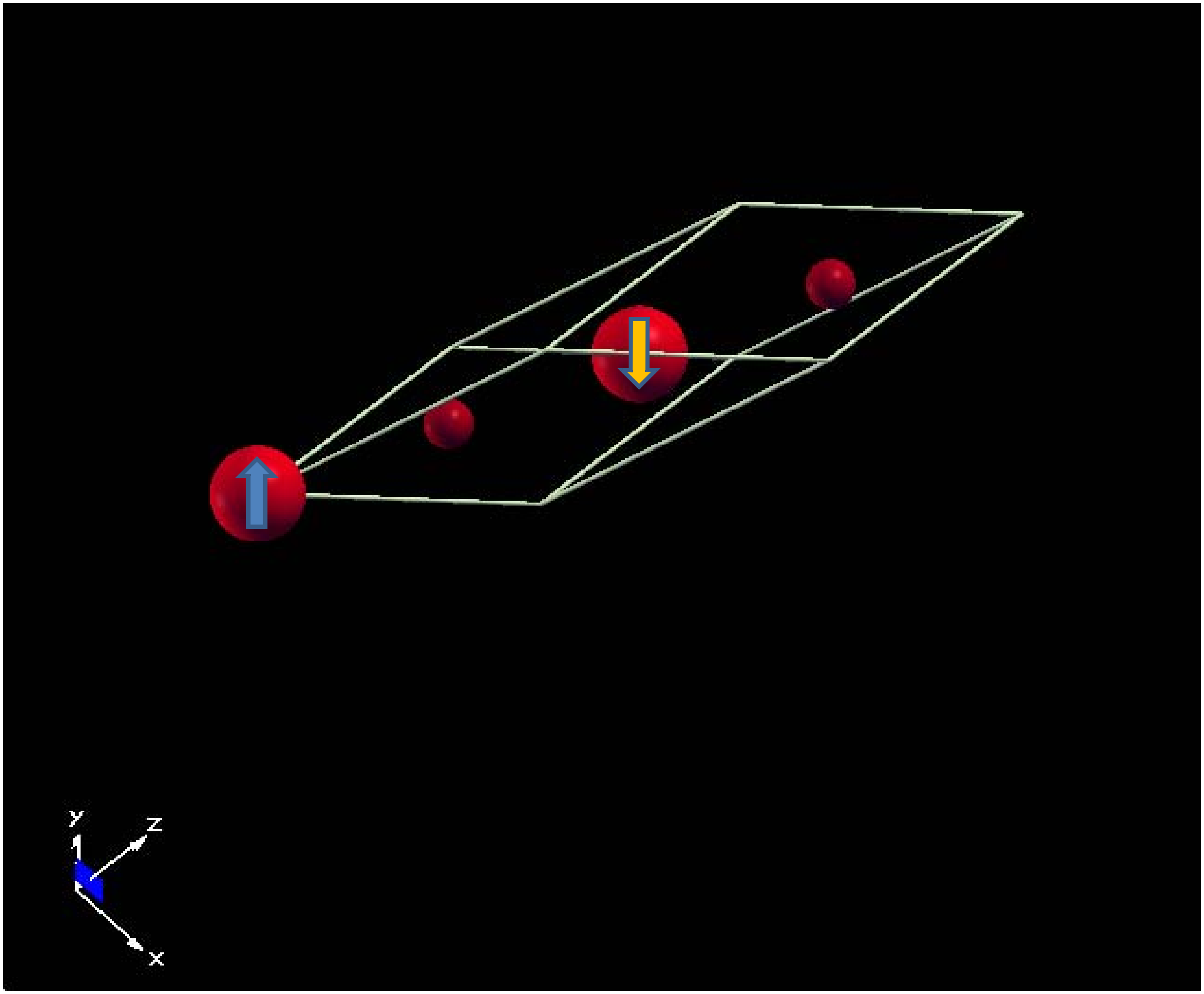
Proto-TMO AF Rock Salt

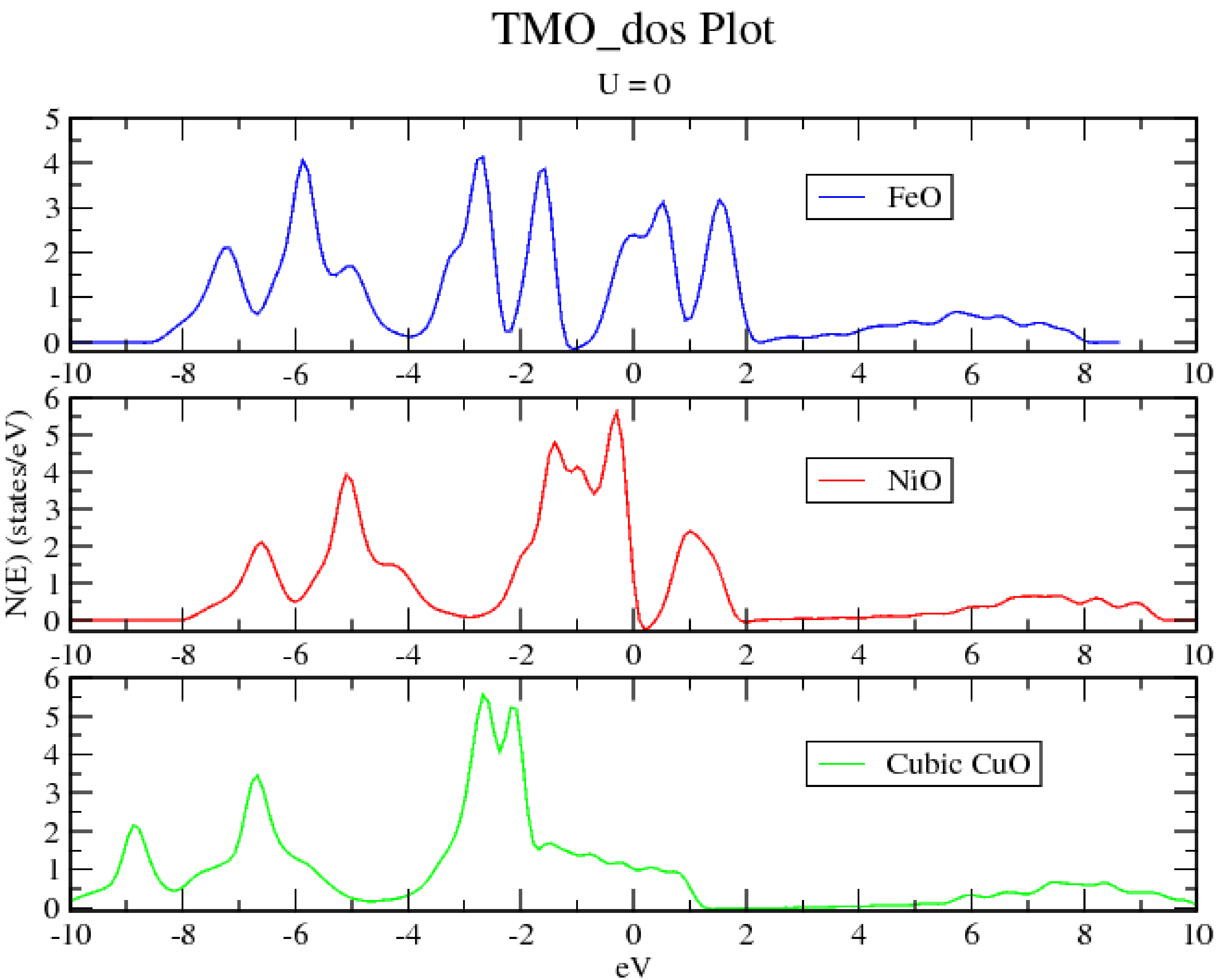


Proto-TMO AF Rock Salt

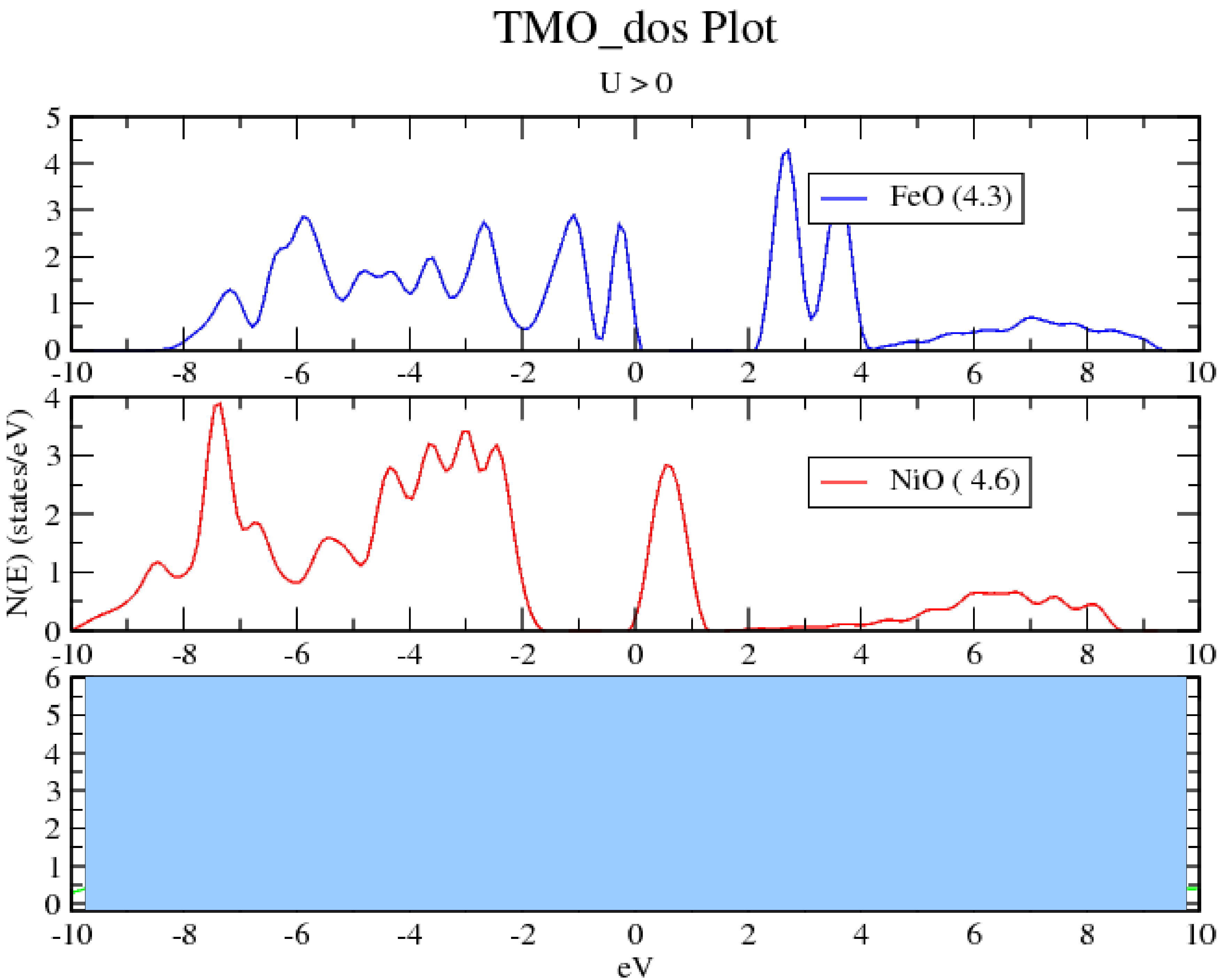



y
x
z


y
z
x

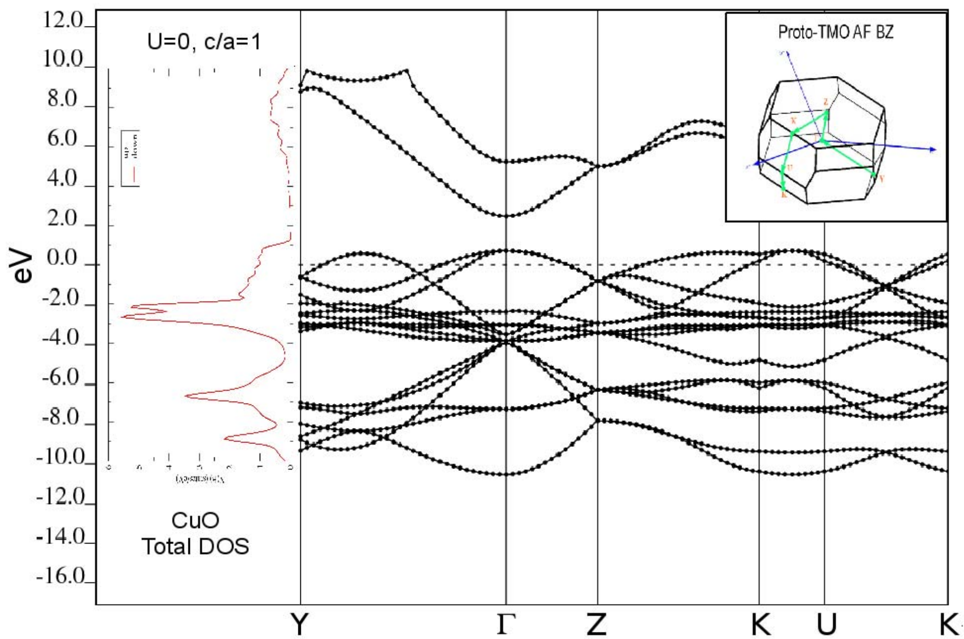


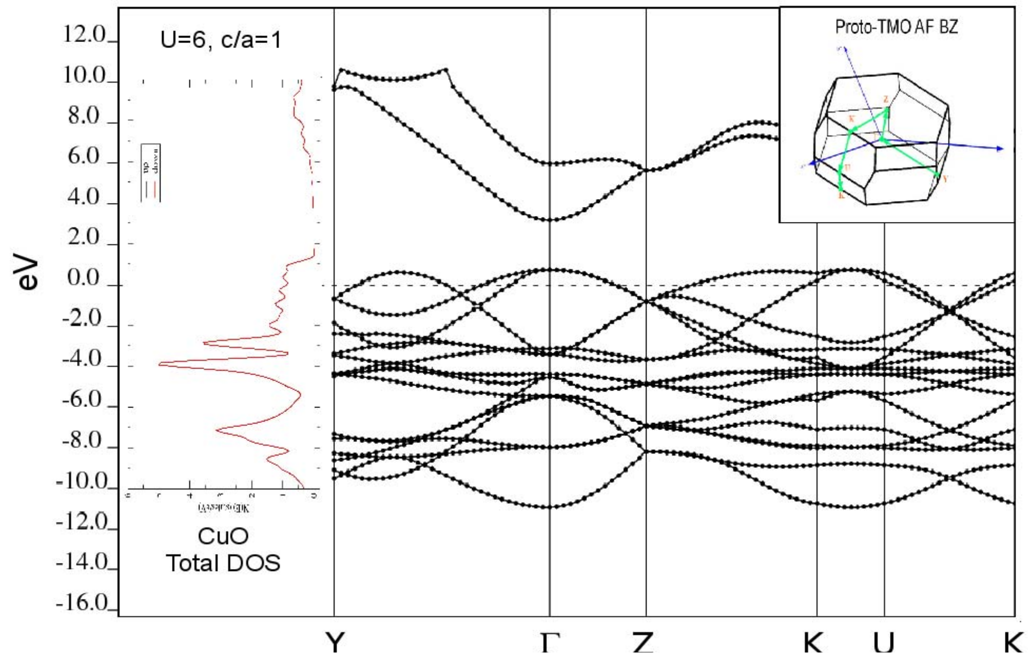
TMO_dos Plot
U = 0
FeO
NiO
Cubic CuO
N(E) (states/eV)
eV

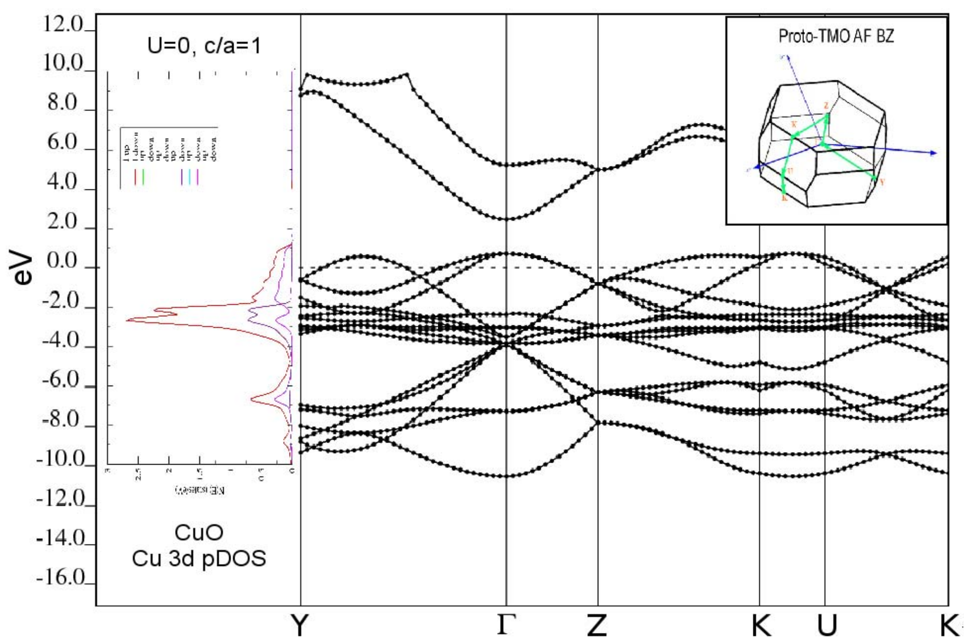


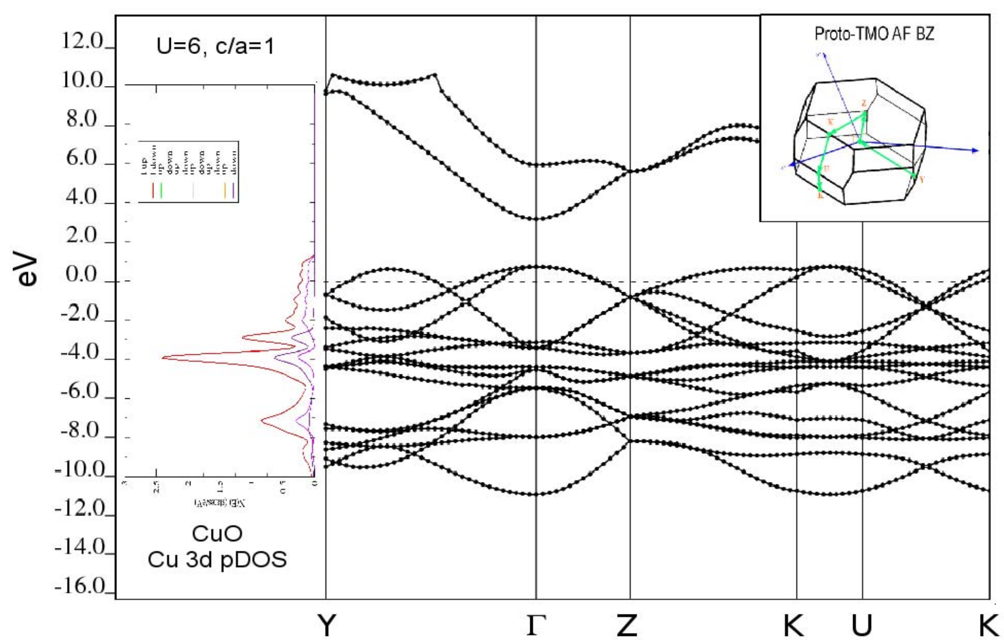
TMO_dos Plot
U > 0
FeO (4.3)
NiO (4.6)
N(E) (states/eV)
eV

Cubic Rocksalt CuO

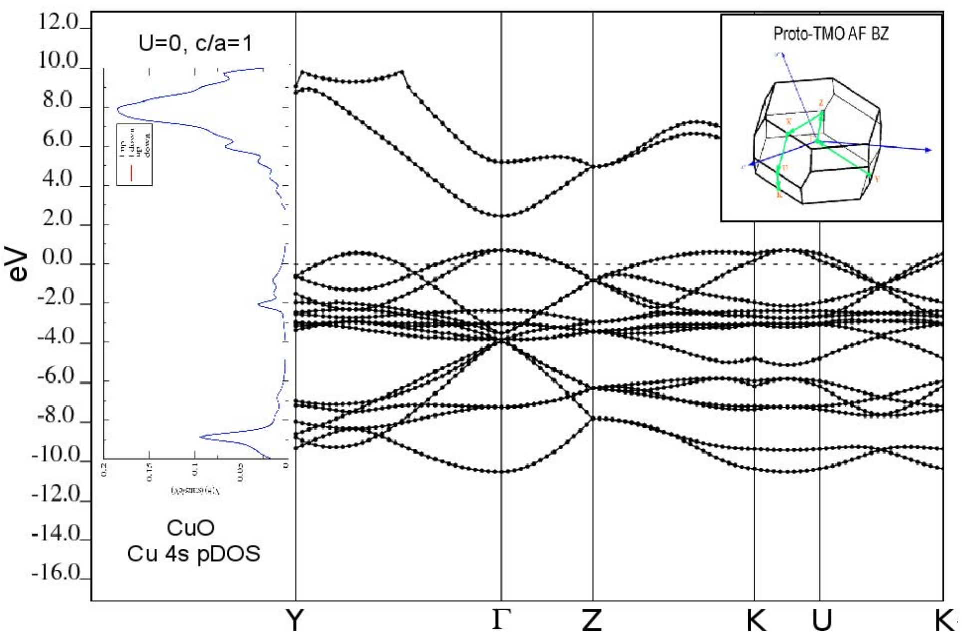


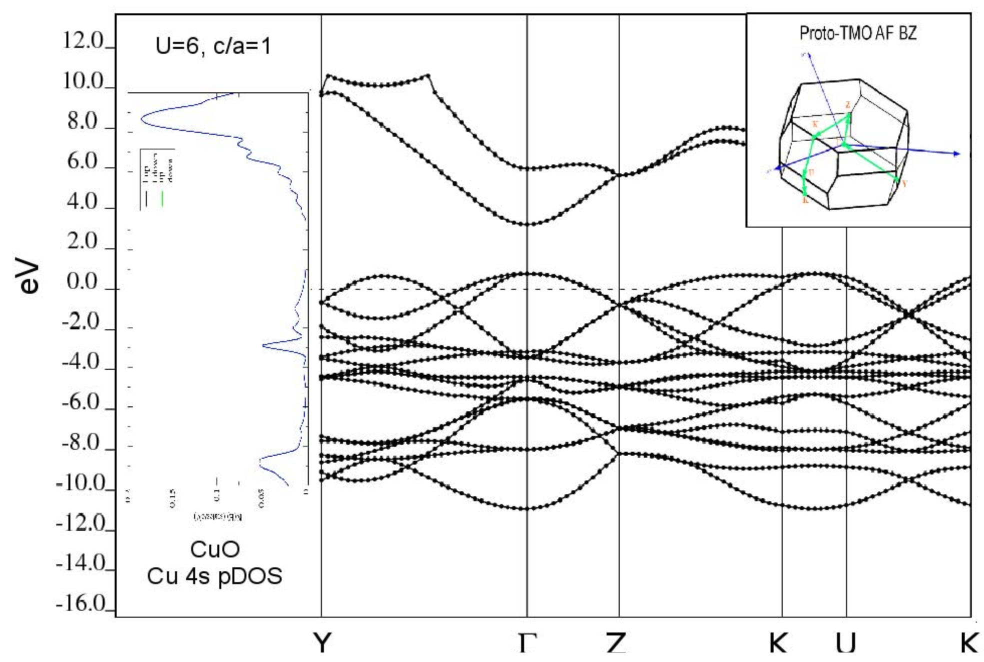


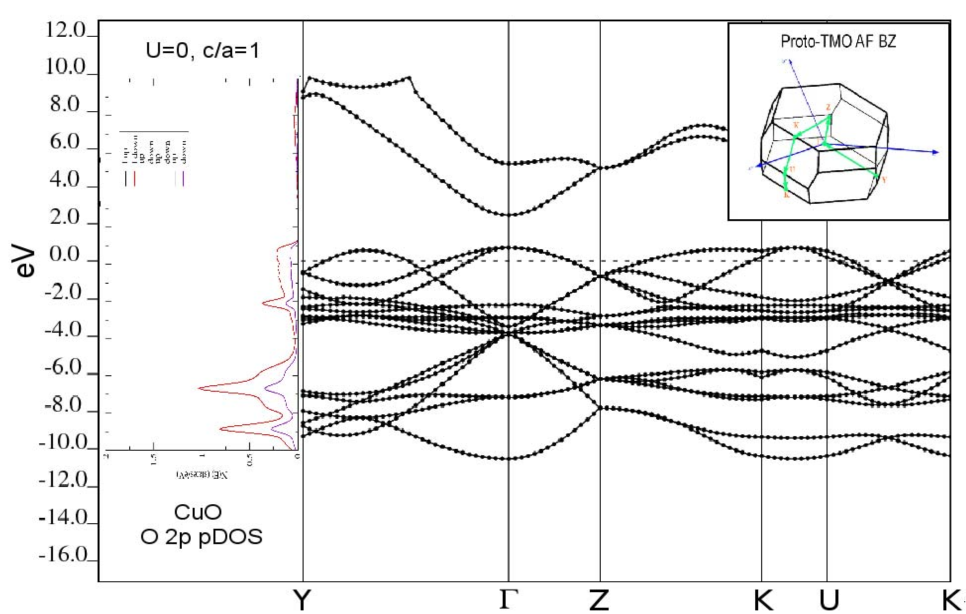


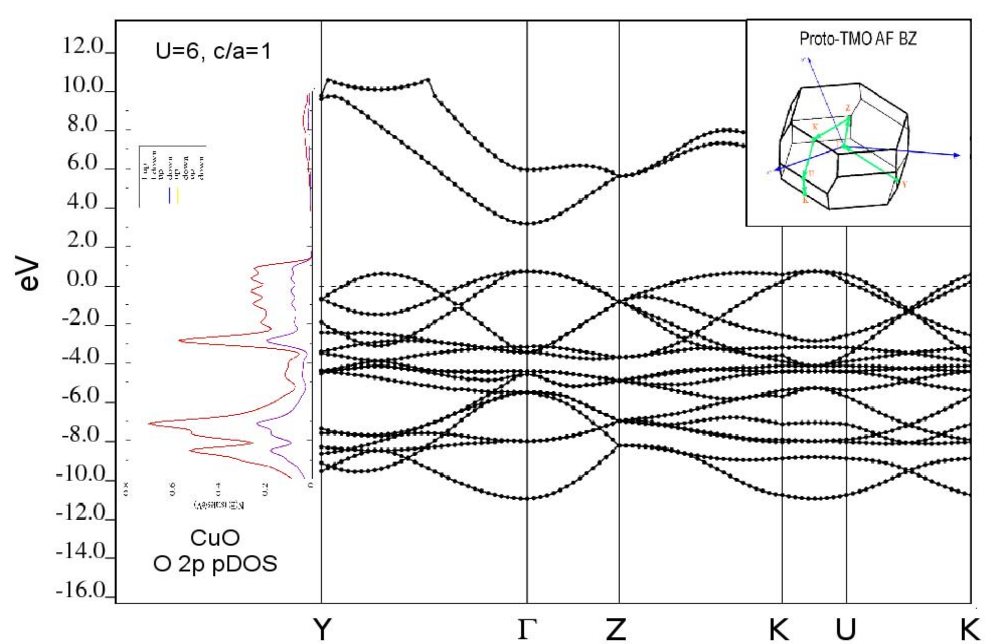


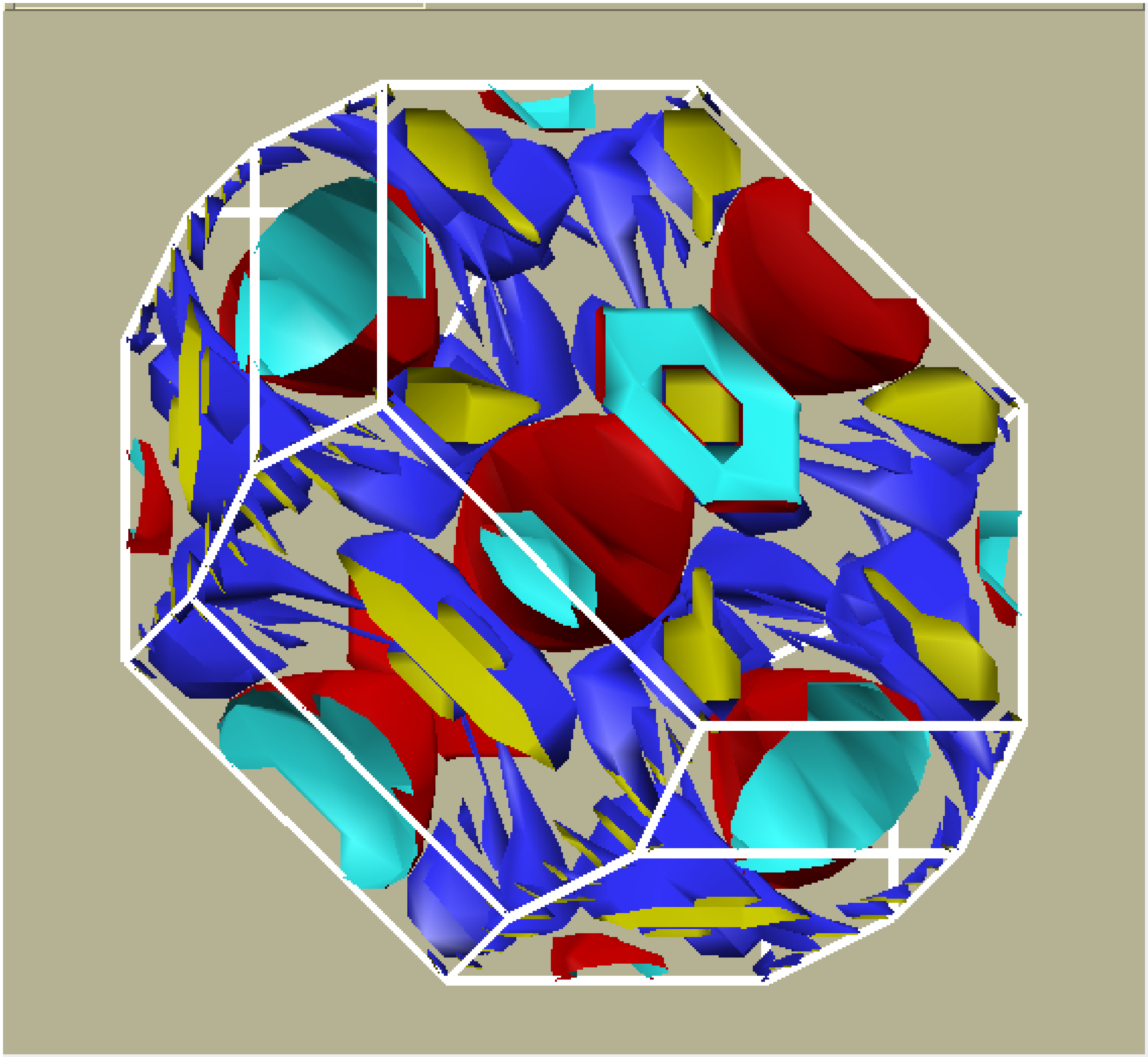
Cubic Rocksalt CuO (Cu 4s & O2p)

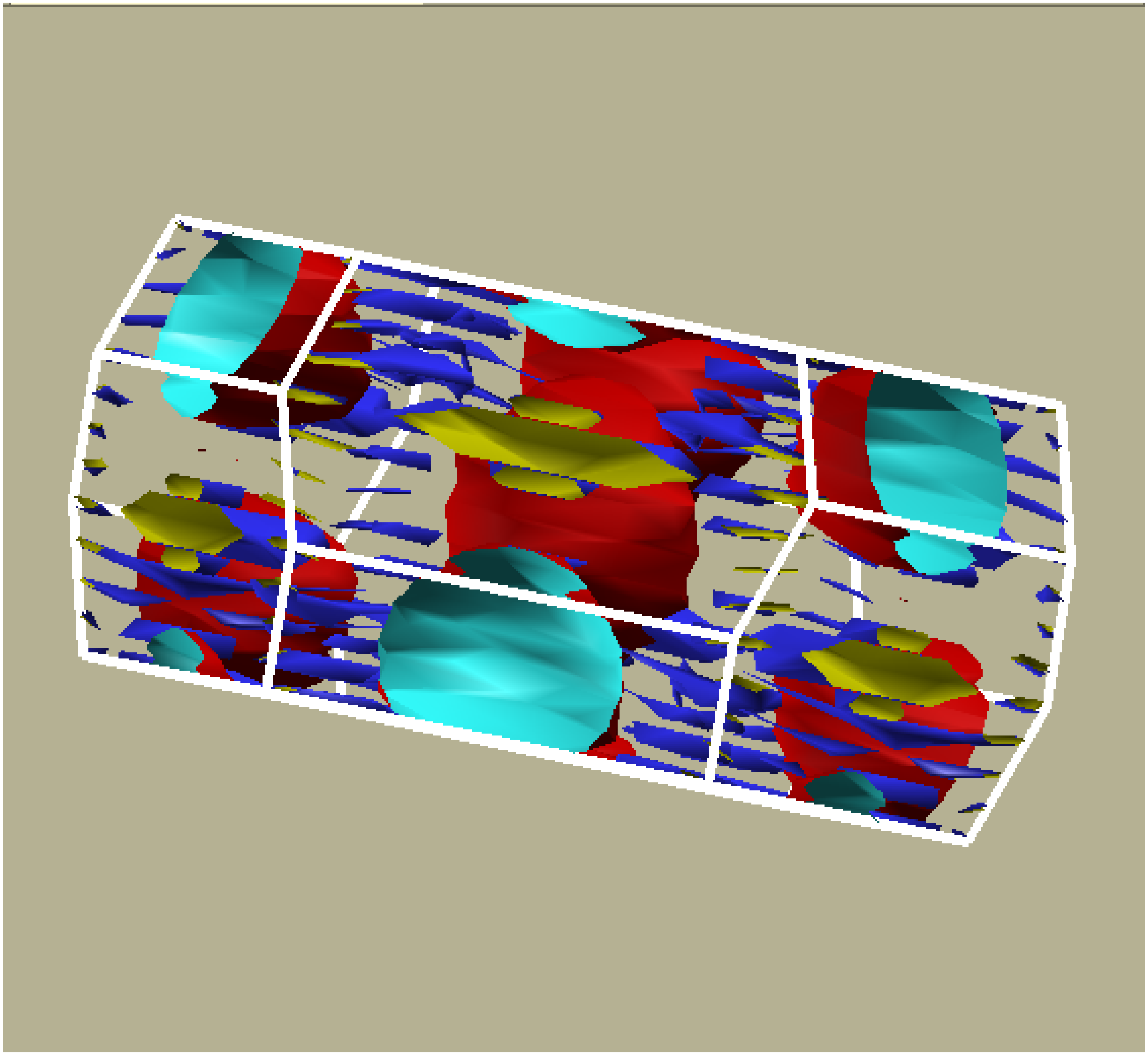




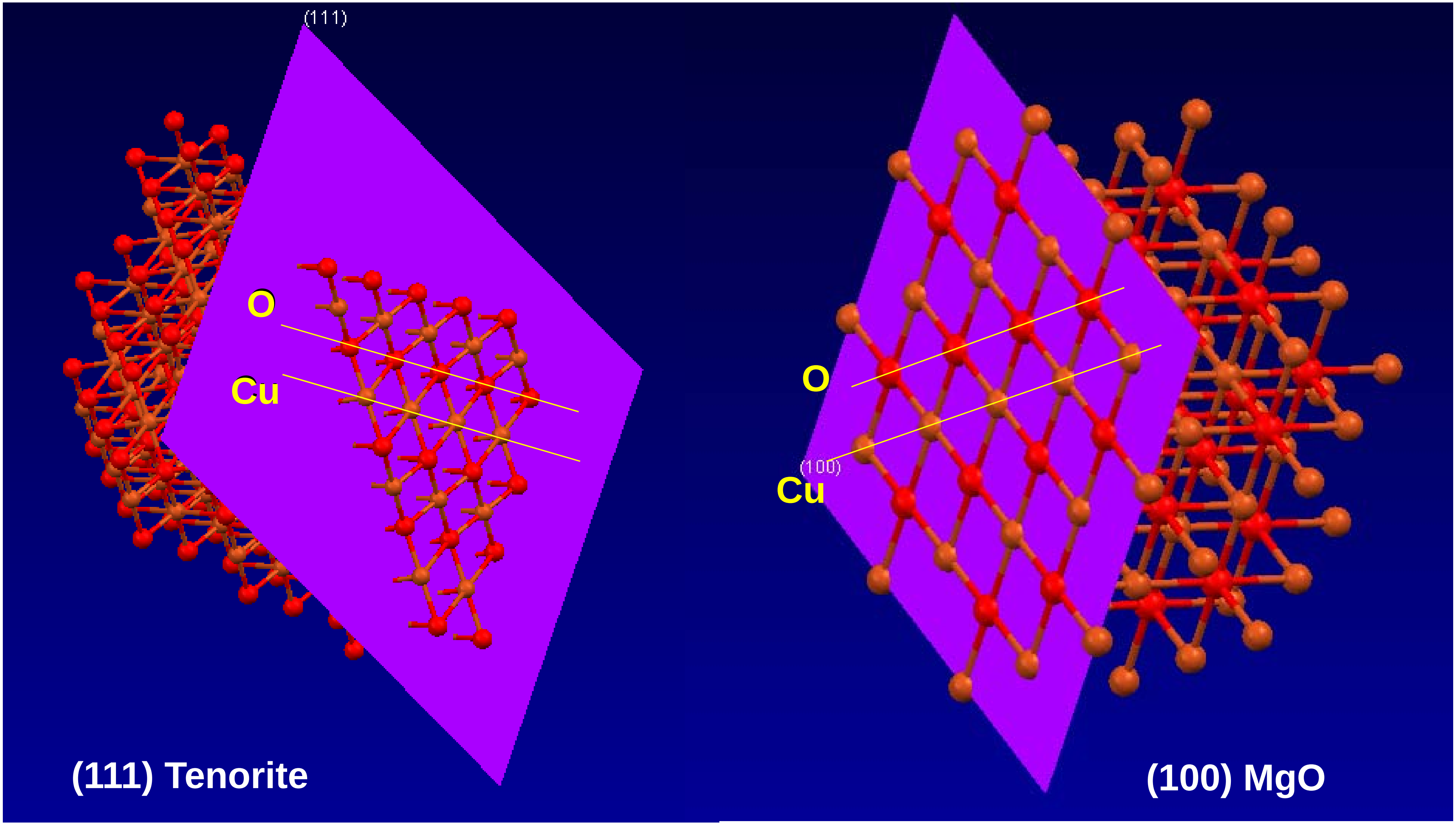








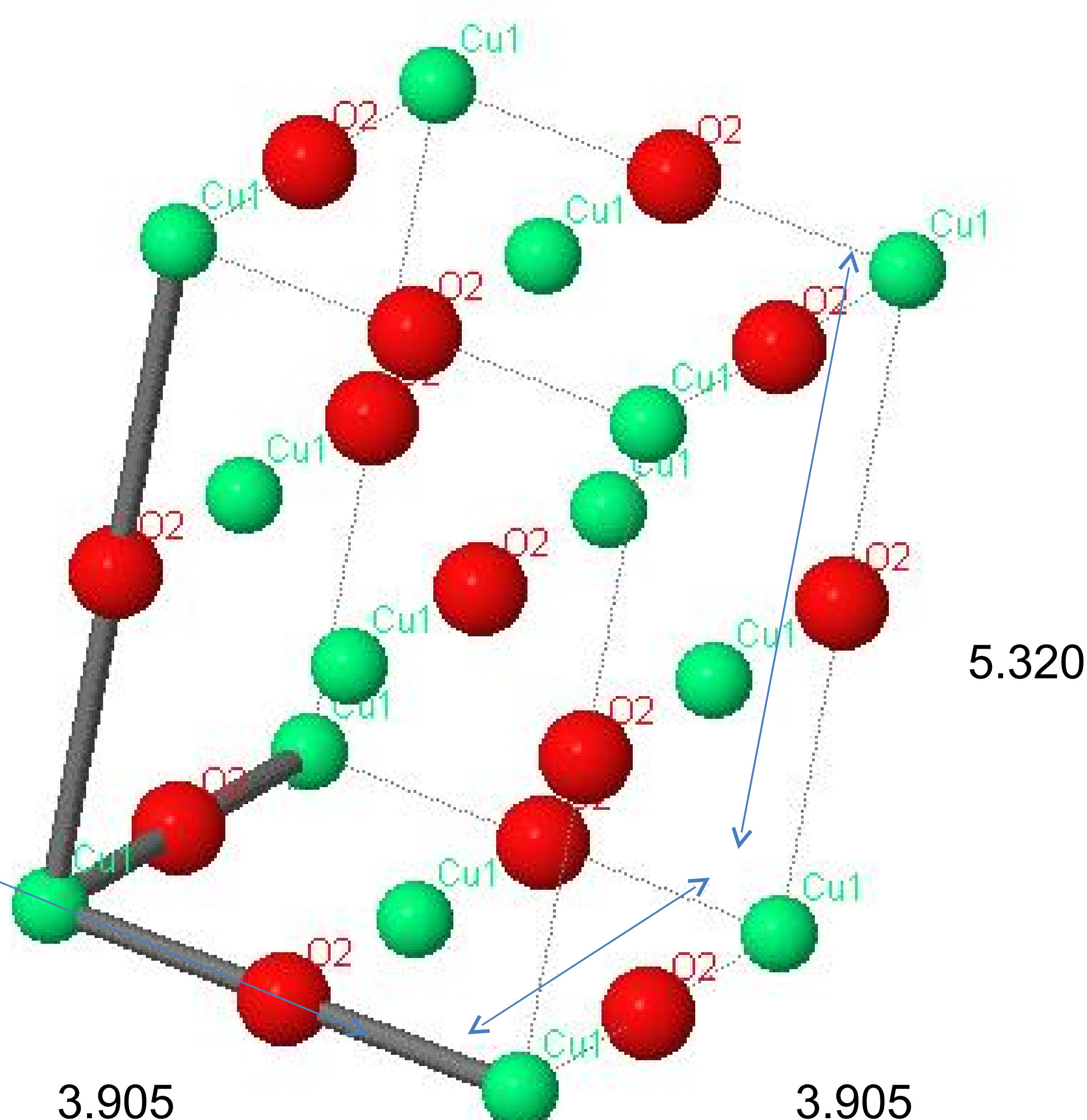
Comparison of Tenorite (111) to CuO – MgO Proxy (100)



Tetragonal CuO

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

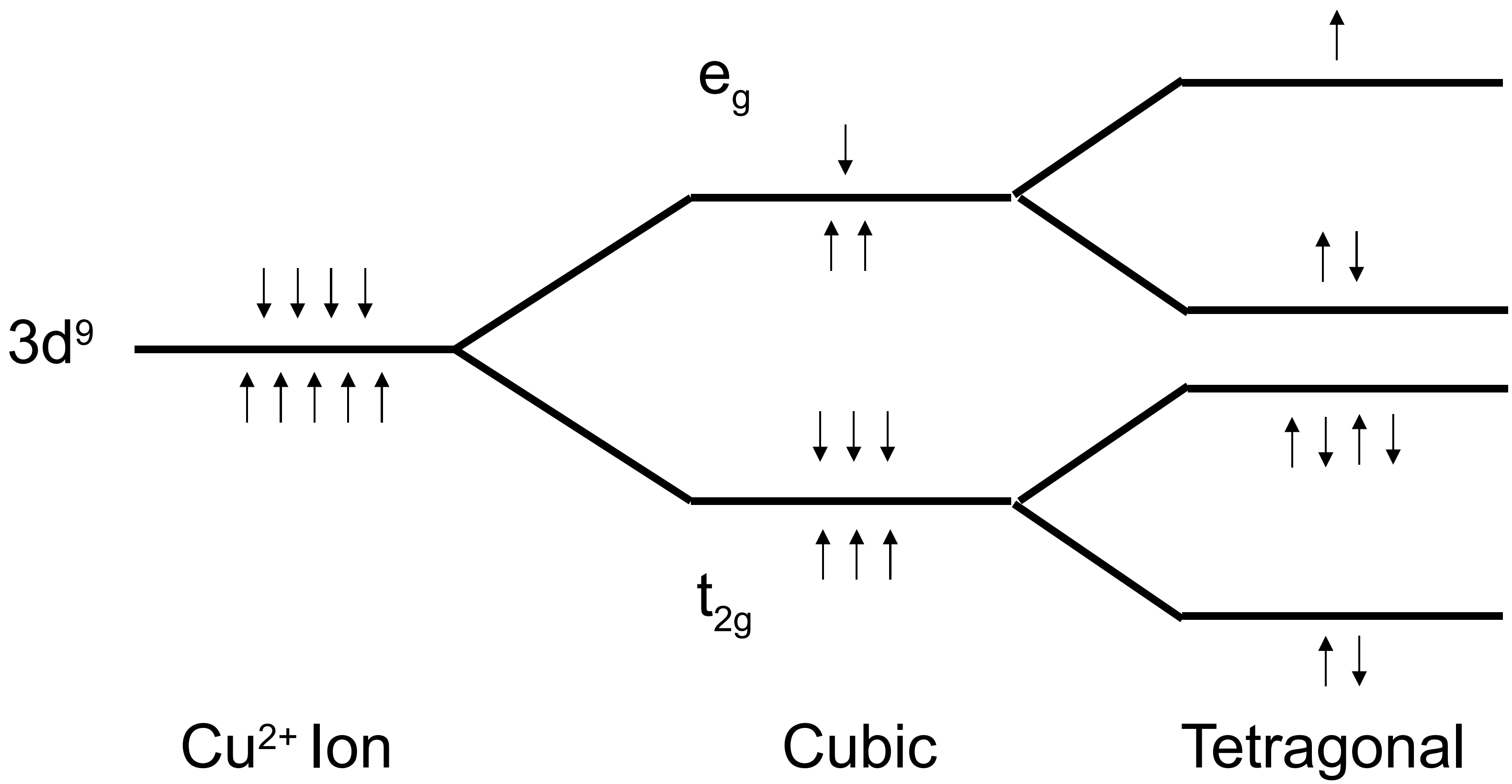
c/a = 1.36



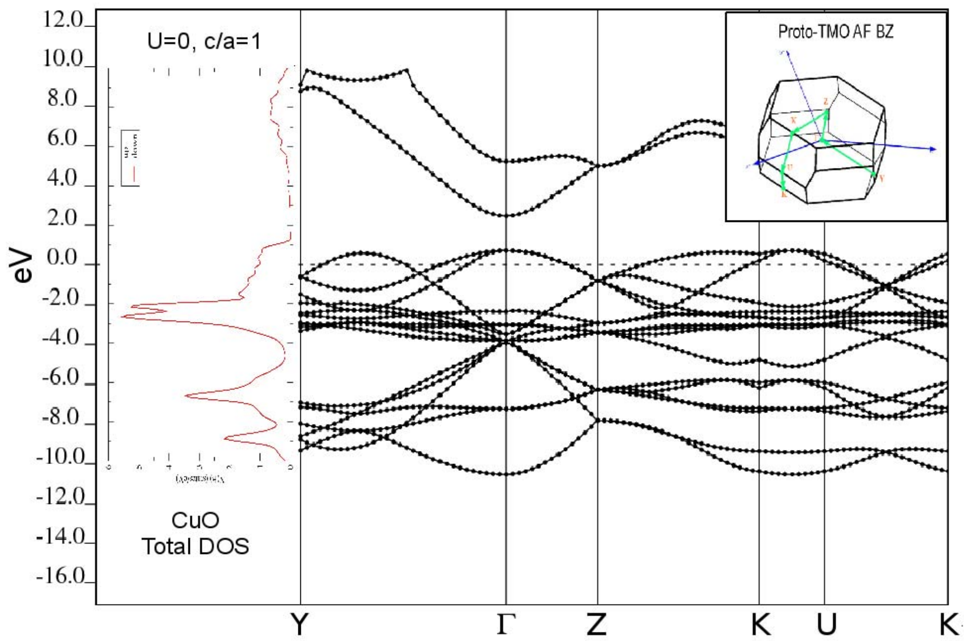
<u>Measurements</u>
<u>(Wolter Siemons)</u>

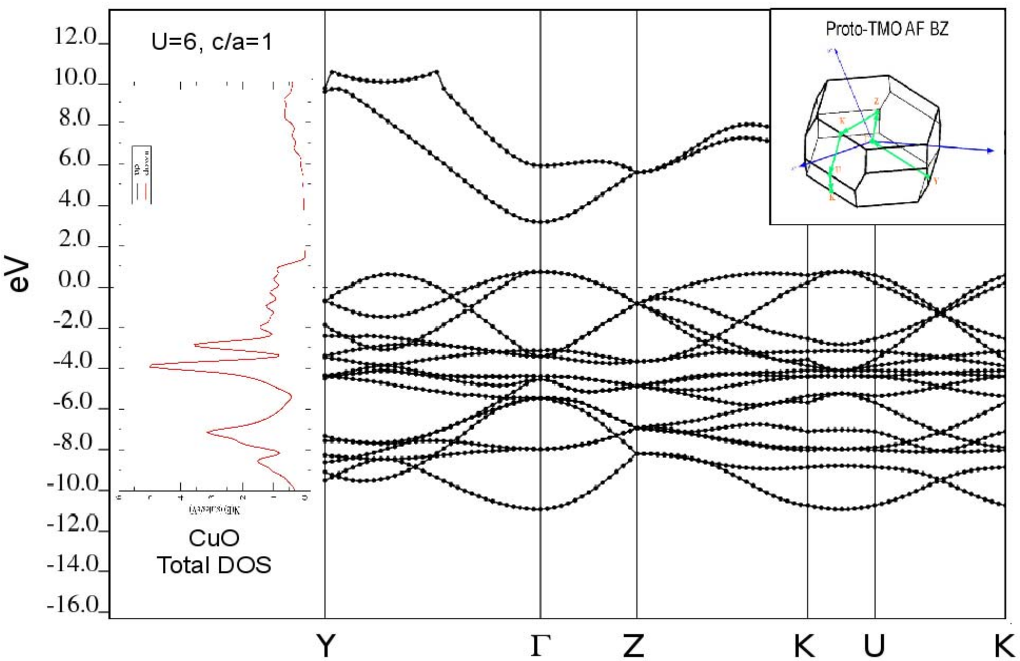
- 2-4 ML epi on STO
- No Fermi Edge
- No Exchange Bias on ferro-SRO (Tc ~ 100-150 K)

Cu2+ 3d Multiplet Splitting (Tetra)

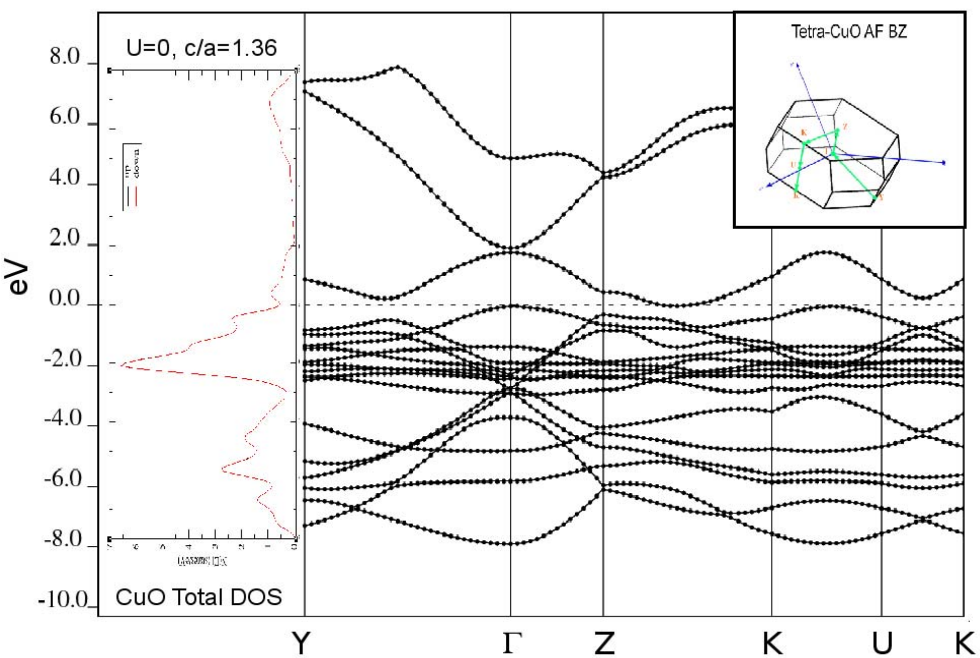


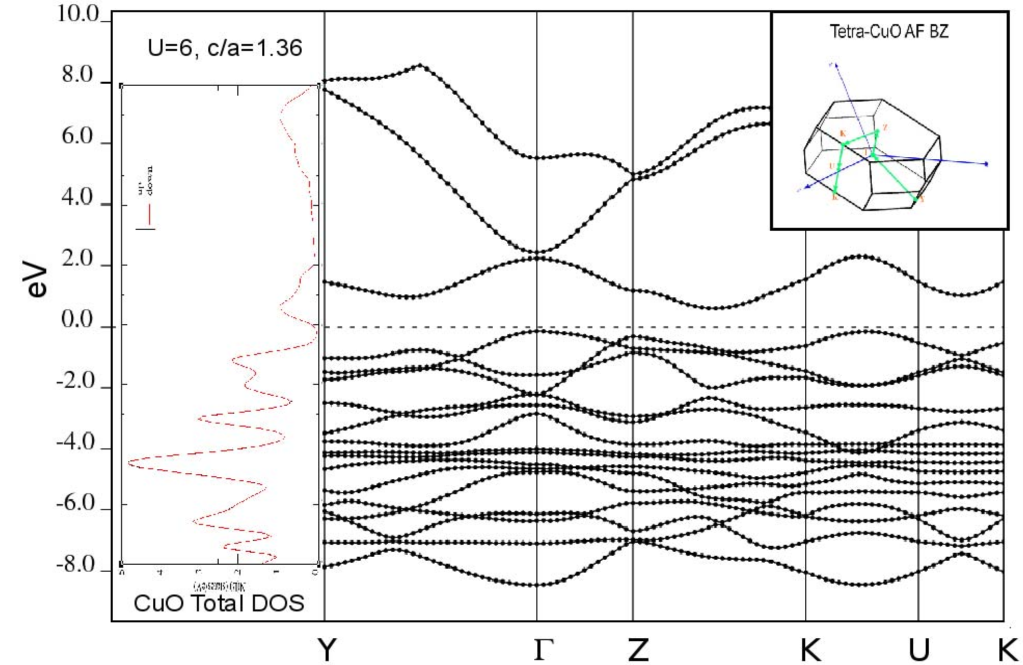
Cubic



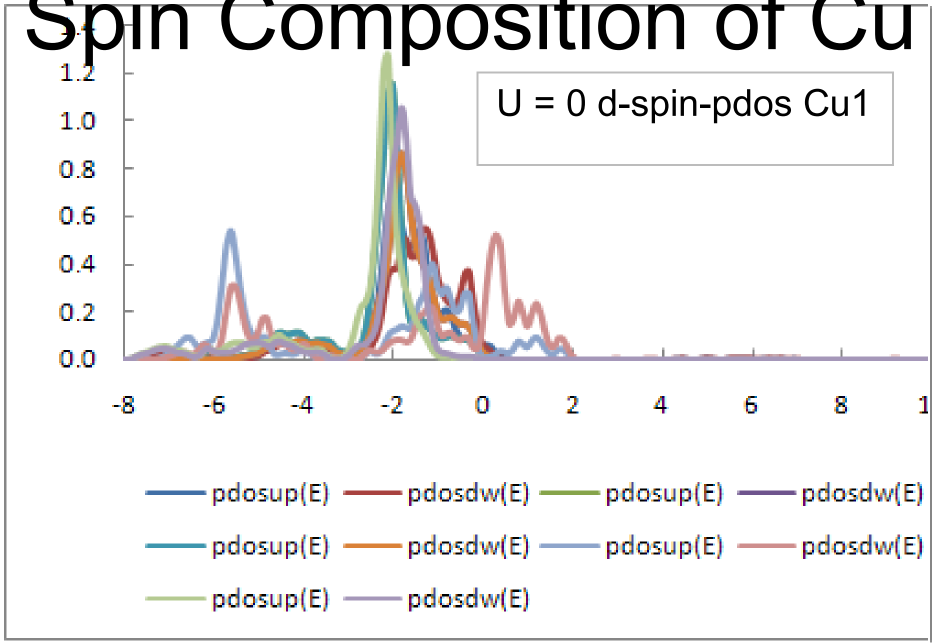


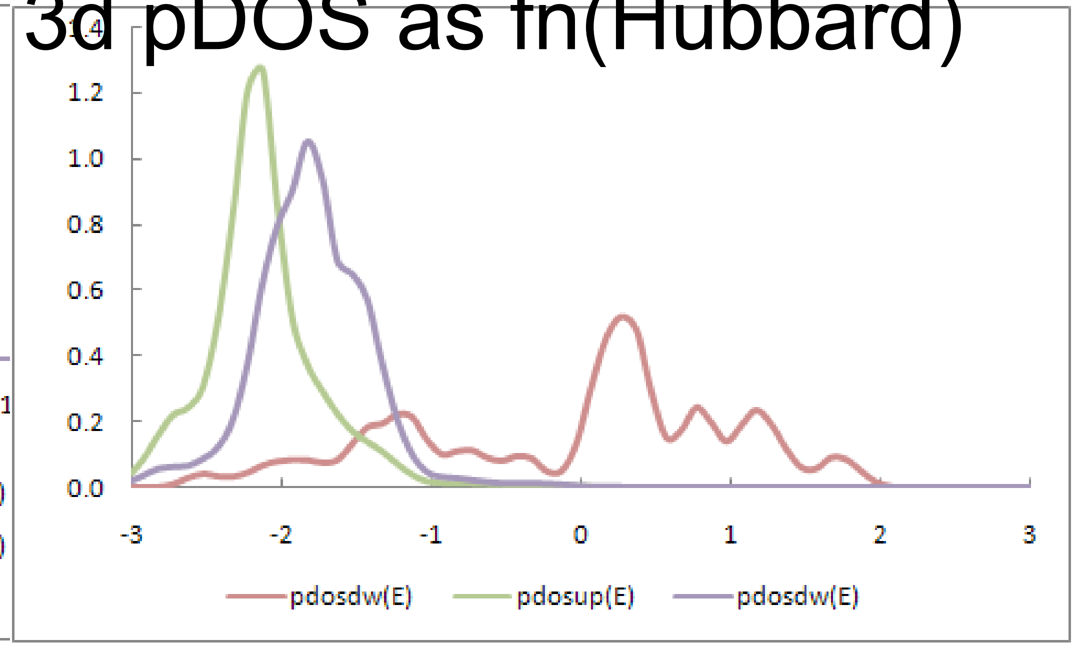
Tetragonal

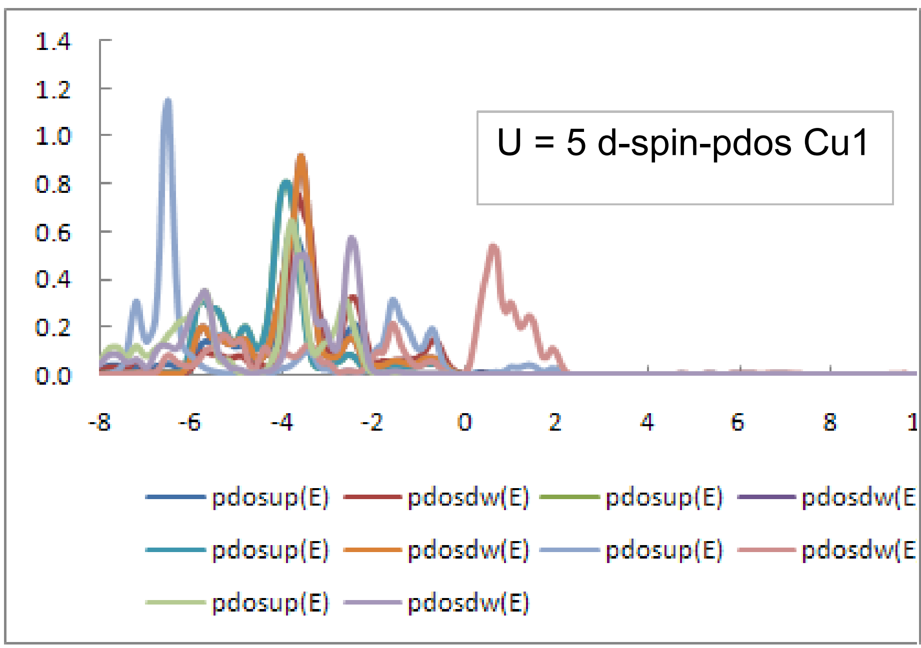


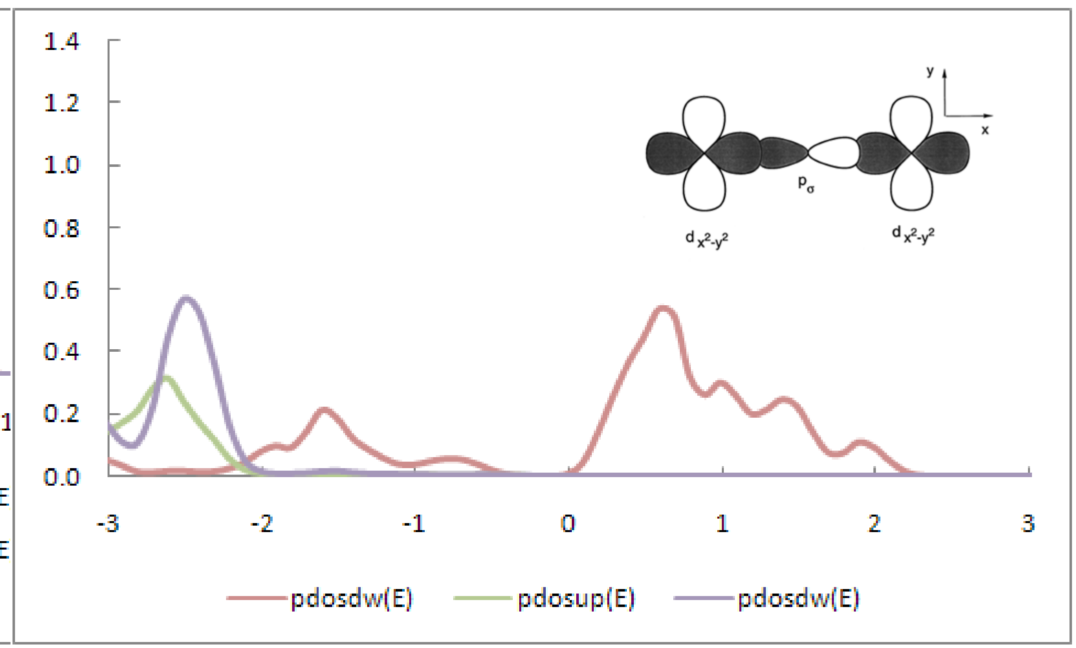


Spin Composition of Cu 3d pDOS as fn(Hubbard)

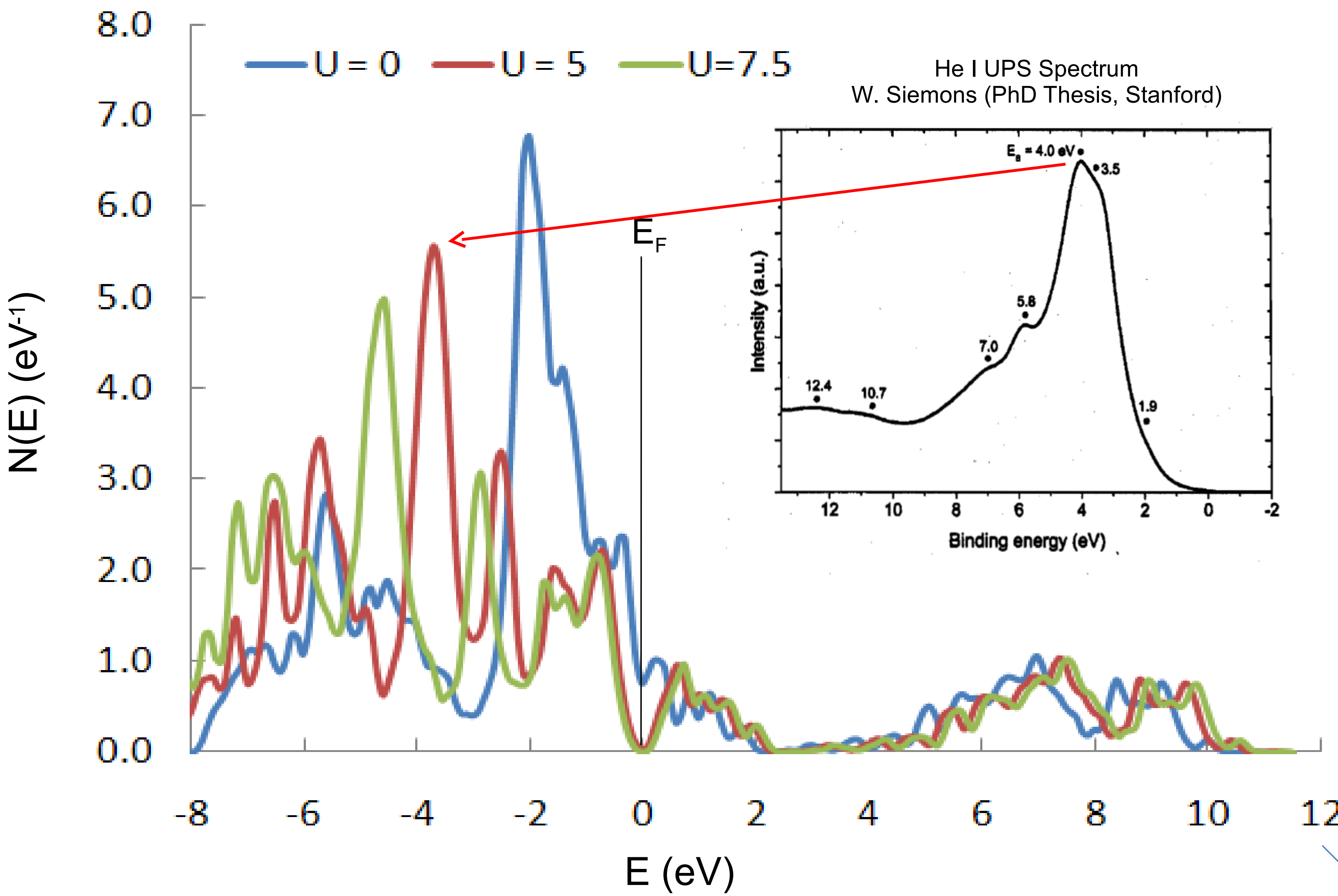






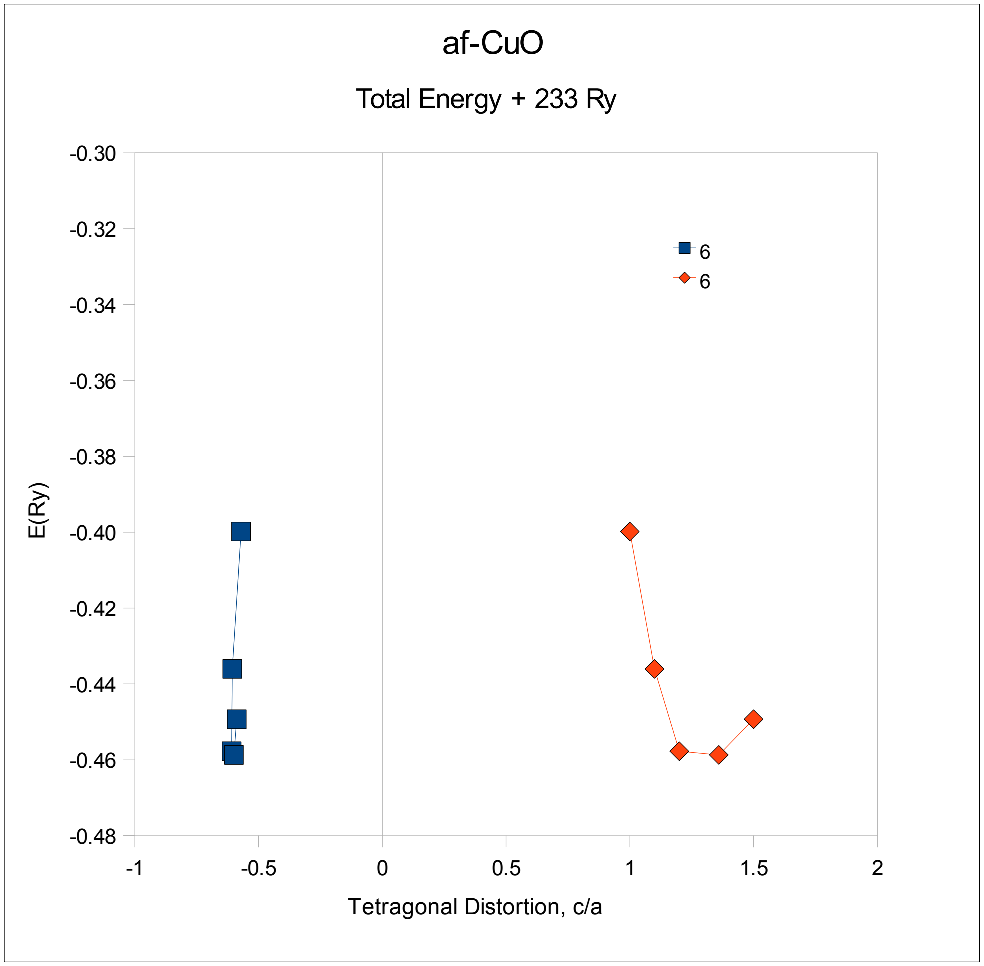


t-CuO Density-of-States

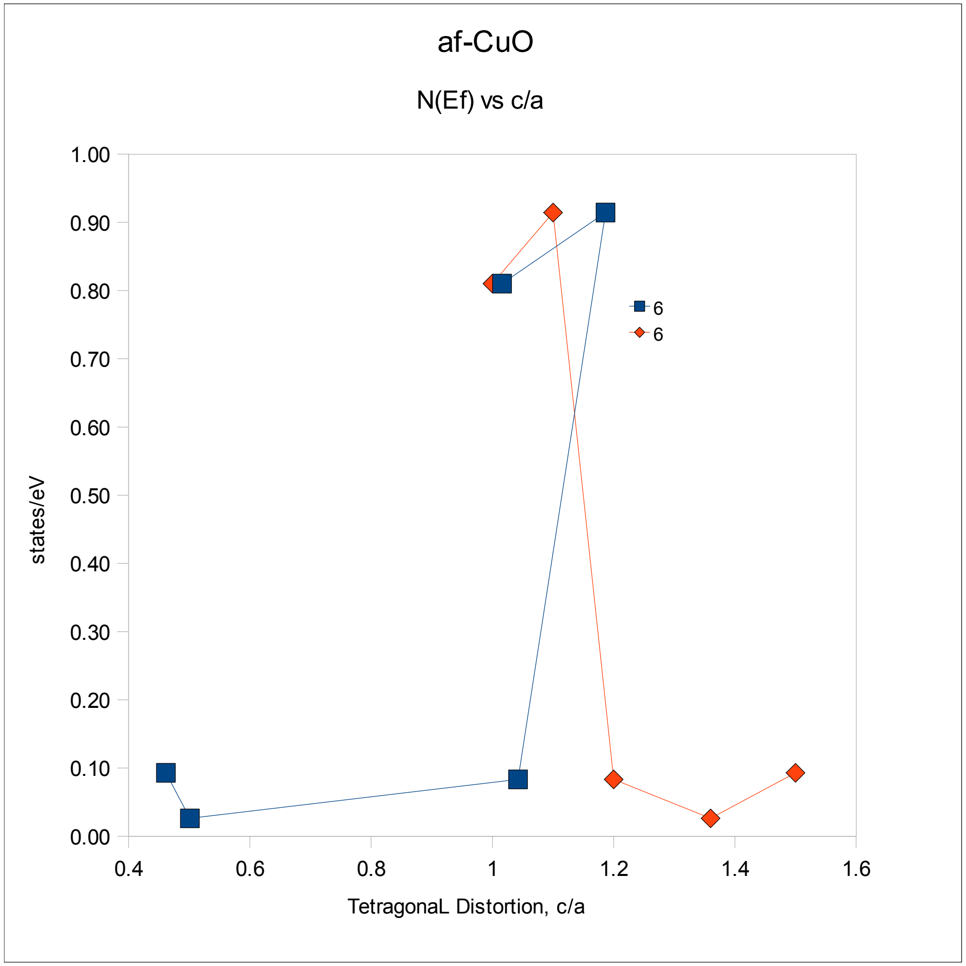


Cubic & Tetragonal CuO
Ground State Properties

Total GS Energy



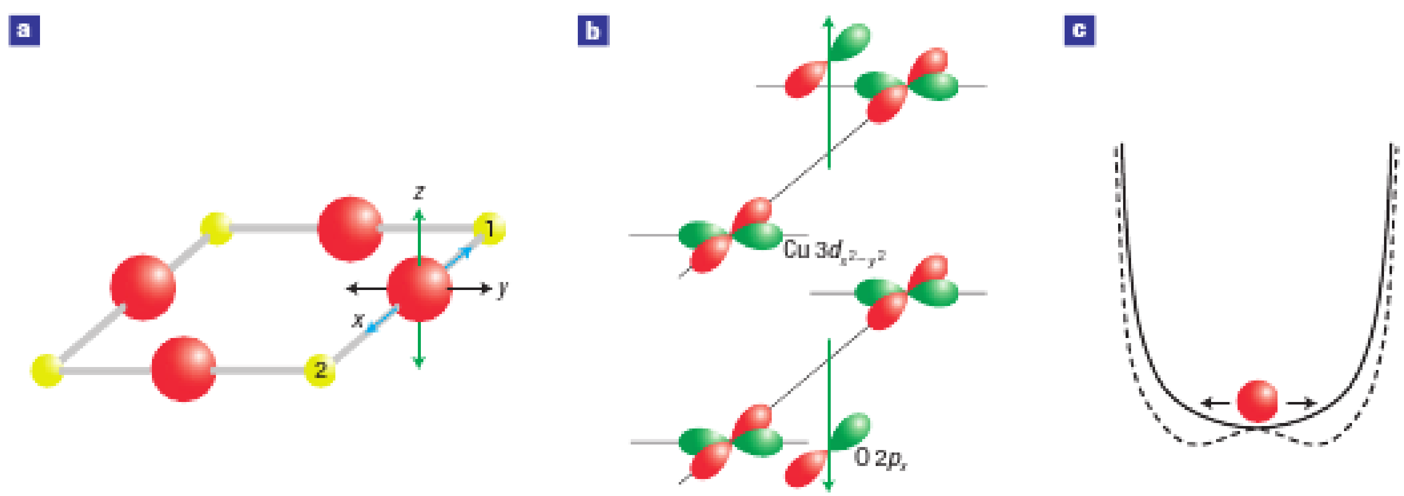
DOS at Fermi Energy



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

<u>Conclusions</u>

- Rocksalt CuO can be used as a proxy material to study HTSC
- Cubic RS CuO is a metal independent of U, subject to J-T distortions

<u>Homework</u>

- Compute e-p coupling as fn(c/a,U), then λ
- Compute μ*, T_N
- Compute Θ_D , then T_C
- Look for anharmicicities a la Newns & Tsuei