Electronic Structure of Cubic Copper Monoxides*

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  - Stanford (Visiting Scholar)
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- Robert H. Hammond
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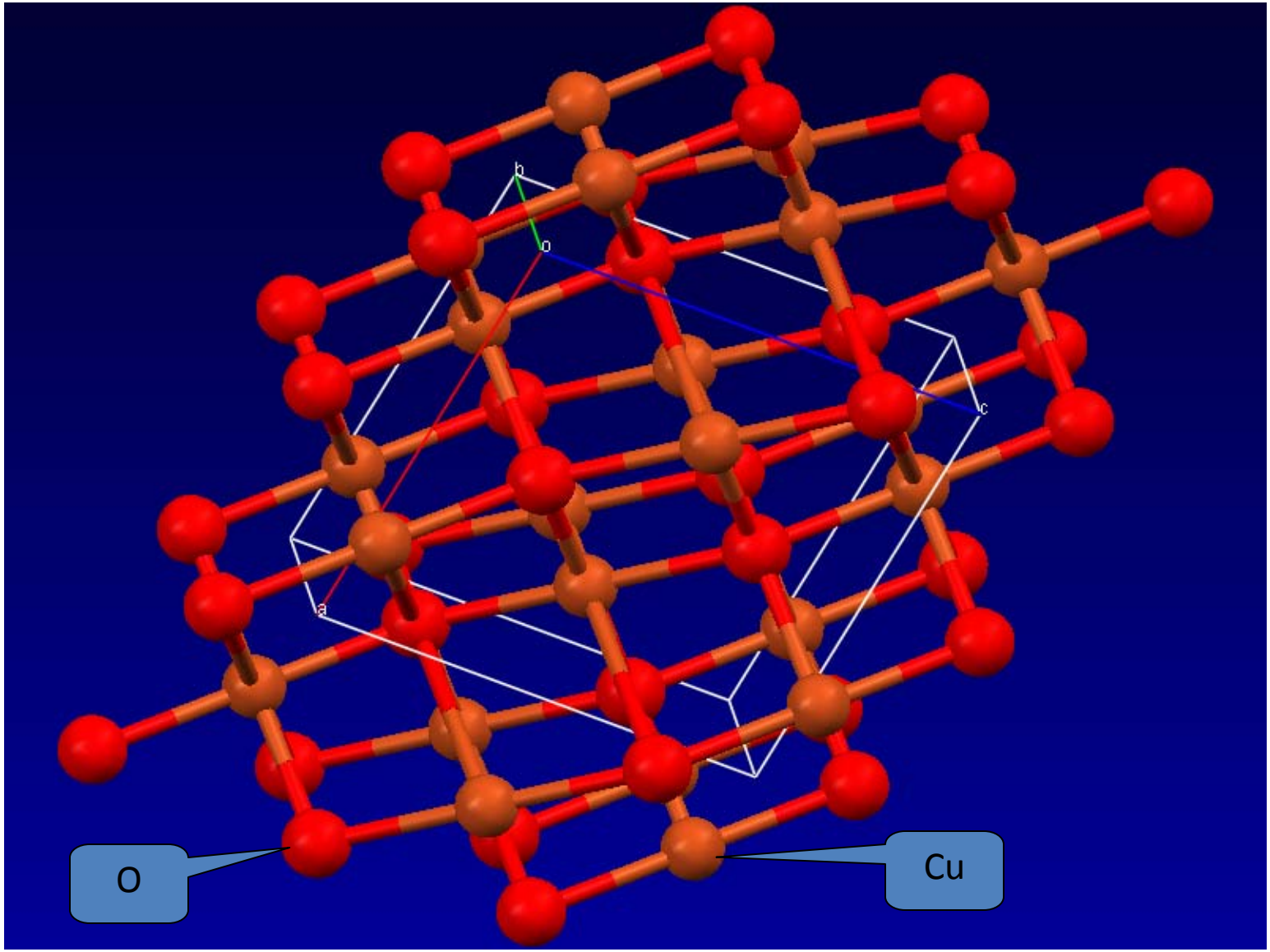
Y23.00007, 12:51 PM, Friday, 14 March
Session Y23: Electronic Structure of Complex Oxides
2008 APS March Meeting, New Orleans, LA

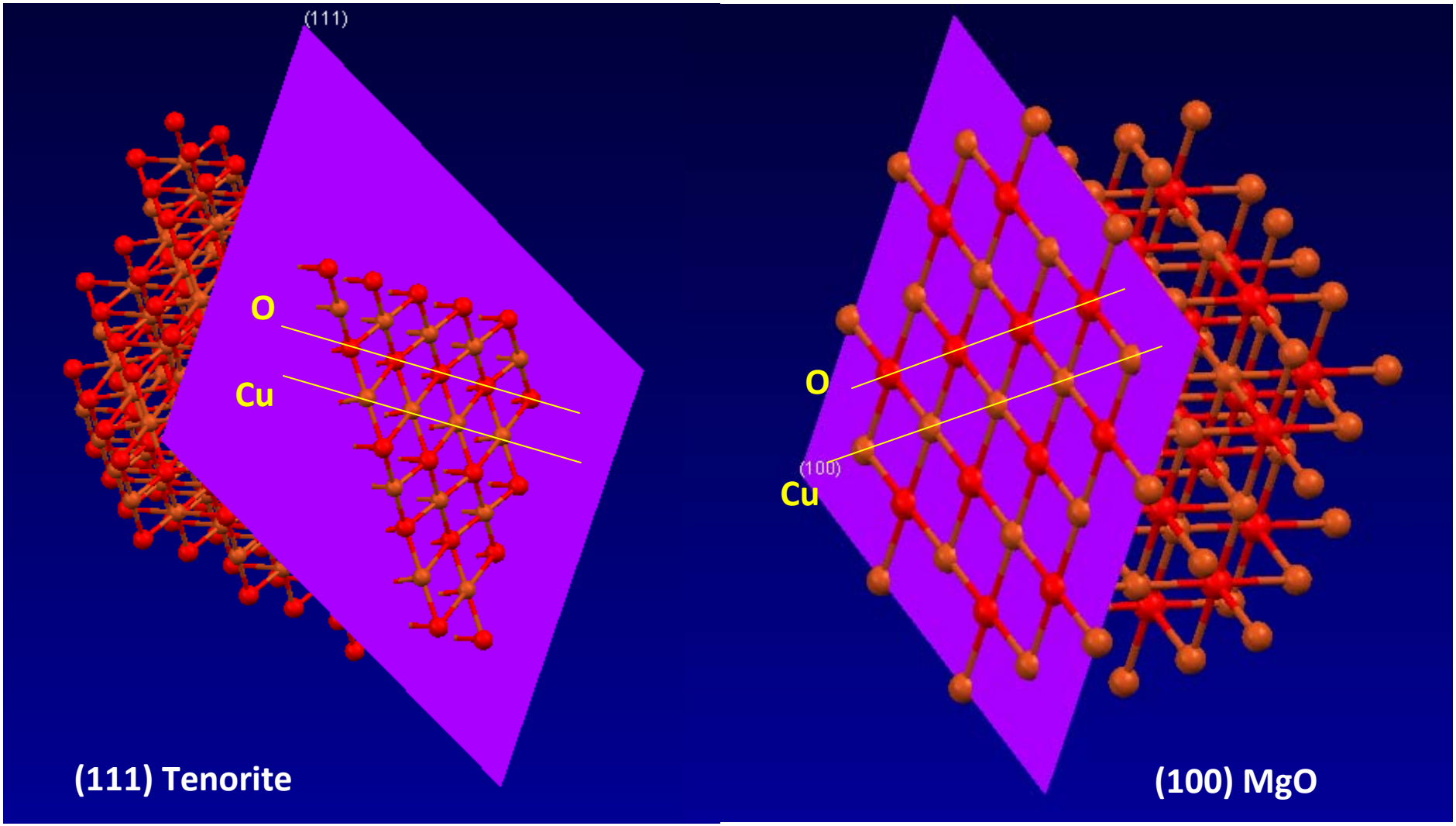
* Research Funded by US AFOSR & EPRI

Tenorite (Monoclinic CuO)

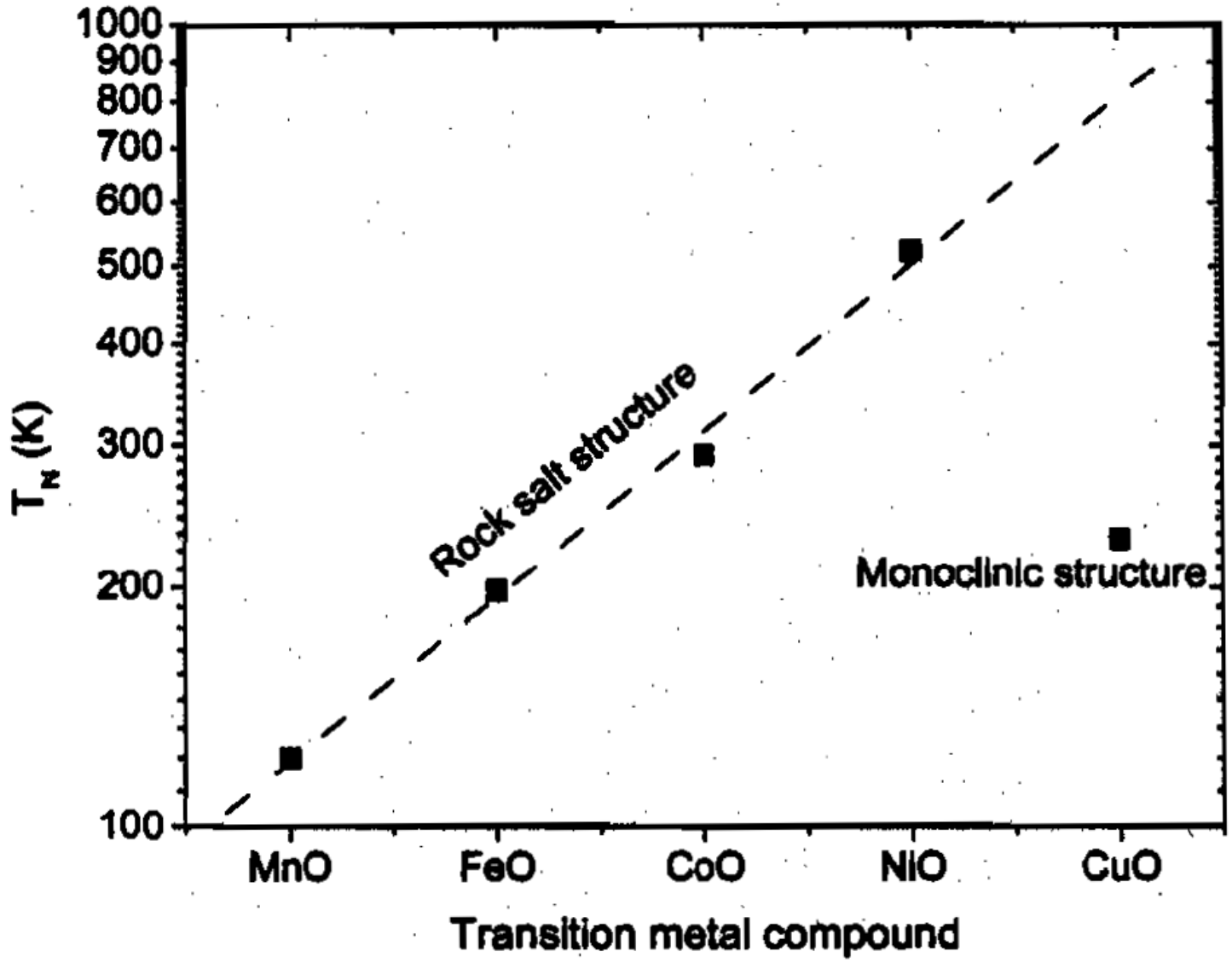


Return

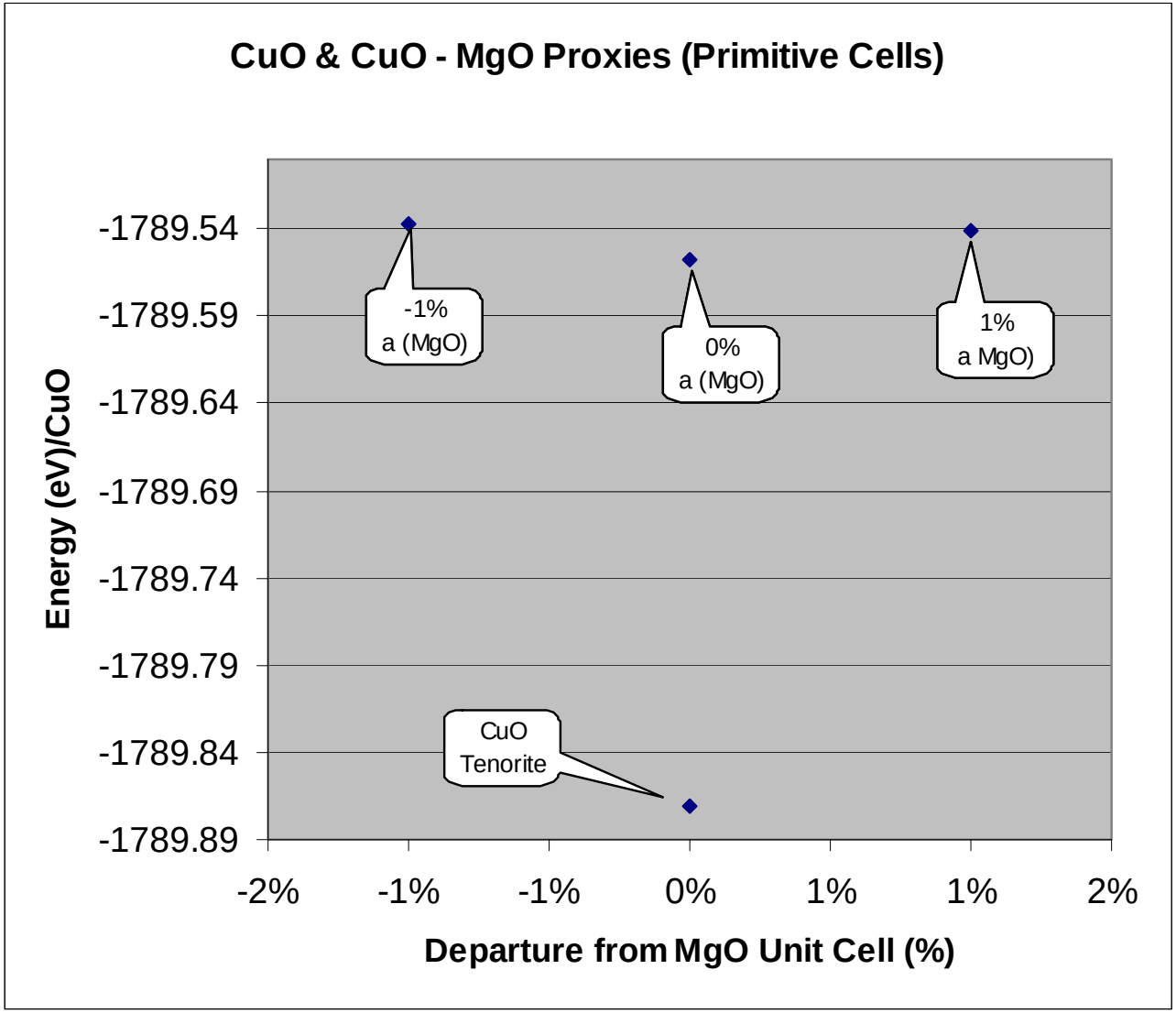
Comparison of Tenorite (111) to CuO – MgO Proxy (100)



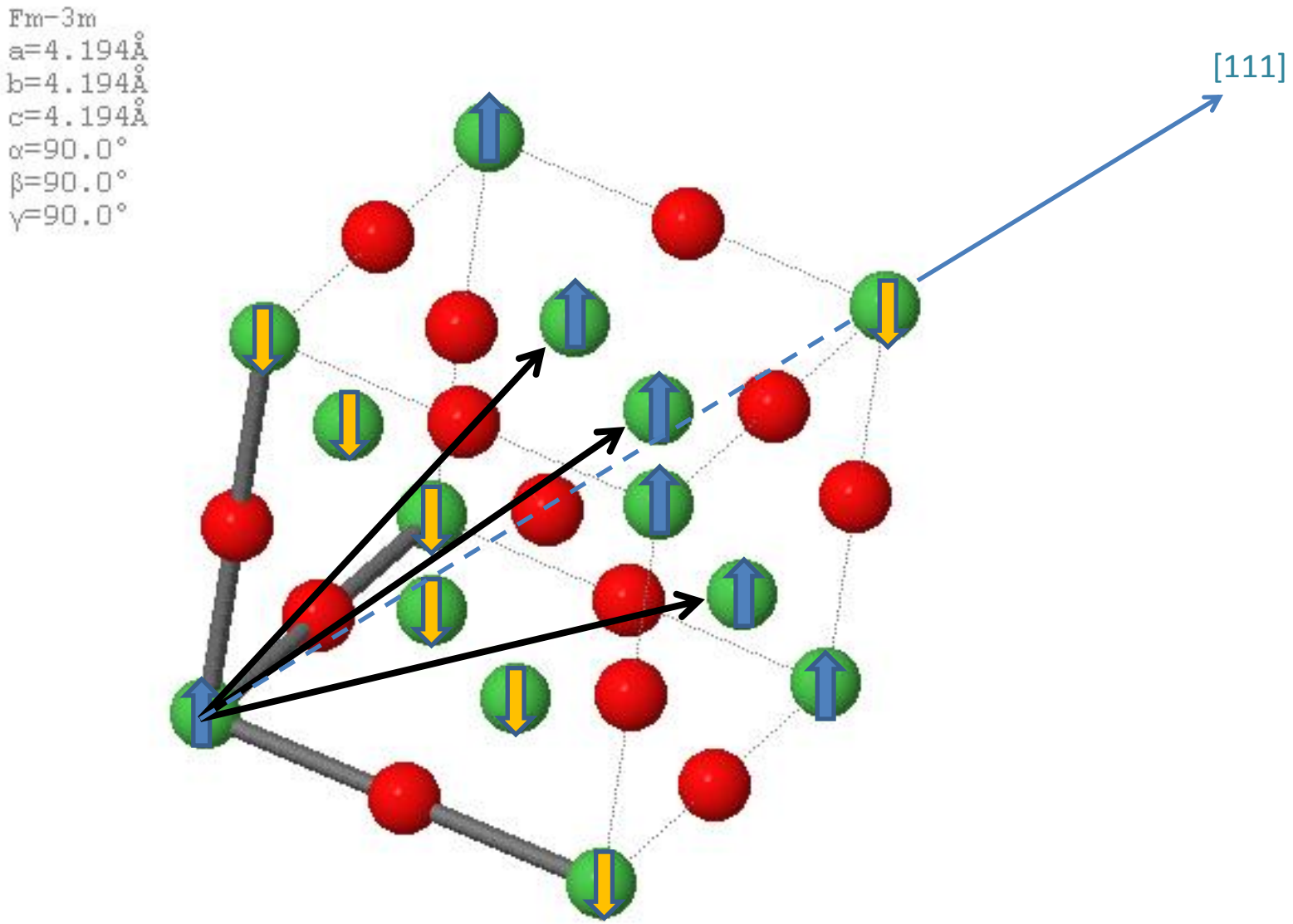
Néel Temperature vs. TMO Atomic Number



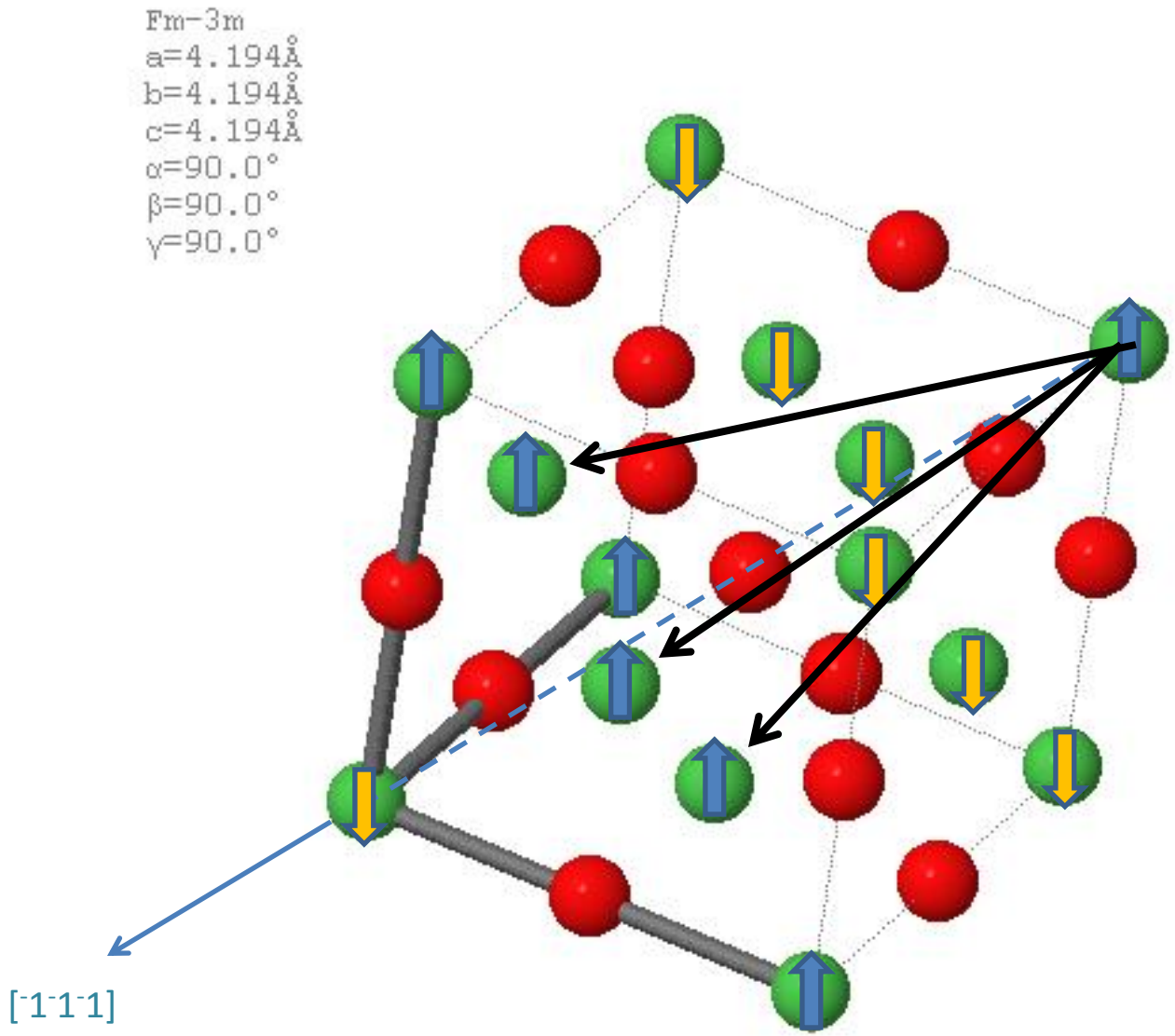
“CuO – MgO Proxy” Converged Energies

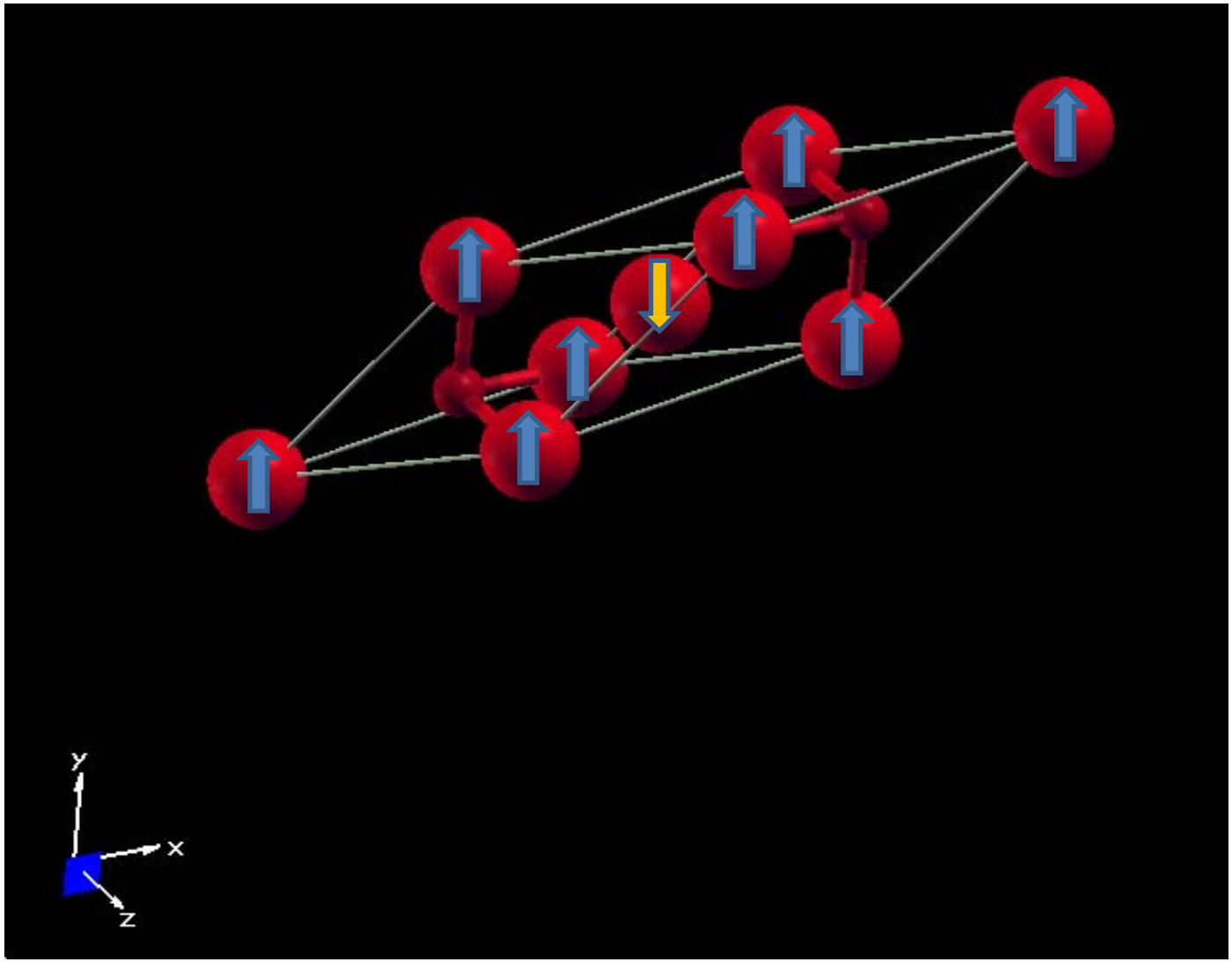


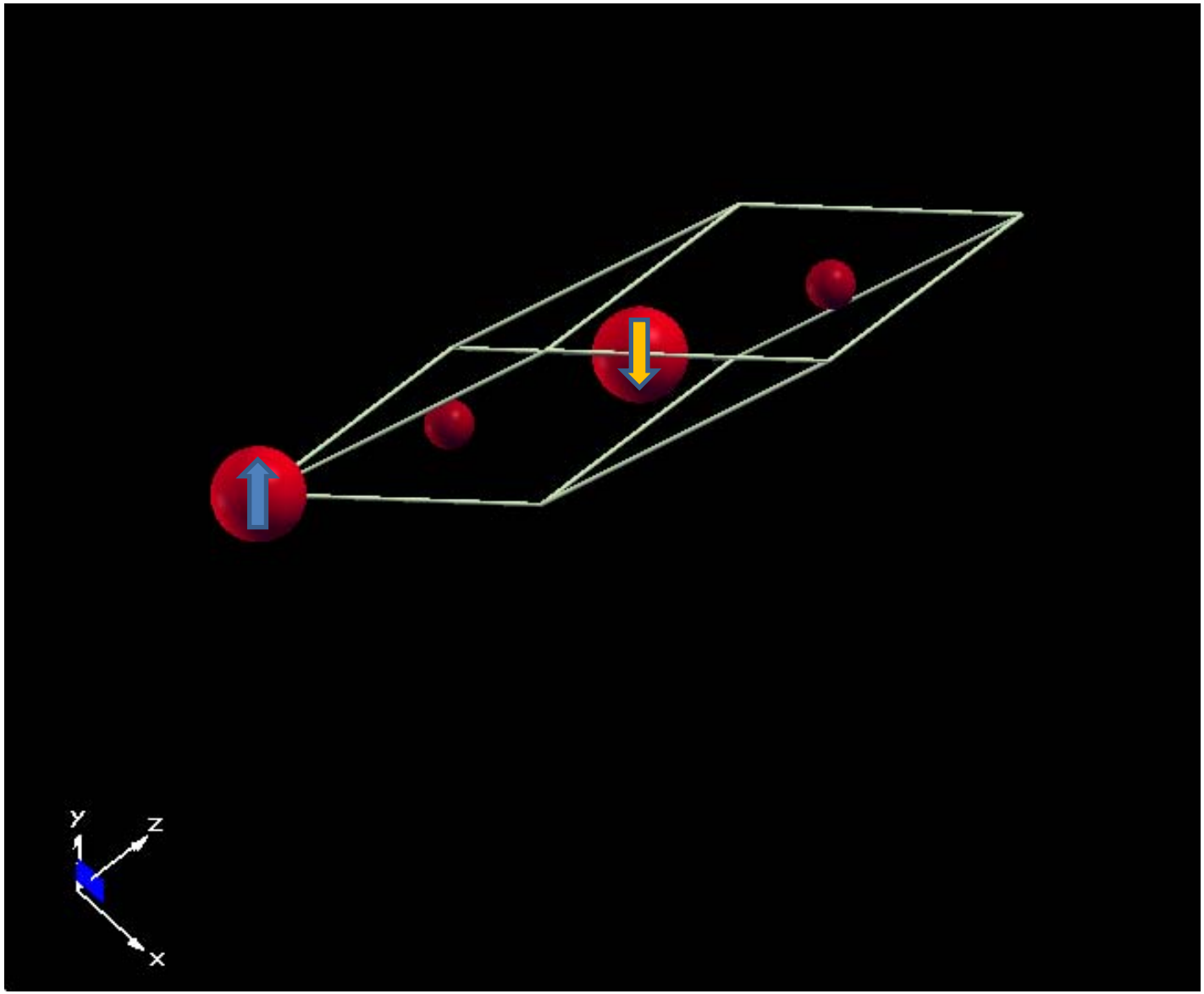
Proto-TMO AF Rock Salt



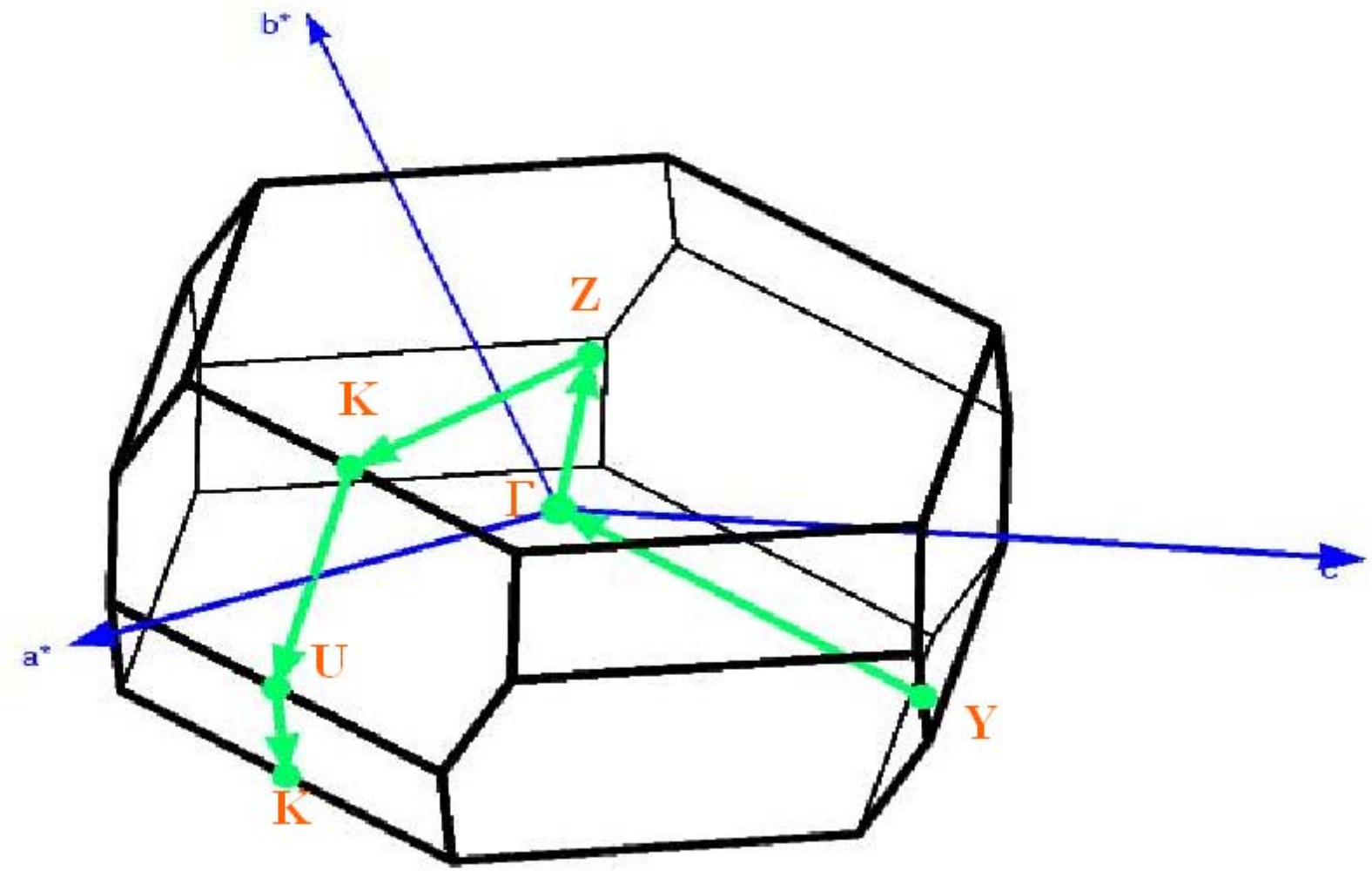
Proto-TMO AF Rock Salt




y
x
z


y
z
x

Proto-TMO AF BZ



Extended Hubbard Hamiltonian

Qualitative Description of the Physical Properties of Antiferromagnetic Insulators

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

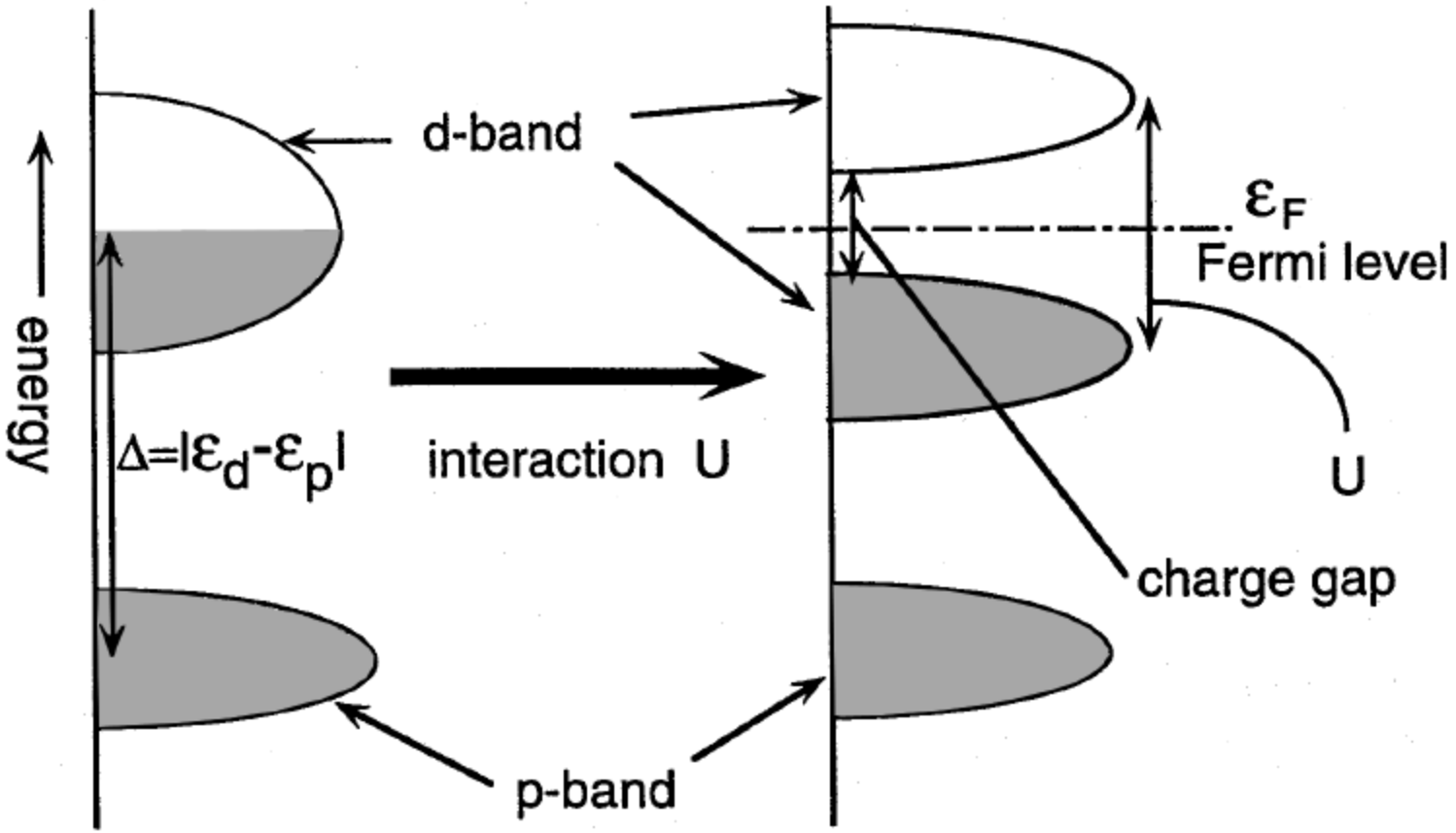
One-electron "band" term

On-site "Hubbard" double occupation coulomb repulsion

Off-site repulsion

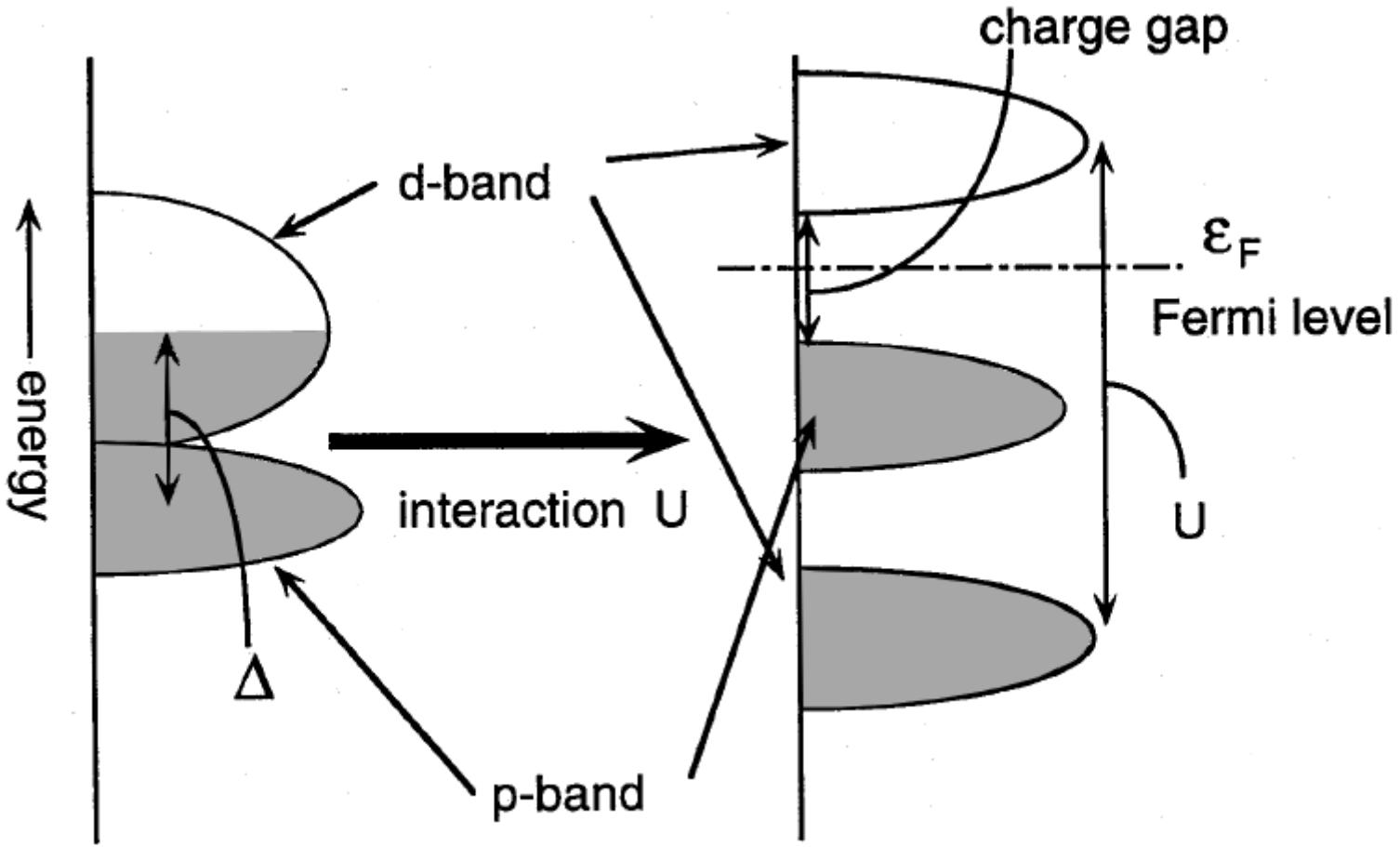
$$kT_N \sim 4t^2 / S^2 U$$

Mott-Hubbard Insulator



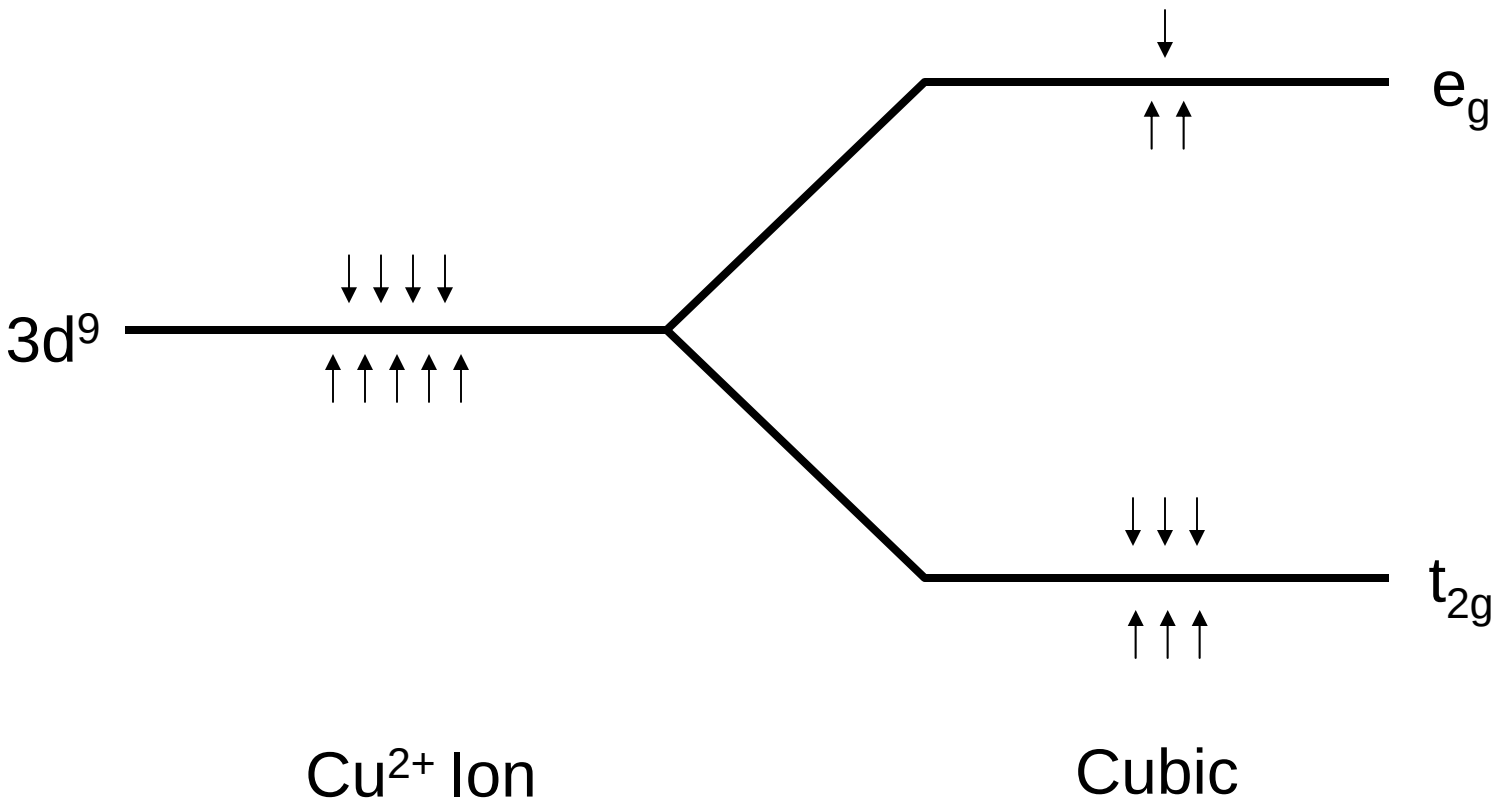
After Imada, et al, RMP 70, 1039 (1998)

Charge Transfer Insulator



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

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



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

On Seeking Insight from Numbers

- "The computer is a tool for clear thinking."

  Freeman Dyson

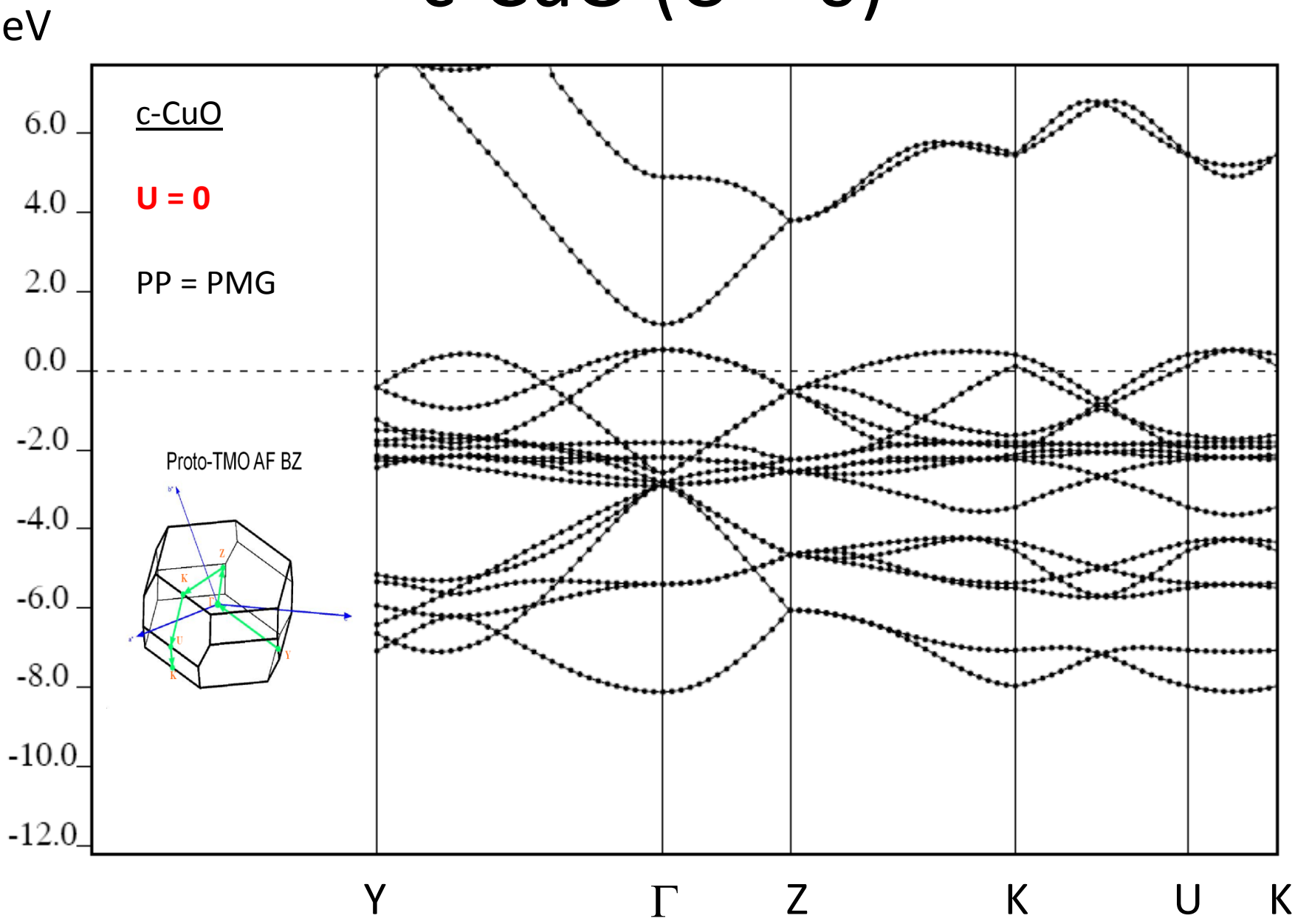
- "Garbage In, Garbage Out"

  Anon., IBM ca. 1954

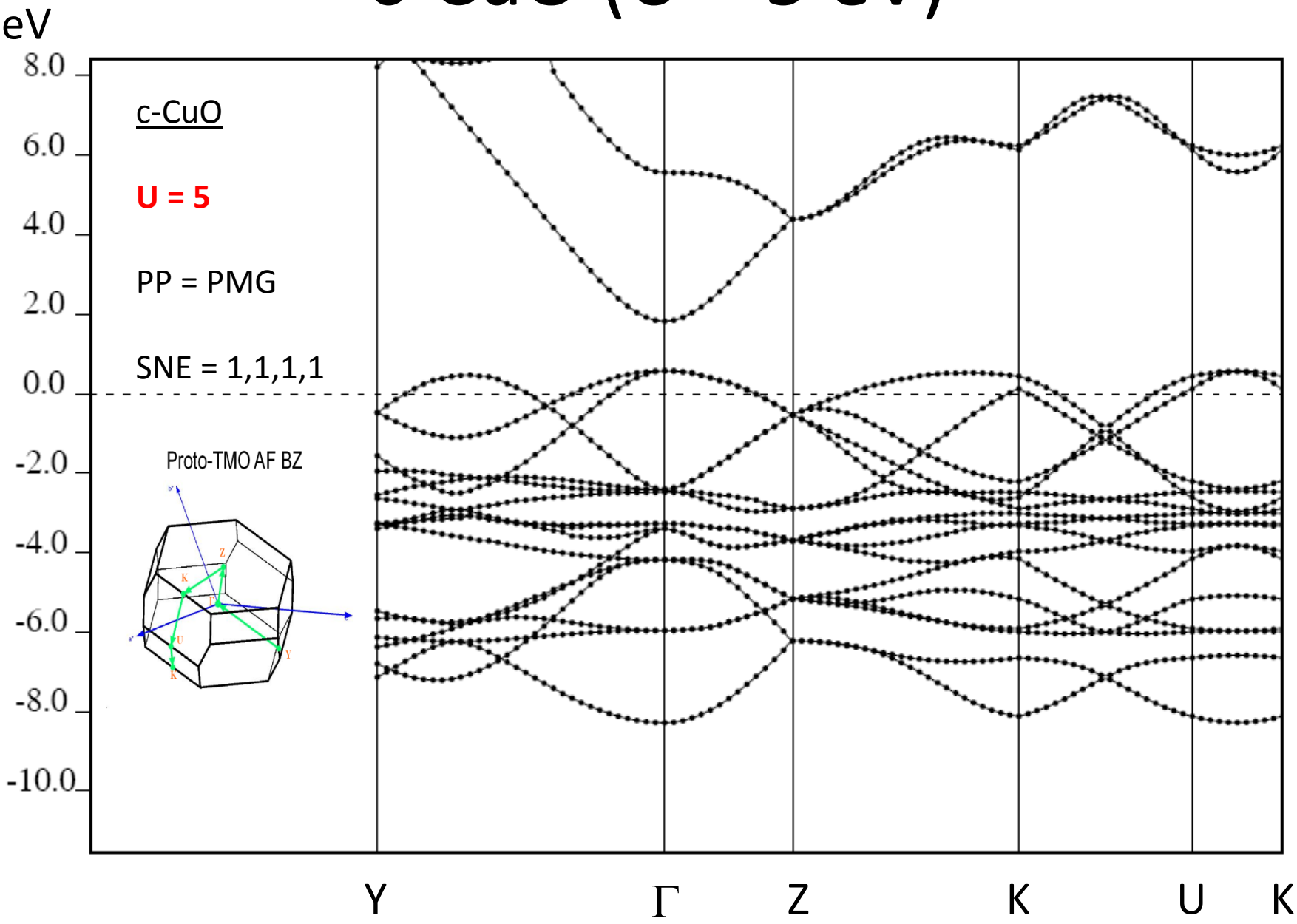
  – Q: "Pray, Mr. Babbage, if you put into the machine wrong figures, will the right answers come out?"

  – A: "I am not able rightly to comprehend the kind of confusion of ideas that could provoke such a question."

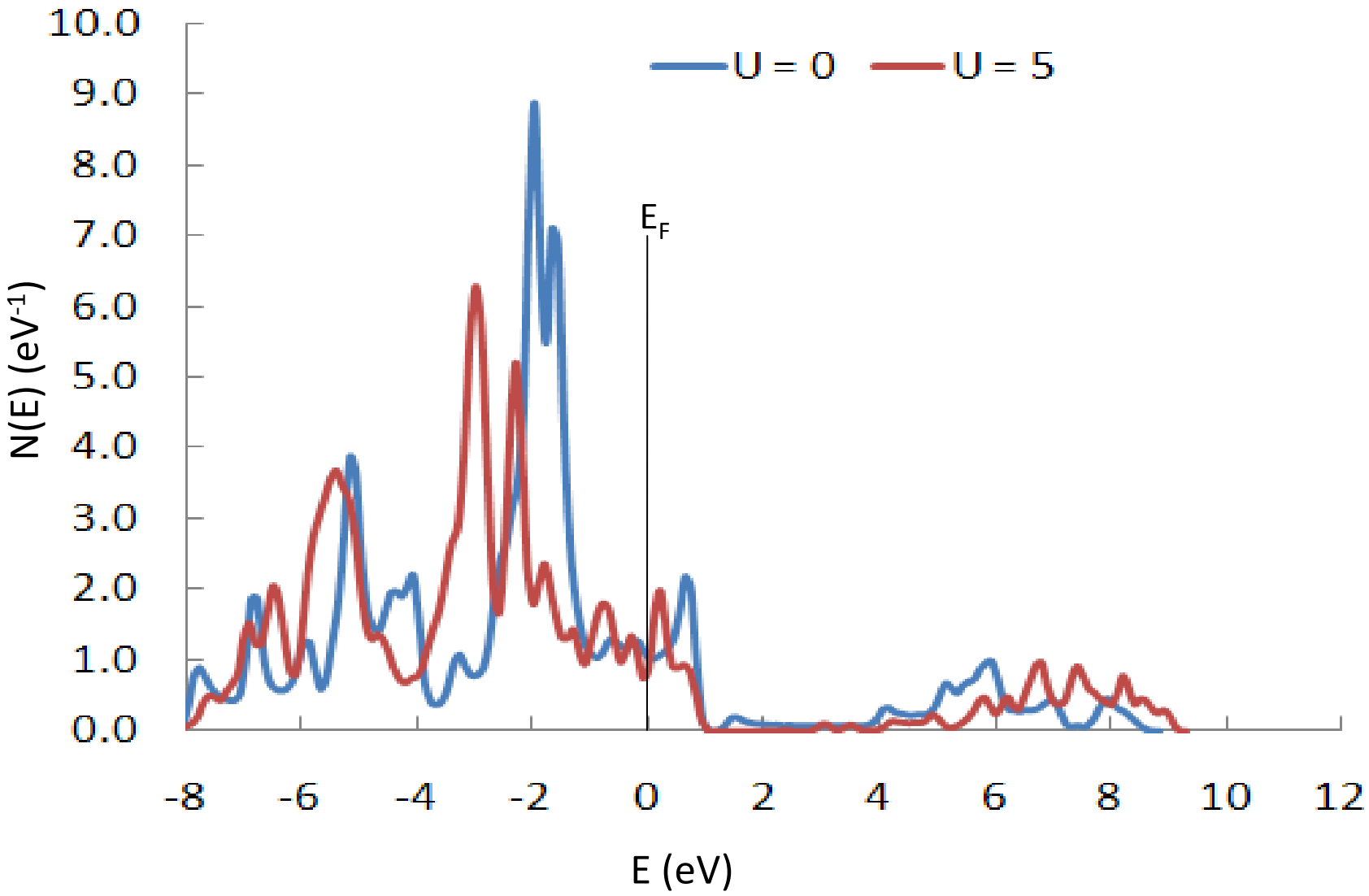
c-CuO (U = 0)

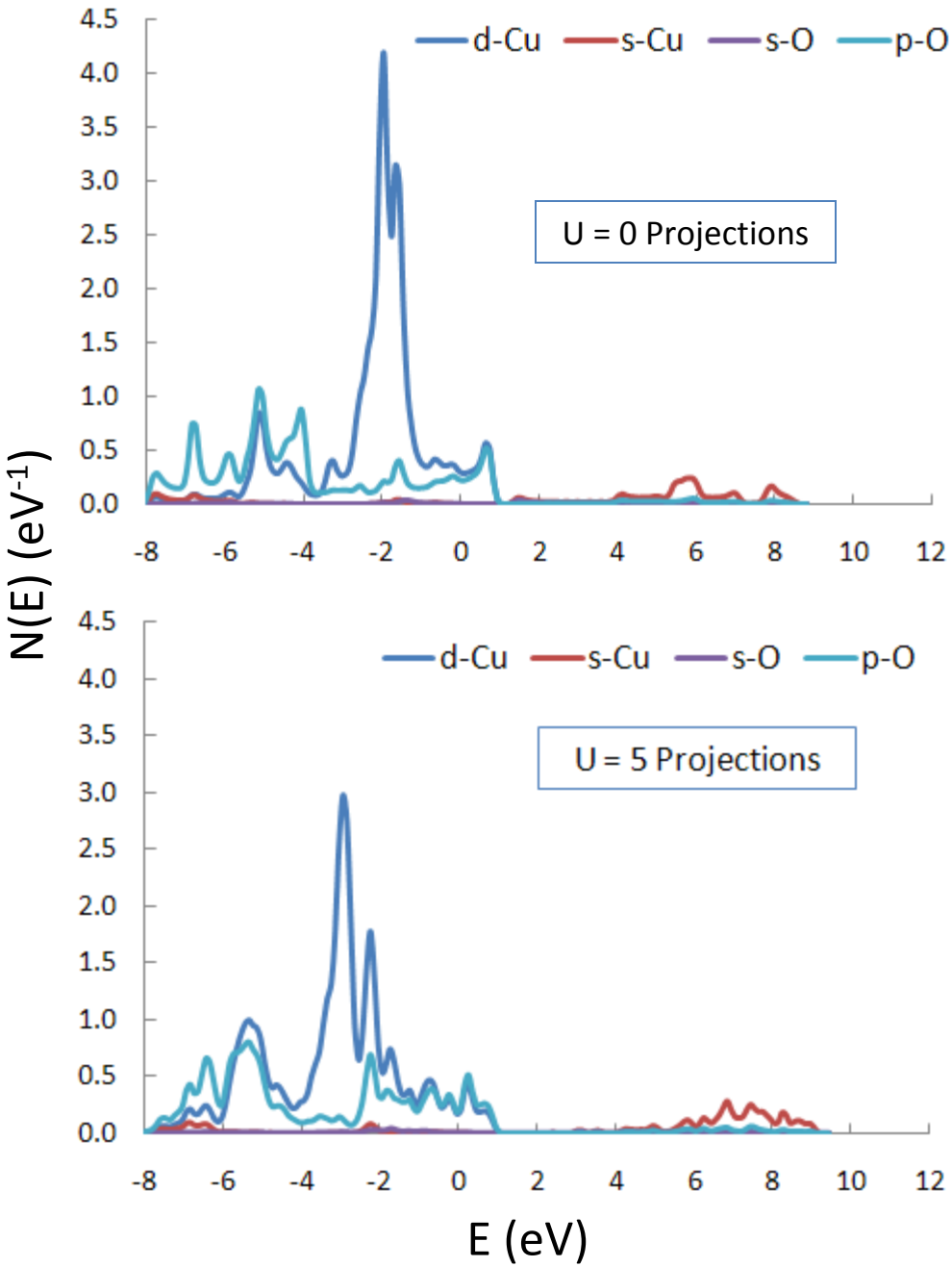

eV
c-CuO
U = 0
PP = PMG
Proto-TMO AF BZ
6.0
4.0
2.0
0.0
-2.0
-4.0
-6.0
-8.0
-10.0
-12.0
Y
Γ
Z
K
U
K

c-CuO (U = 5 eV)


eV
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
-6.0
-8.0
-10.0
c-CuO
U = 5
PP = PMG
SNE = 1,1,1,1
Proto-TMO AF BZ
Y
Γ
Z
K
U
K

c-CuO Density-of-States



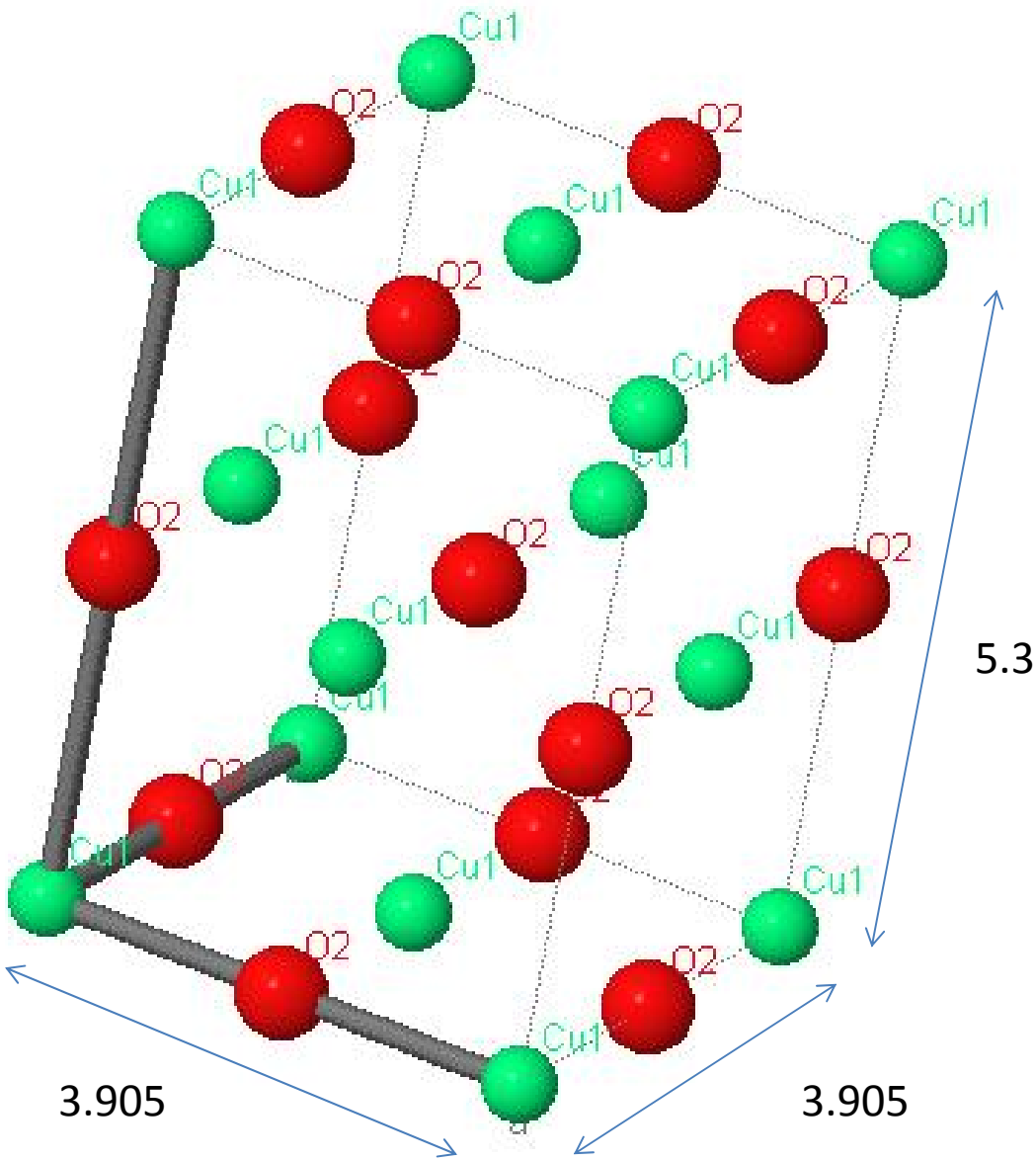


DOS Projected on PP Orbitals

Tetragonal CuO

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

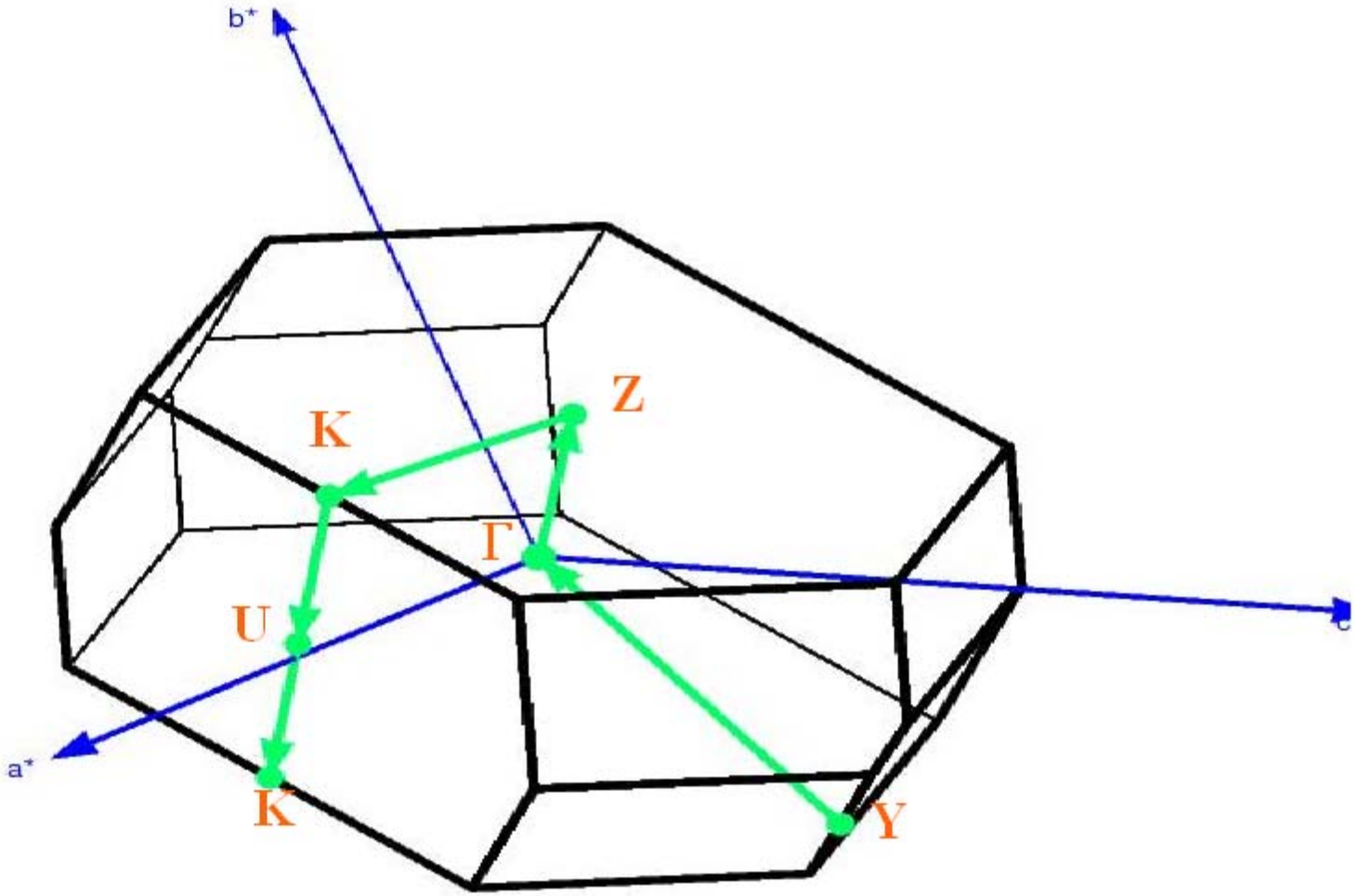
c/a = 1.36



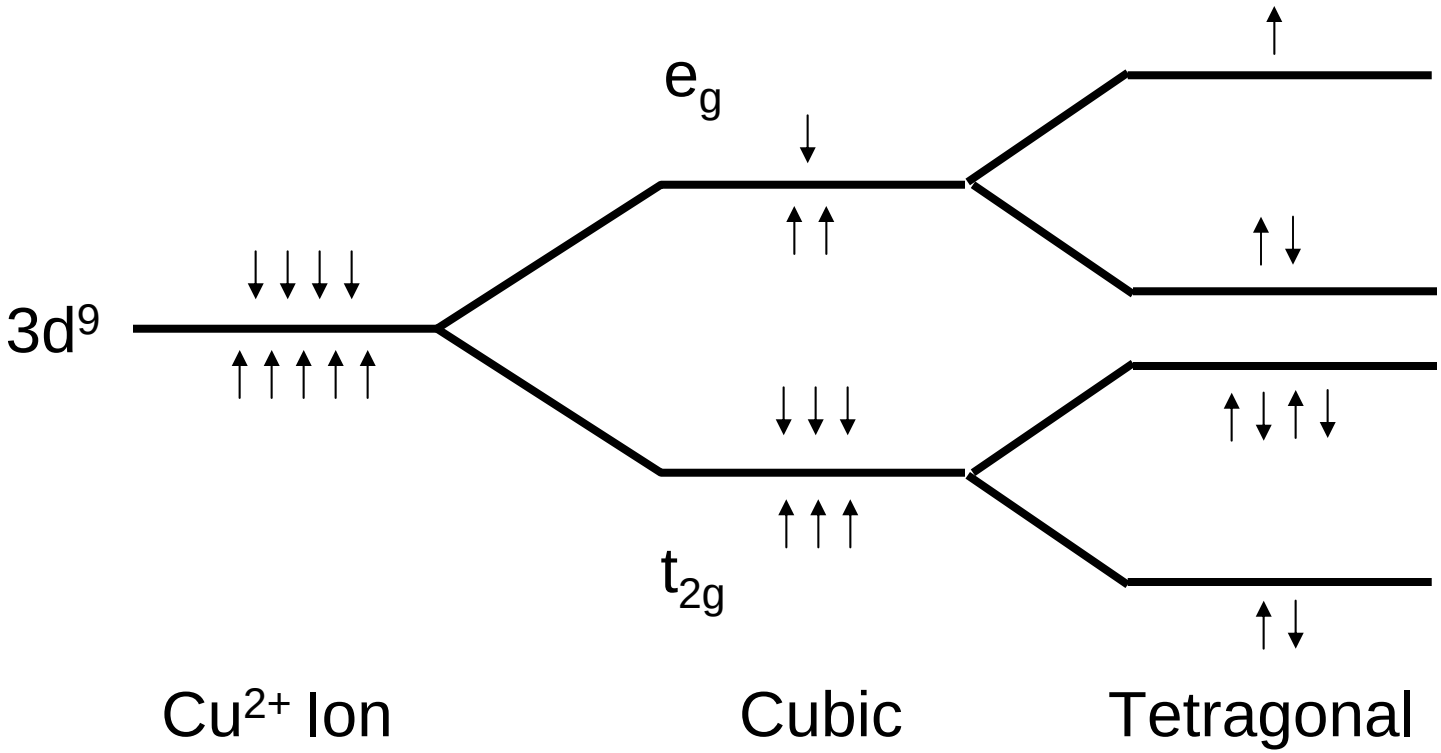
Measurements

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

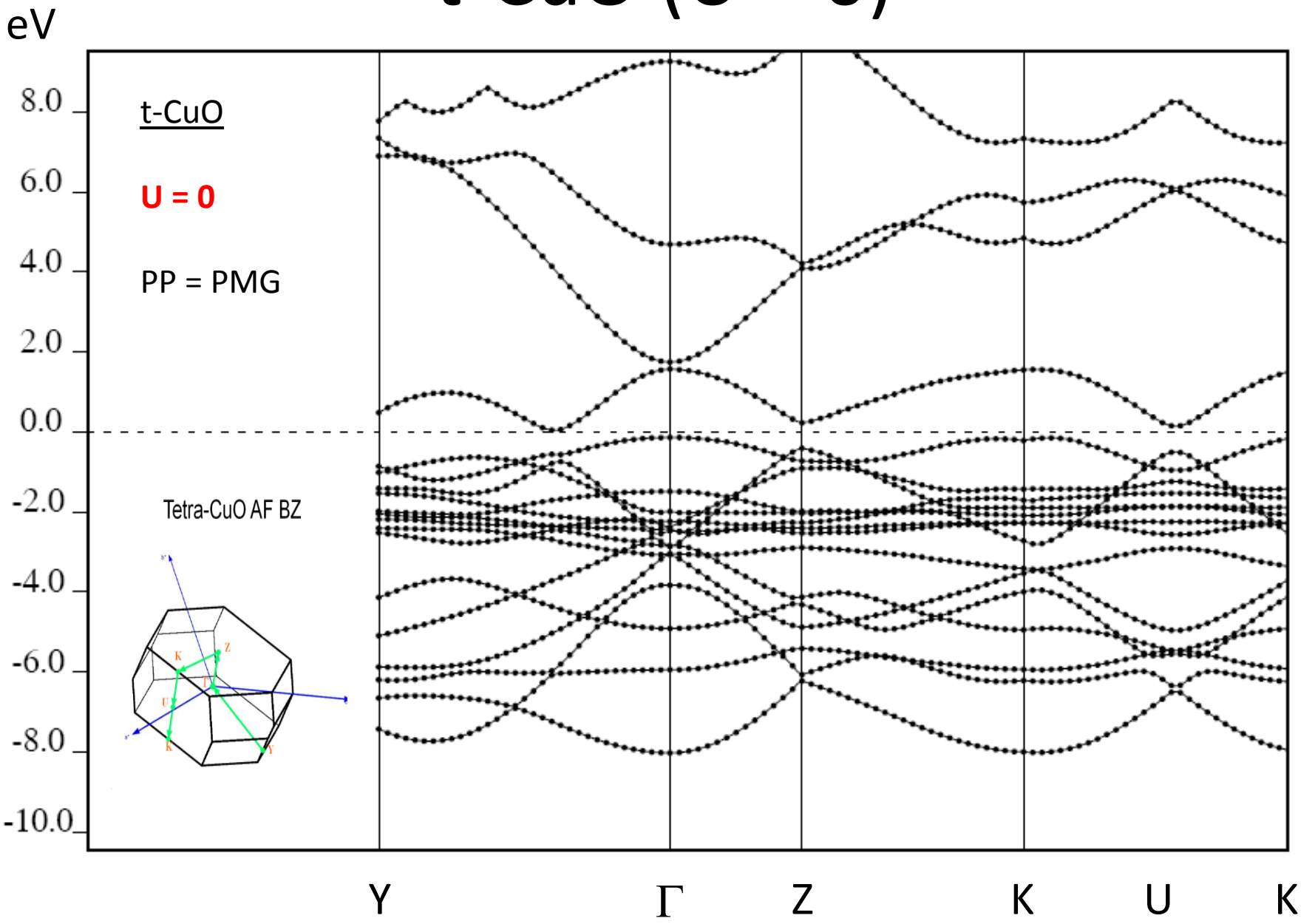
Tetra-CuO AF BZ



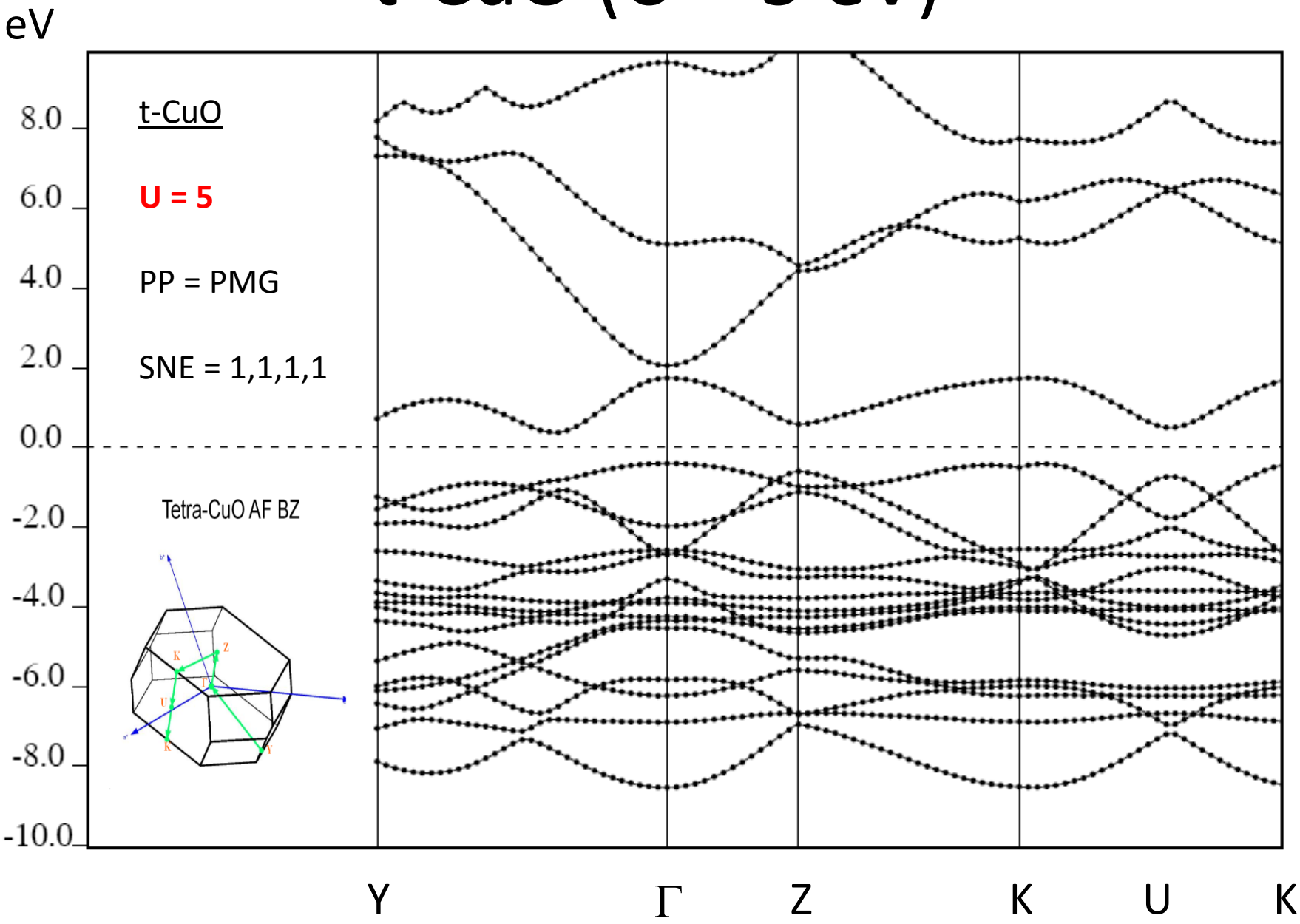
Cu2+ 3d Multiplet Splitting (Tetra)



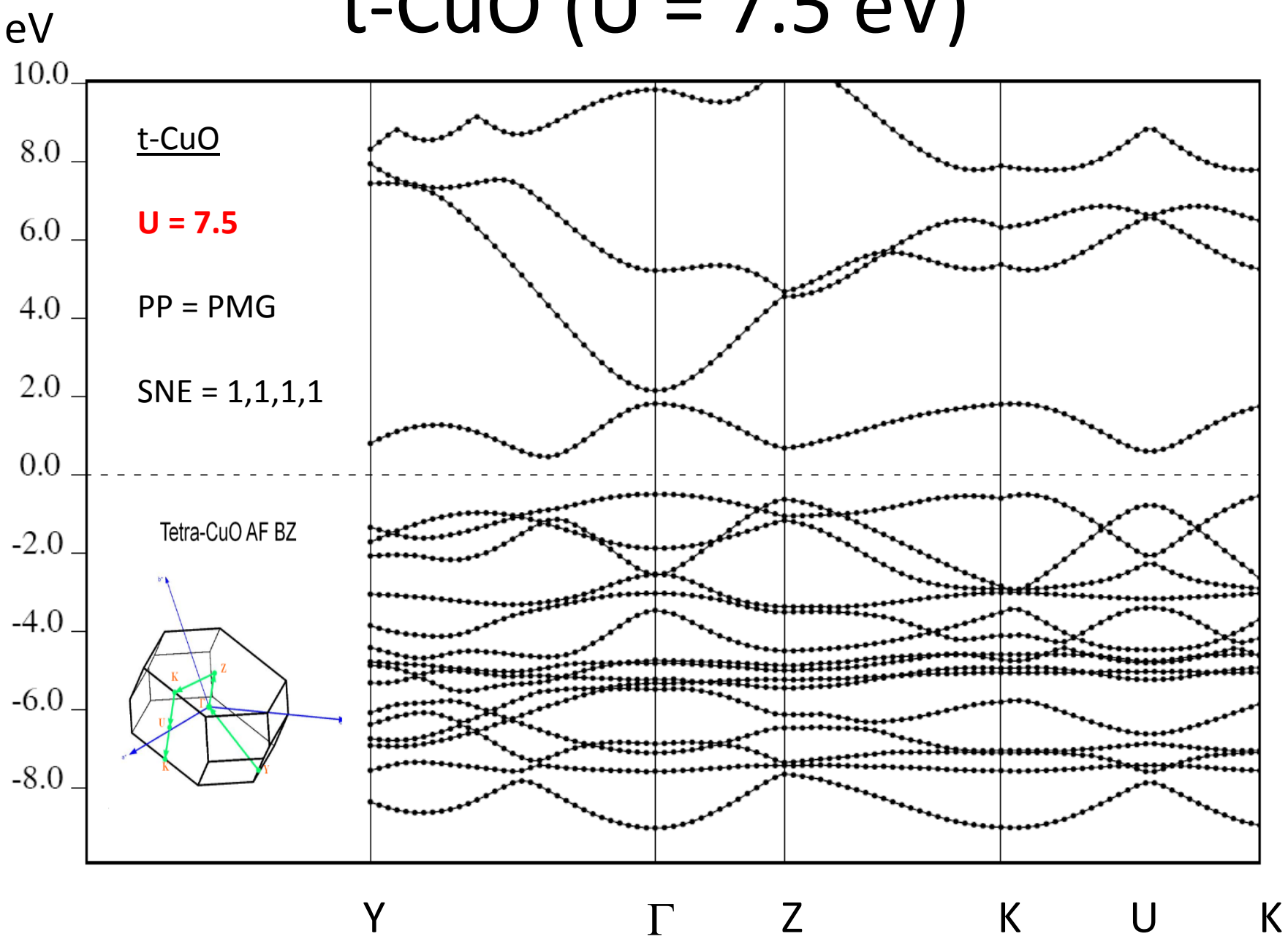
t-CuO (U = 0)


eV
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
-6.0
-8.0
-10.0
t-CuO
U = 0
PP = PMG
Tetra-CuO AF BZ
Y
Γ
Z
K
U
K

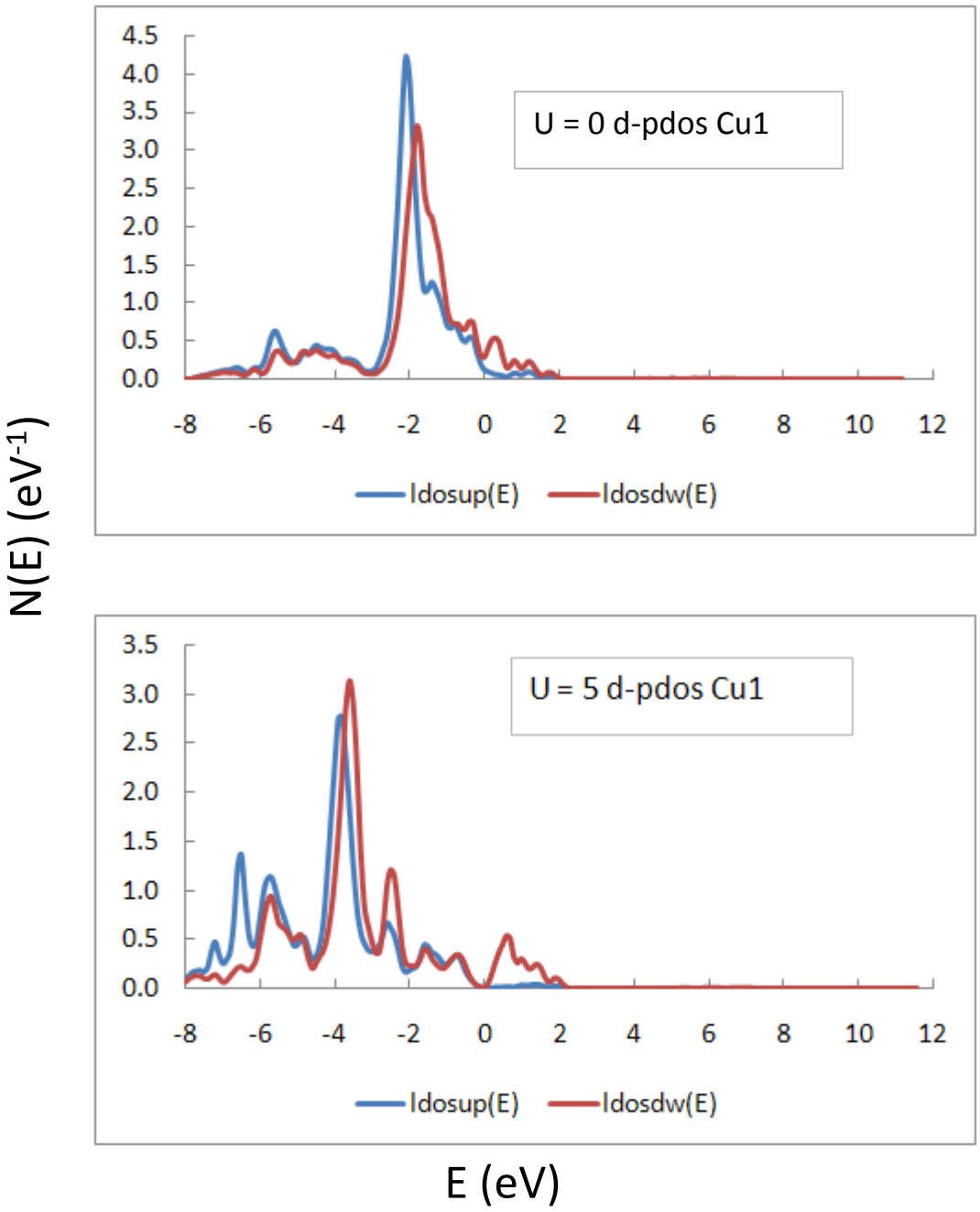
t-CuO (U = 5 eV)


eV
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
-6.0
-8.0
-10.0
t-CuO
U = 5
PP = PMG
SNE = 1,1,1,1
Tetra-CuO AF BZ
Y
Γ
Z
K
U
K

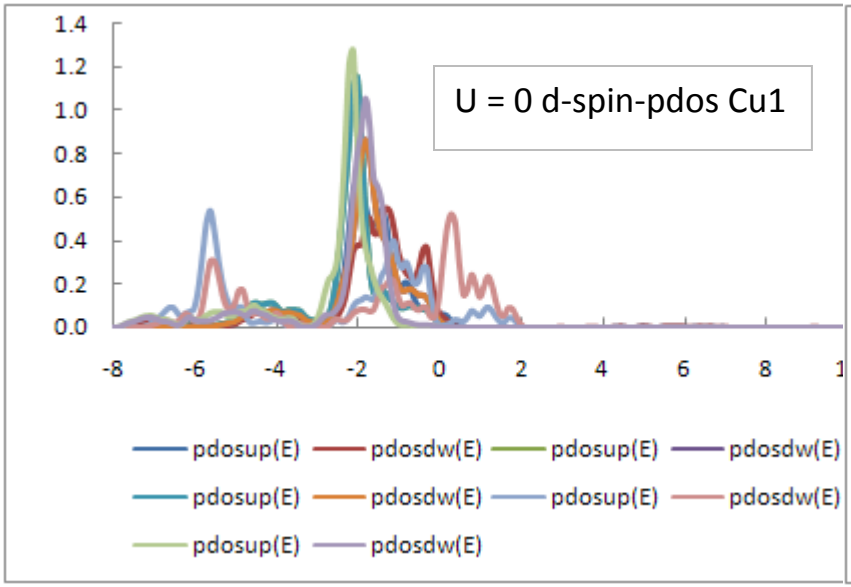
t-CuO (U = 7.5 eV)

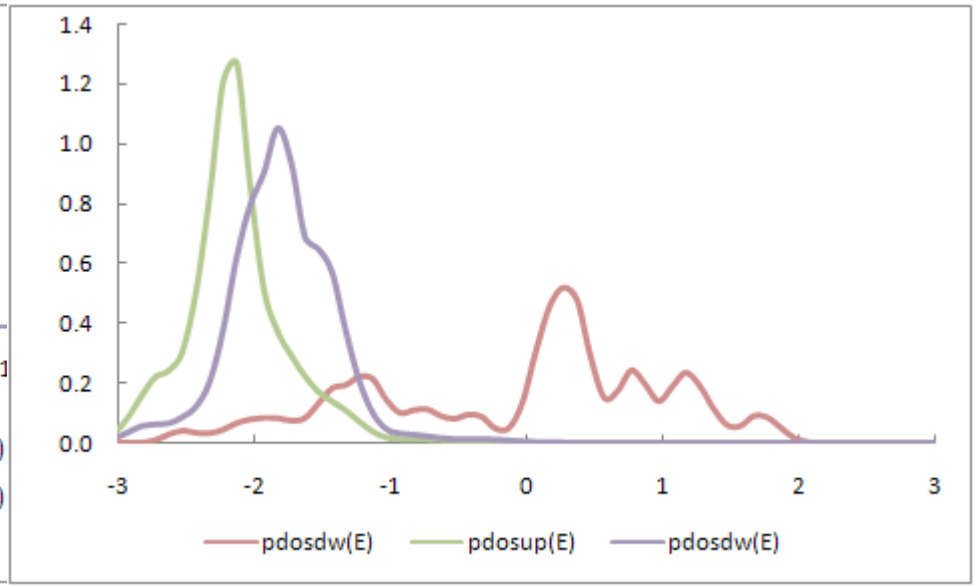

eV
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
-6.0
-8.0
t-CuO
U = 7.5
PP = PMG
SNE = 1,1,1,1
Tetra-CuO AF BZ
Y
Γ
Z
K
U
K

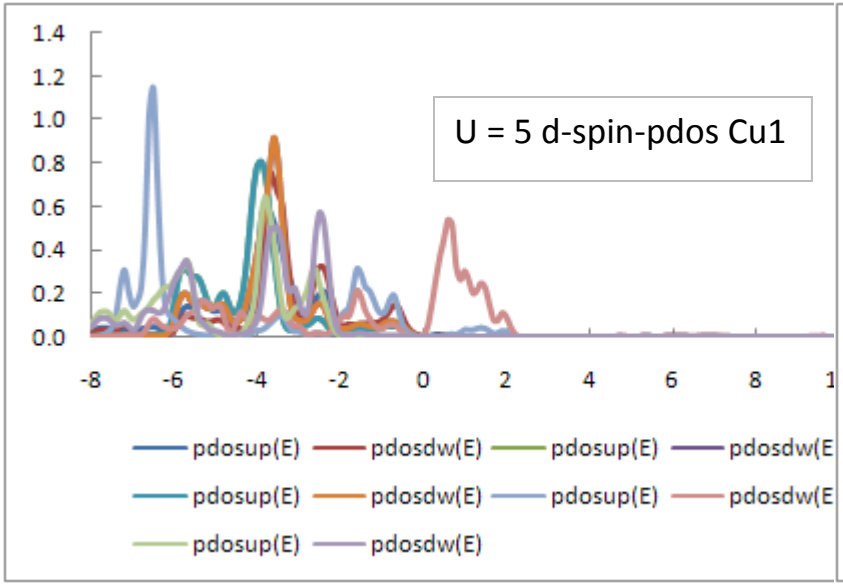
Spin-DOS Projected on Cu 3d-Orbitals As Function of Hubbard U

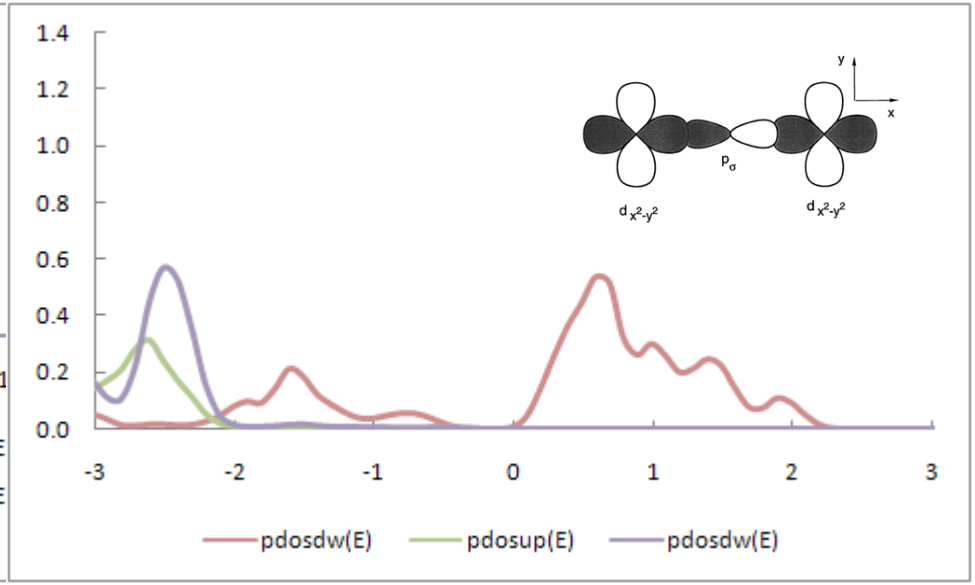


Spin Composition of Cu 3d pDOS as fn(Hubbard)

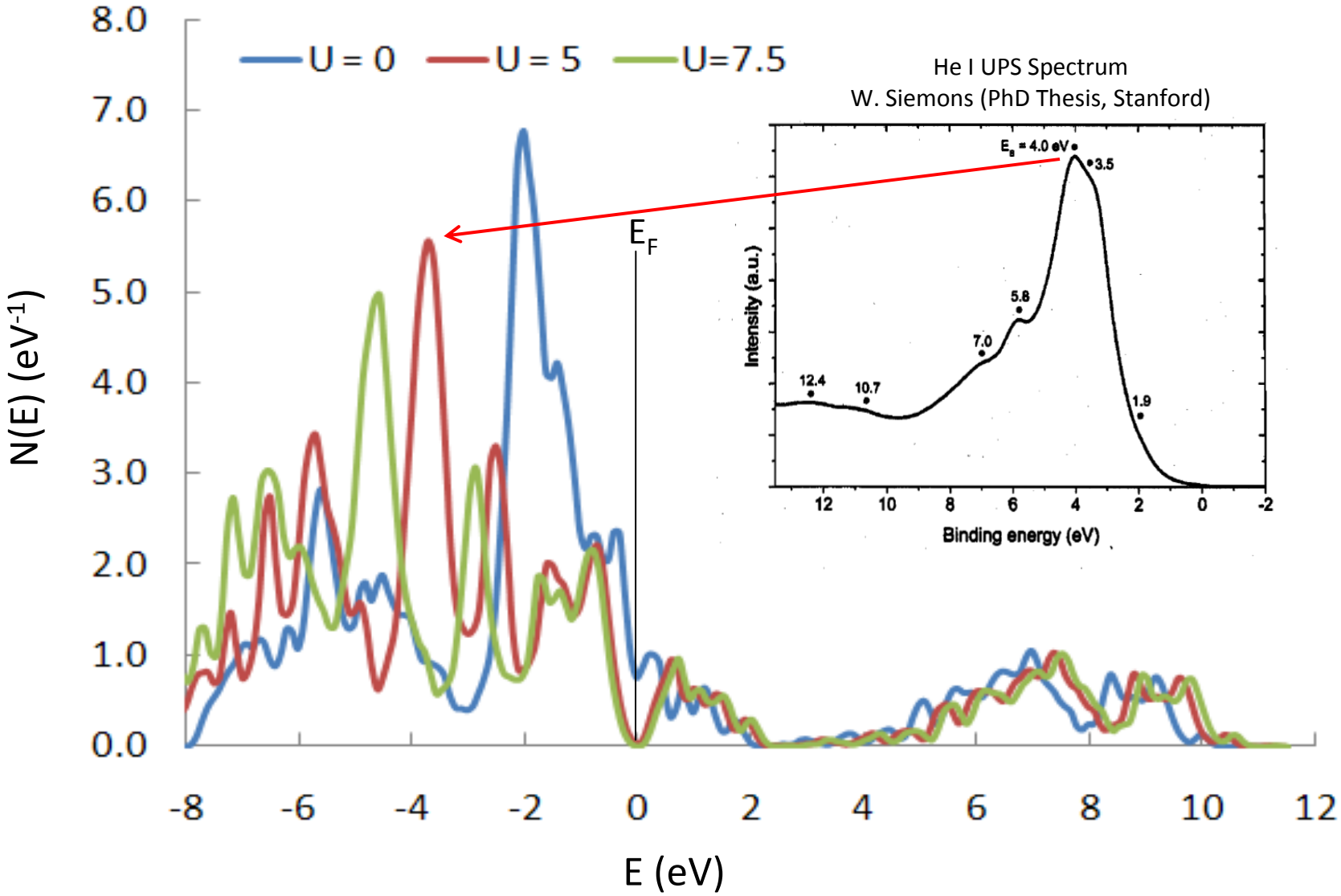






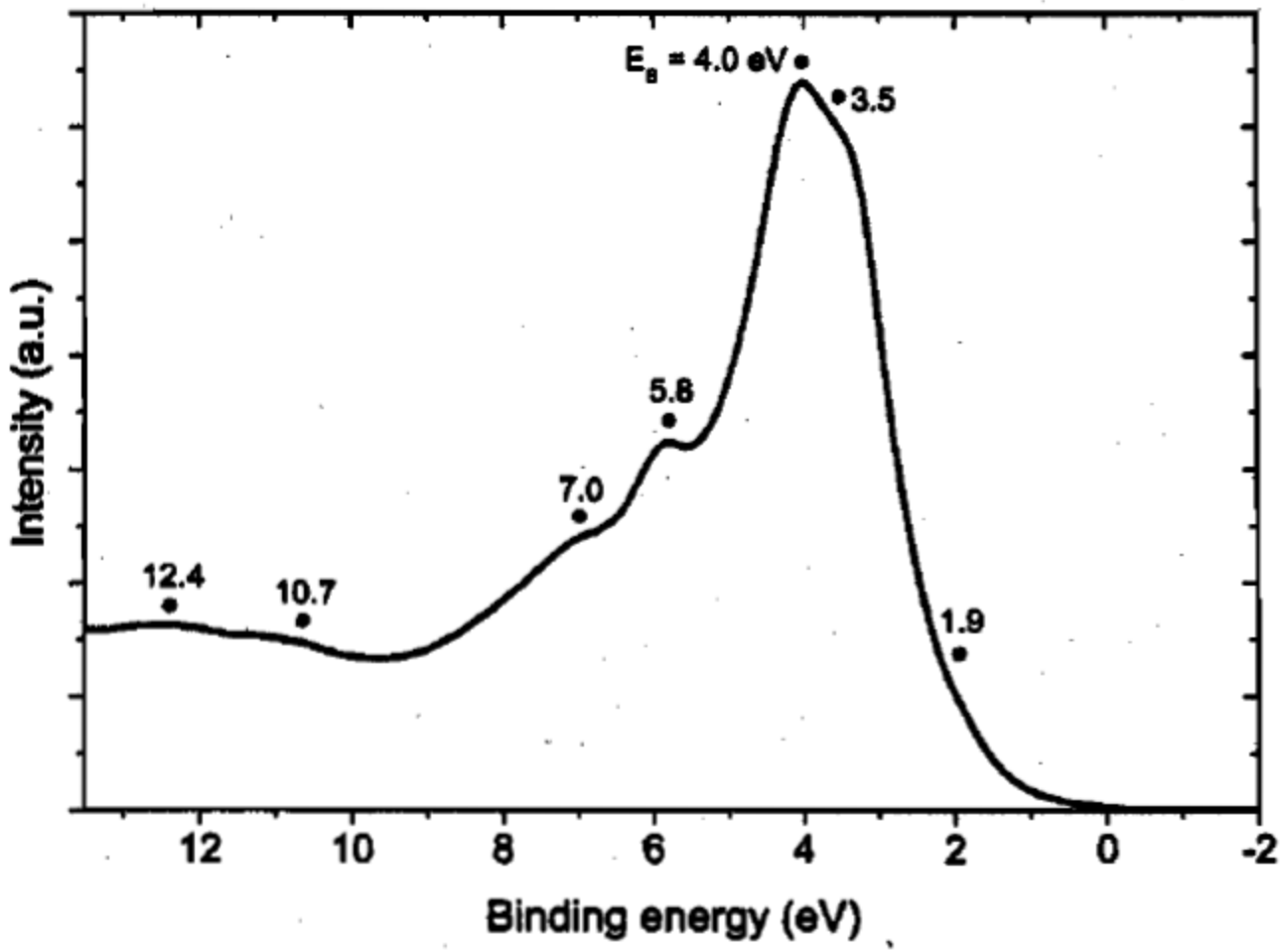


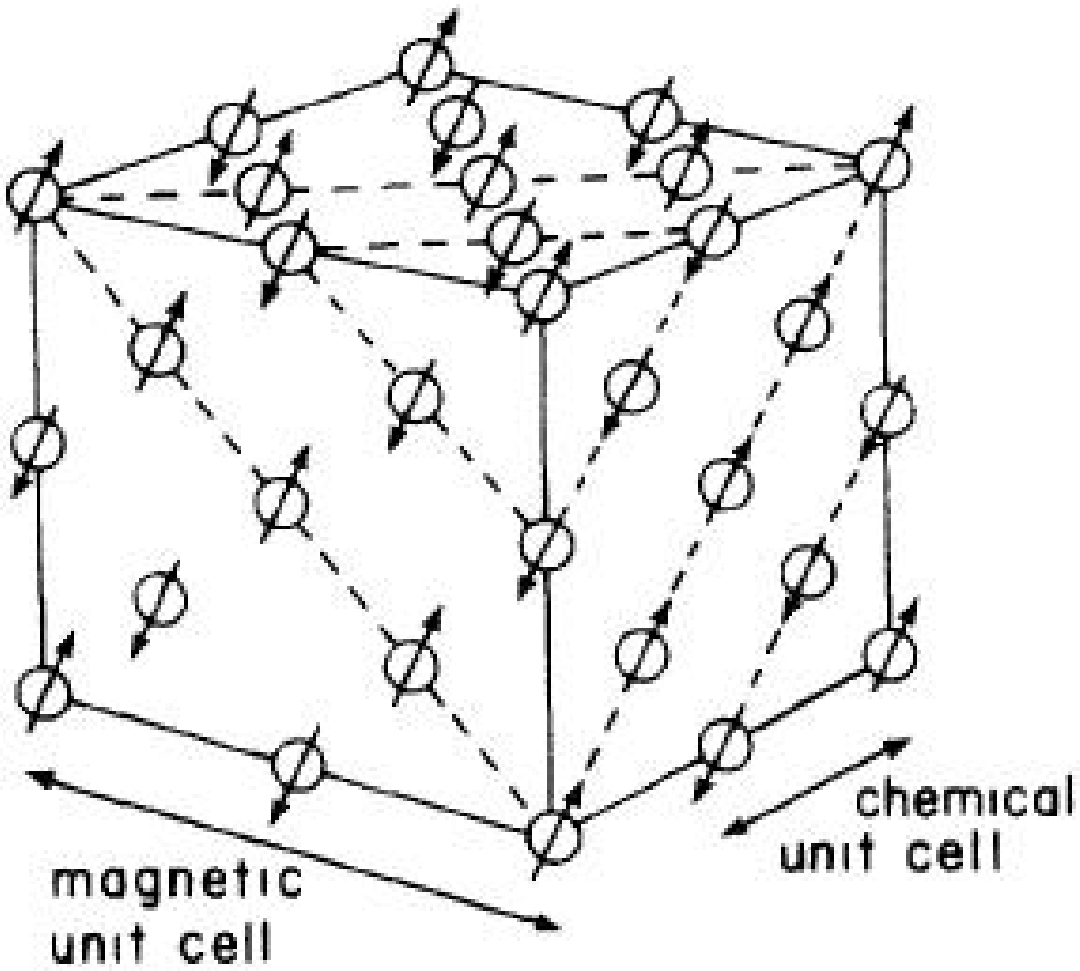
t-CuO Density-of-States

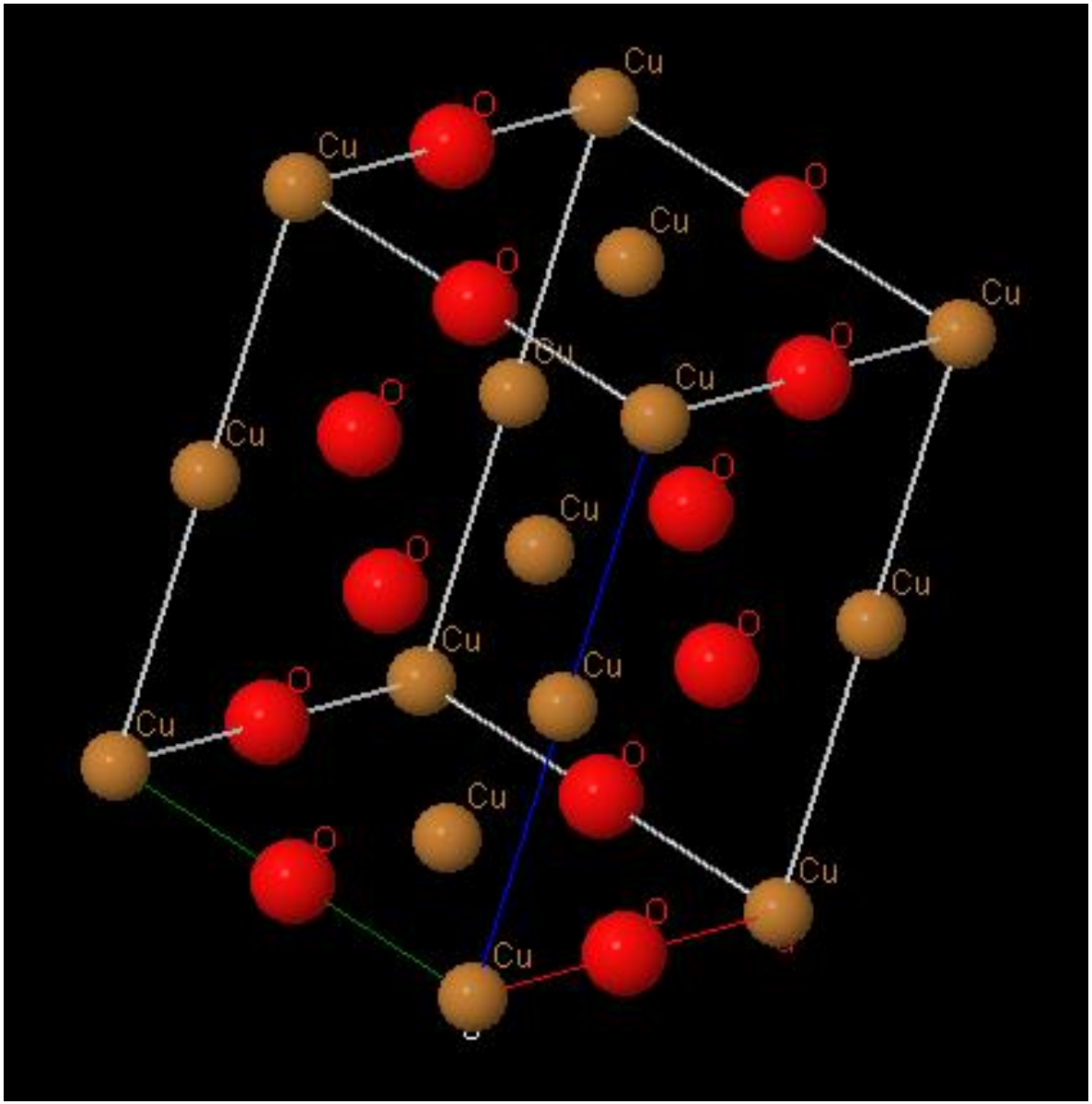


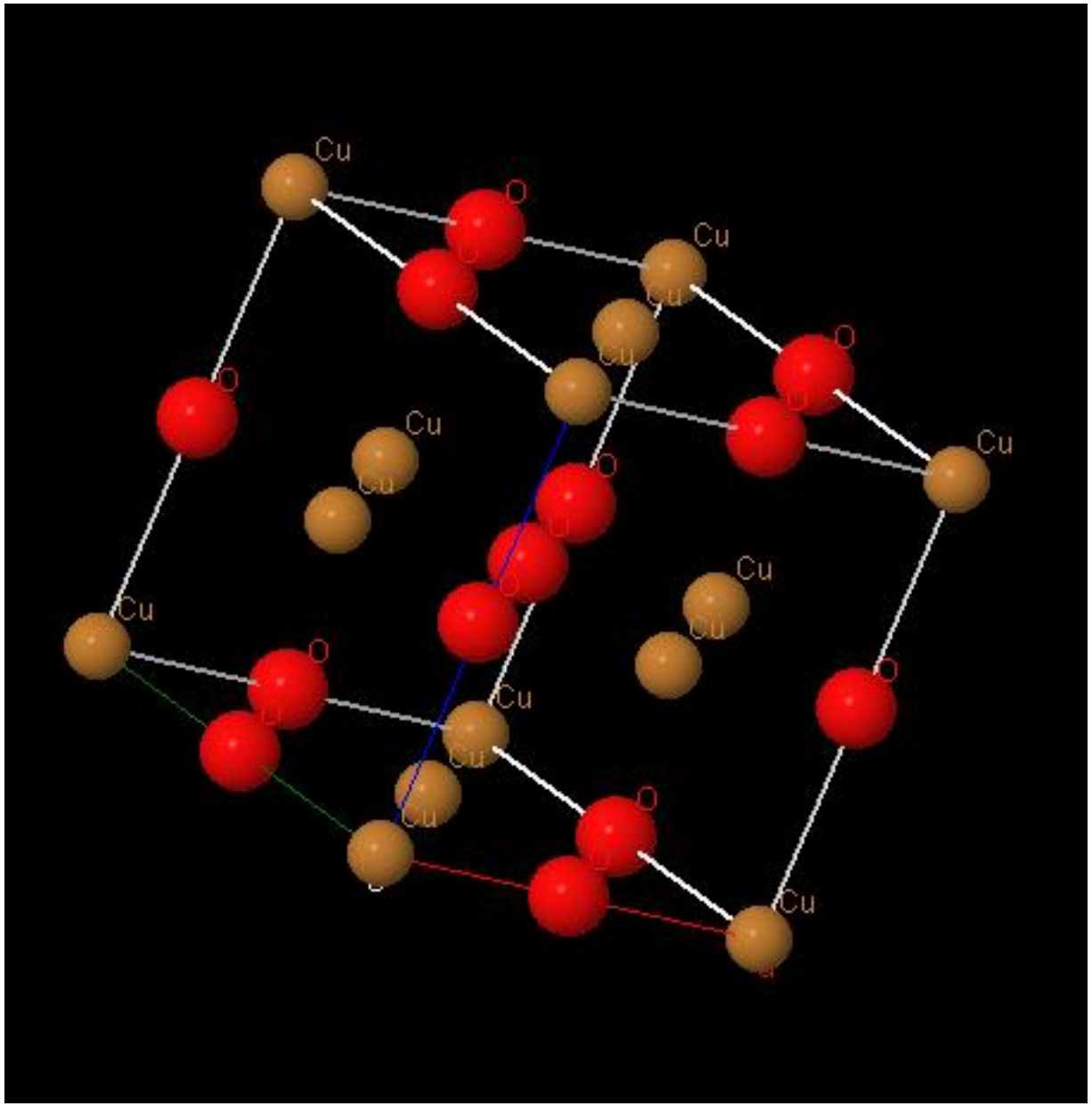
Conclusions & Homework

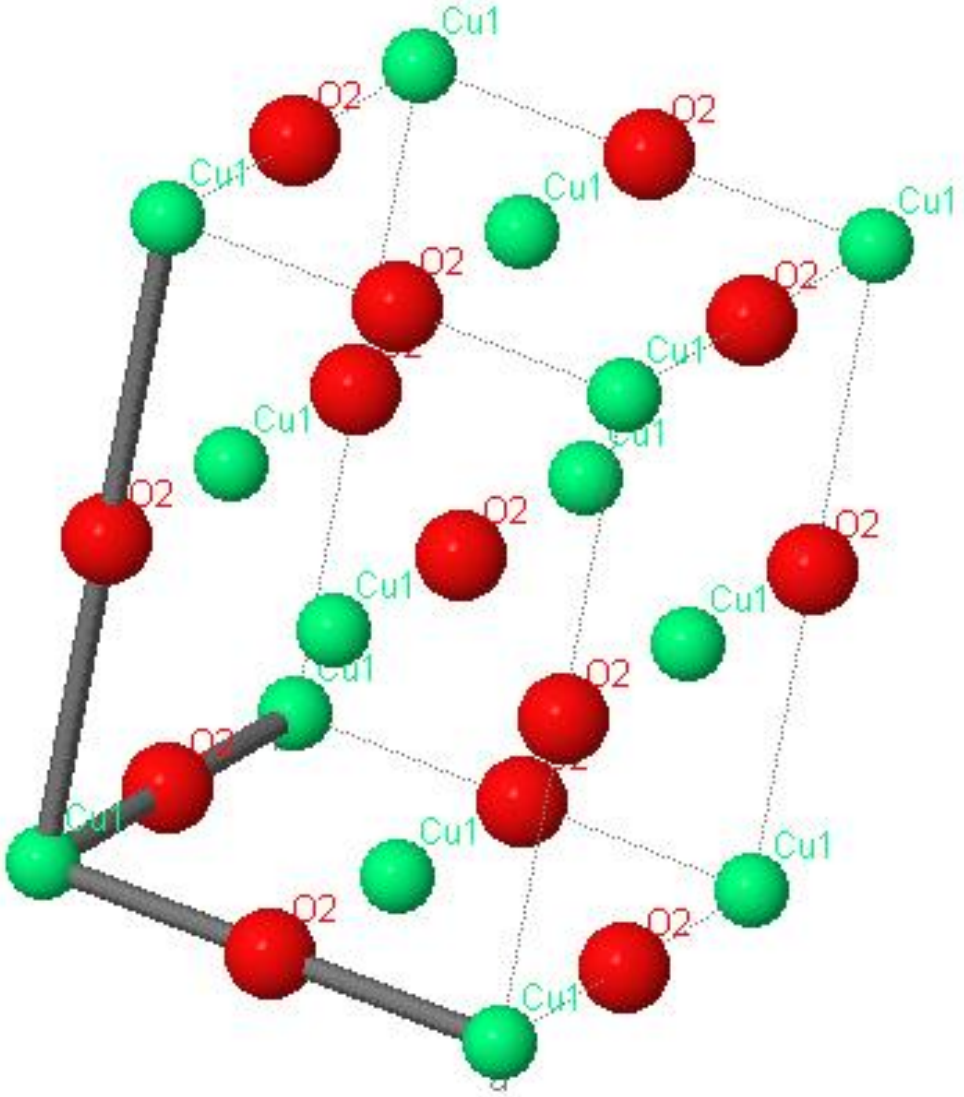
- If you could make it, cubic rock salt copper monoxide would be a metal!
- Distortions (J-T?) are necessary to "spread" the Cu $3d^{10}$ multiplet allowing Hubbard to separate spins creating the $3d^9$ AF ground state and thus HTS.
- To-do
  - Check the LDA+U PW-PP package on tenorite
  - Compute "tetragonal supercell" to get to CuO plane properties.
  - Then "dope" and perform e-p calculation to "see what happens."


E_g = 4.0 eV
3.5
5.8
7.0
12.4
10.7
1.9
Intensity (a.u.)
12
10
8
6
4
2
0
-2
Binding energy (eV)


chemical
unit cell
magnetic
unit cell


Cu
O
Cu
O
Cu
O
Cu
O
Cu
Cu
Cu
O
Cu
O
Cu
O
Cu
O
Cu
Cu
Cu
O
Cu
O
Cu
O
Cu
O
Cu
Cu
O
Cu
O


Cu
O
Cu
O
Cu
Cu
O
Cu
Cu
O
Cu
Cu
O
Cu
O
Cu
Cu
O
Cu


Cu1
O2
Cu1
O2
Cu1
Cu1
O2
O2
Cu1
Cu1
Cu1
O2
O2
O2
Cu1
Cu1
O2
Cu1
Cu1
O2
Cu1
O2
Cu1

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

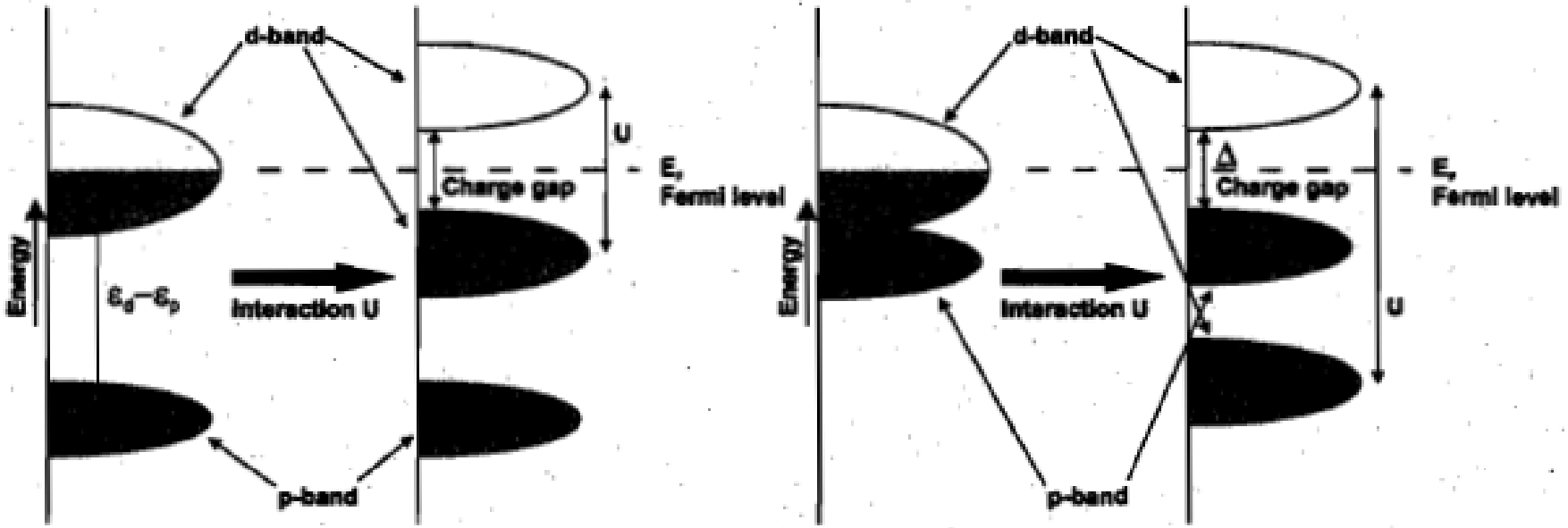
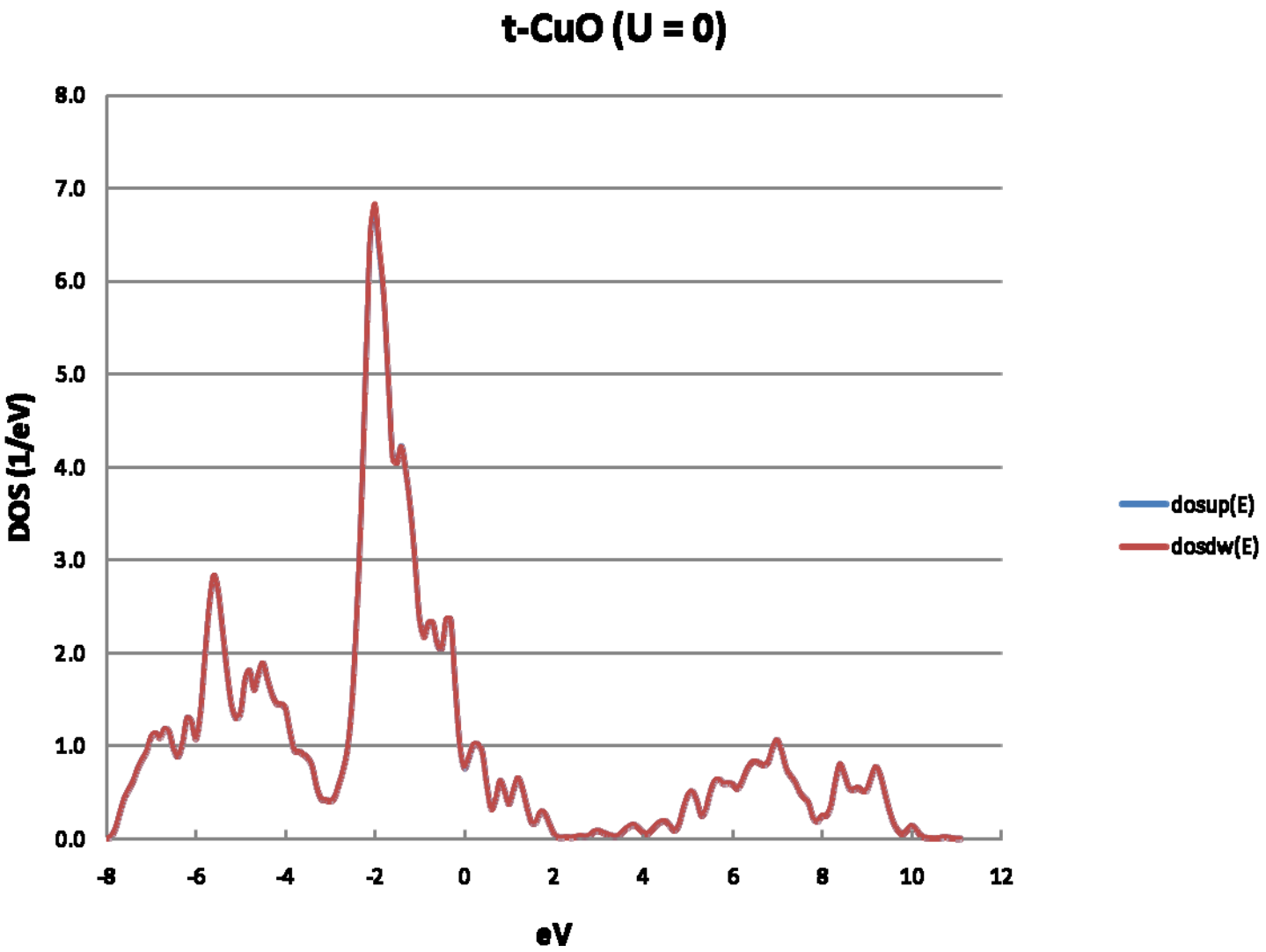
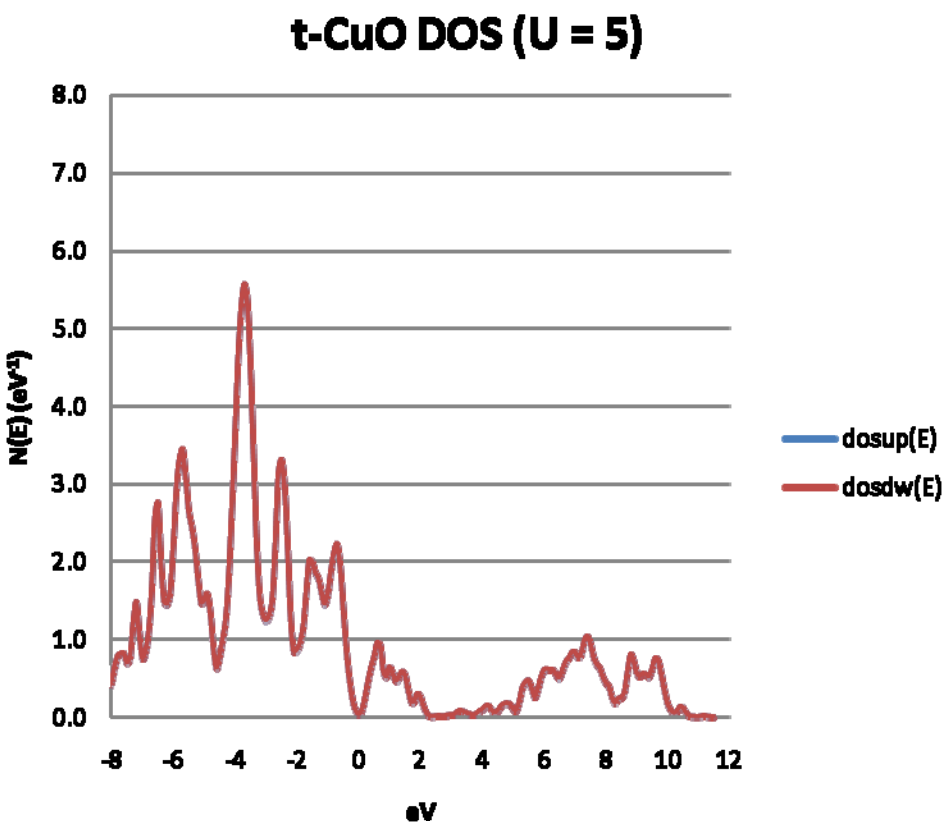
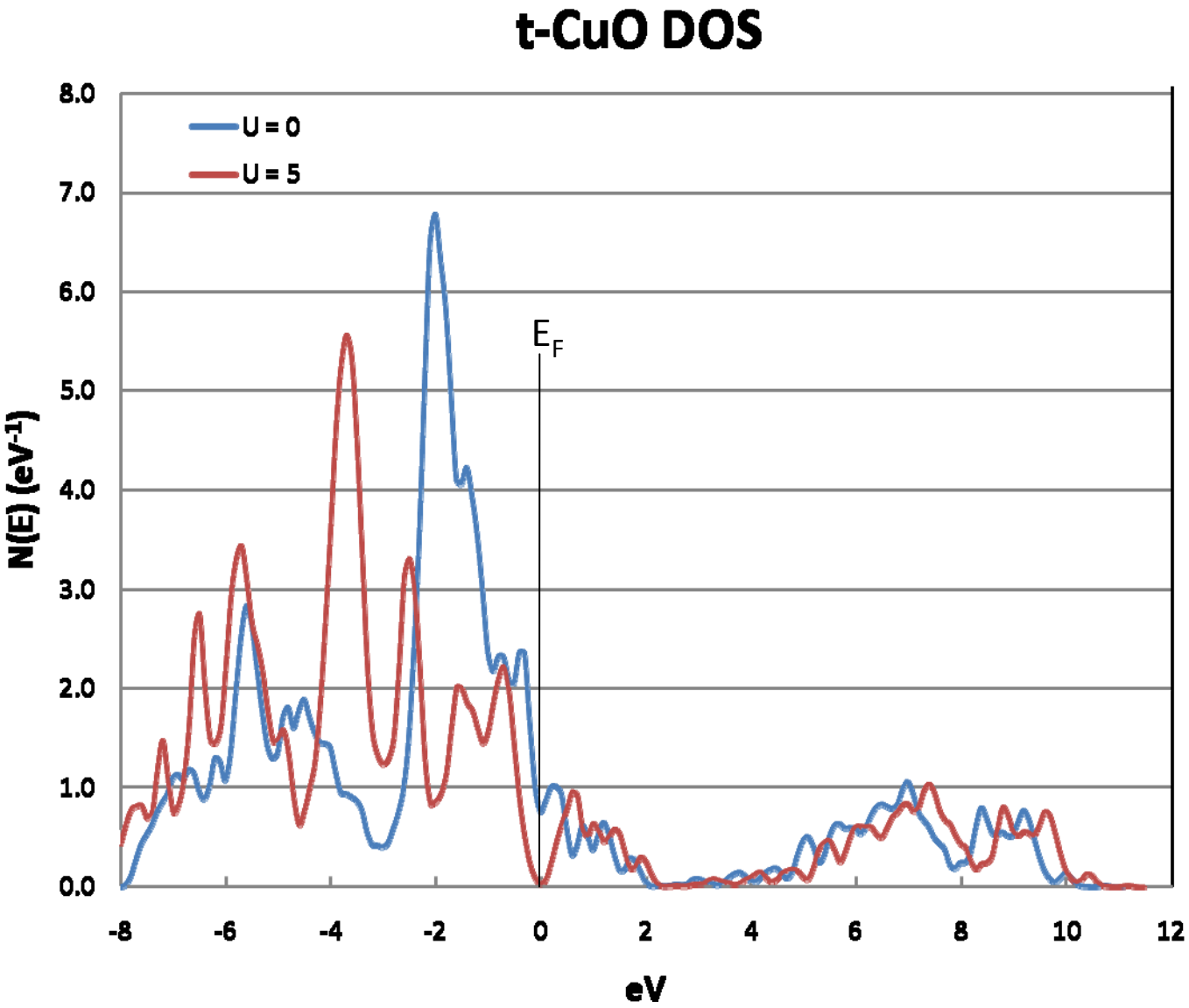


Figure 5.3: *Schematic illustration of the energy levels for a Mott-Hubbard insulator (left) and a charge-transfer insulator (right). The interaction on the d-site results in a splitting of the d-band and a charge gap formed by the upper and lower Hubbard band in the Mott-Hubbard insulator case or the upper Hubbard band and the p-band in the charge-transfer case. After Imada, Fujimori, and Tokura.*[80]


t-CuO (U = 0)
DOS (1/eV)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-8
-6
-4
-2
0
2
4
6
8
10
12
eV
dosup(E)
dosdw(E)


t-CuO DOS (U = 5)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
N(E) (eV⁻¹)
-8
-6
-4
-2
0
2
4
6
8
10
12
eV
dosup(E)
dosdw(E)


t-CuO DOS
U = 0
U = 5
E_F
N(E) (eV-1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-8
-6
-4
-2
0
2
4
6
8
10
12
eV

Insight from Numbers

- "The universe is of two indivisible elements…tiny particles and the void."

  Democritos, after Leucippus, 4th Century BC

- "The computer is a tool for clear thinking."

  Freeman Dyson, 20th Century AD

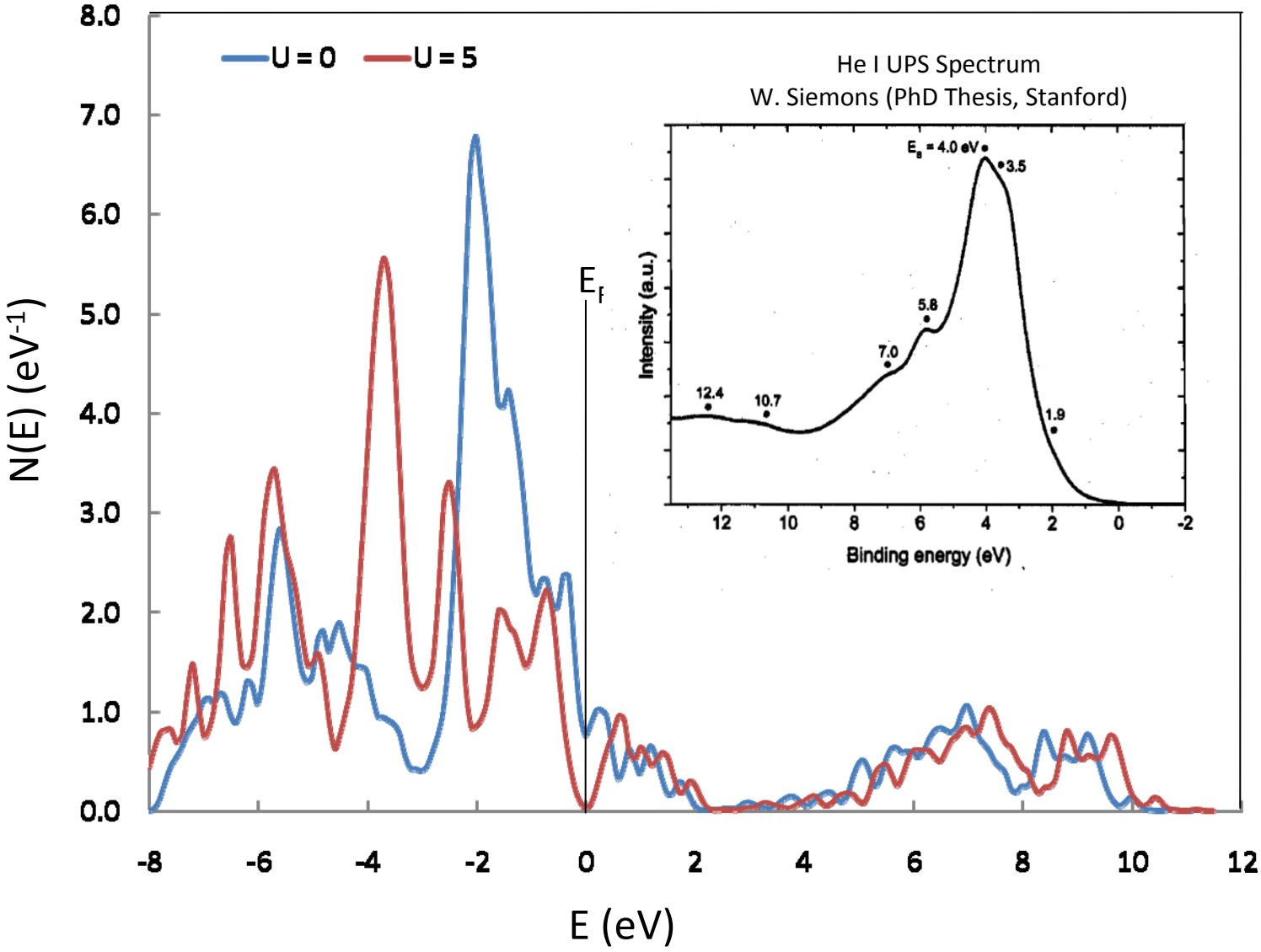
- "Garbage In, Garbage Out"

  Anon., IBM ca. 1954

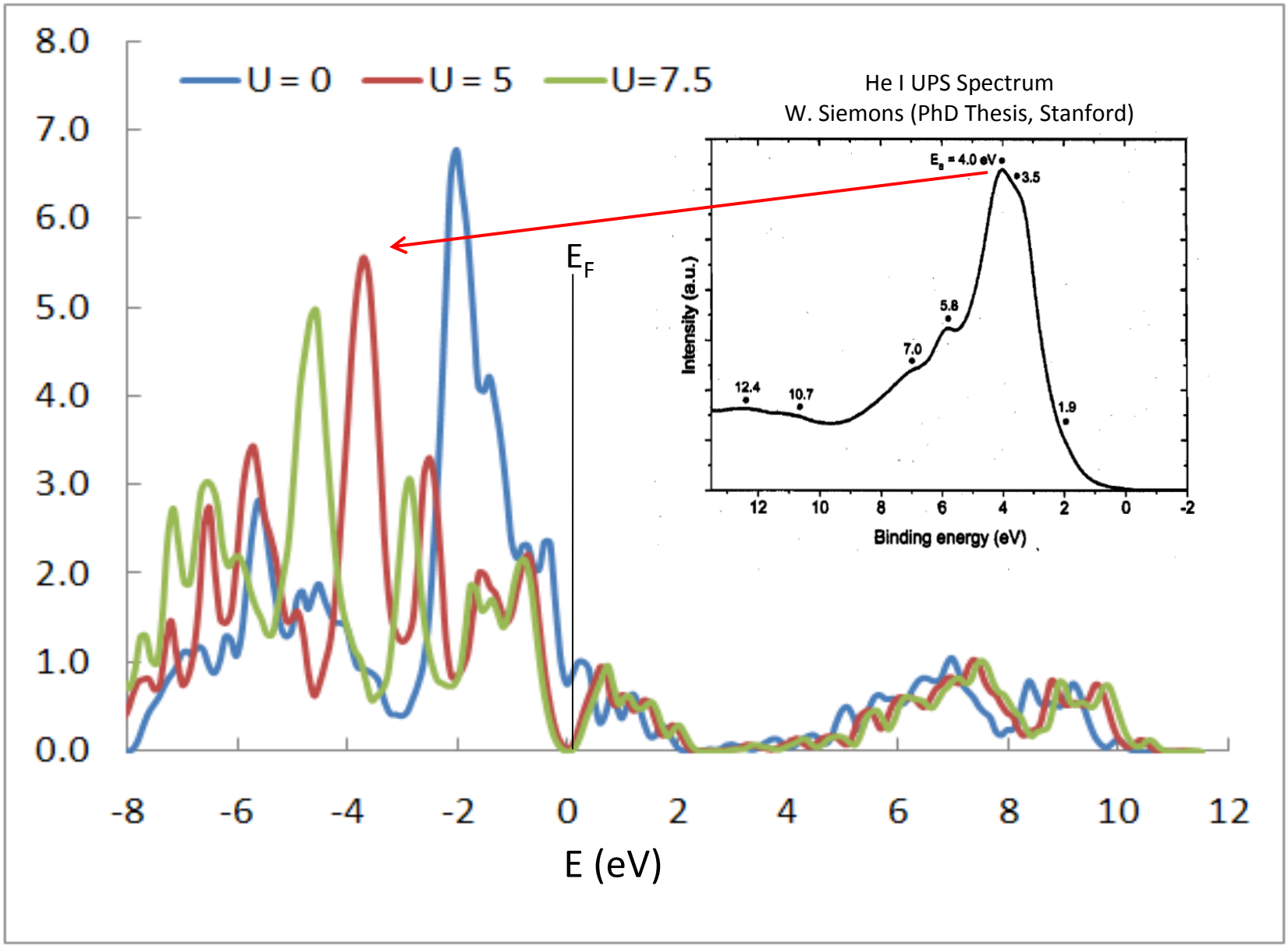
  – Q: "Pray, Mr. Babbage, if you put into the machine wrong figures, will the right answers come out?"

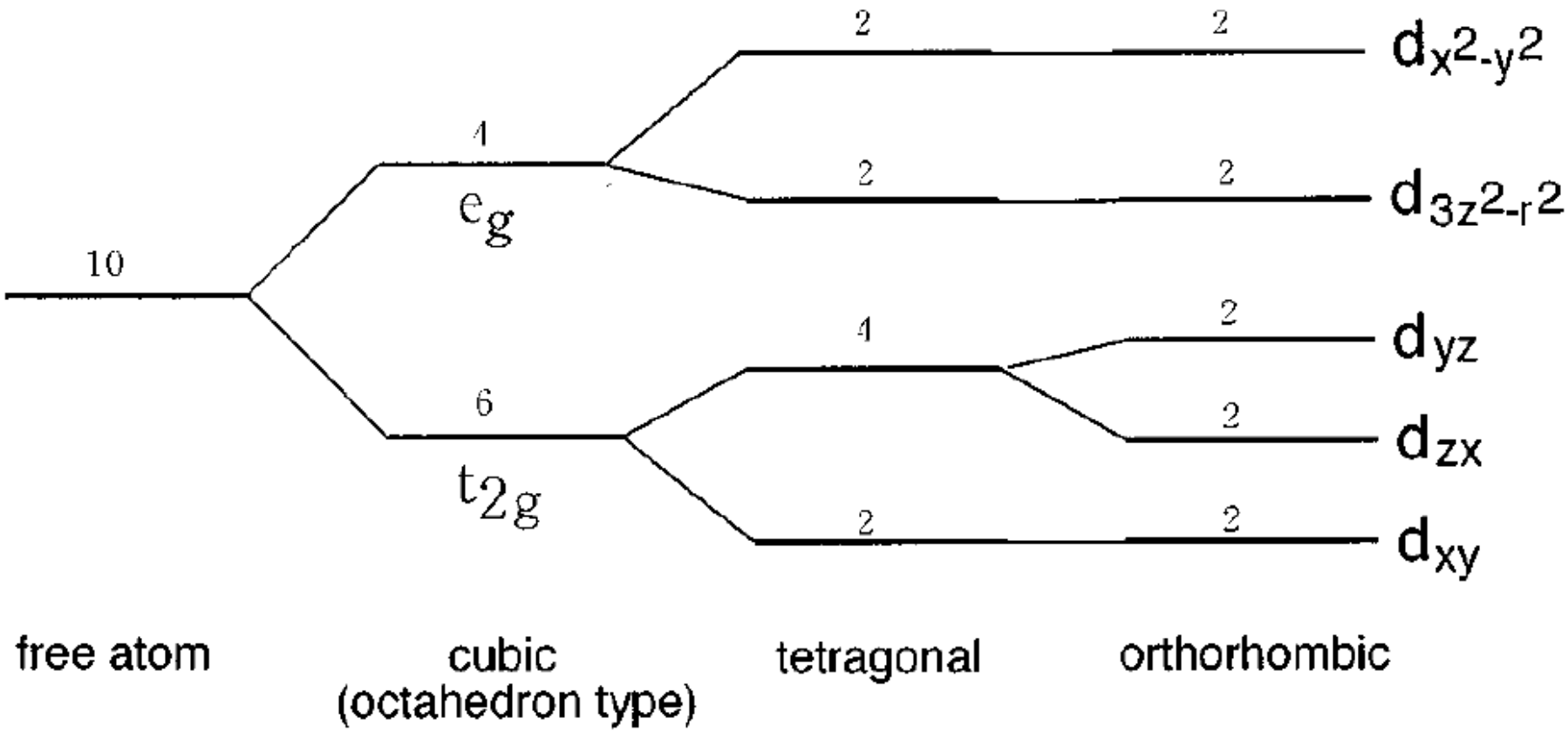
  – A: "I am not able rightly to comprehend the kind of confusion of ideas that could provoke such a question."

t-CuO Density-of-States

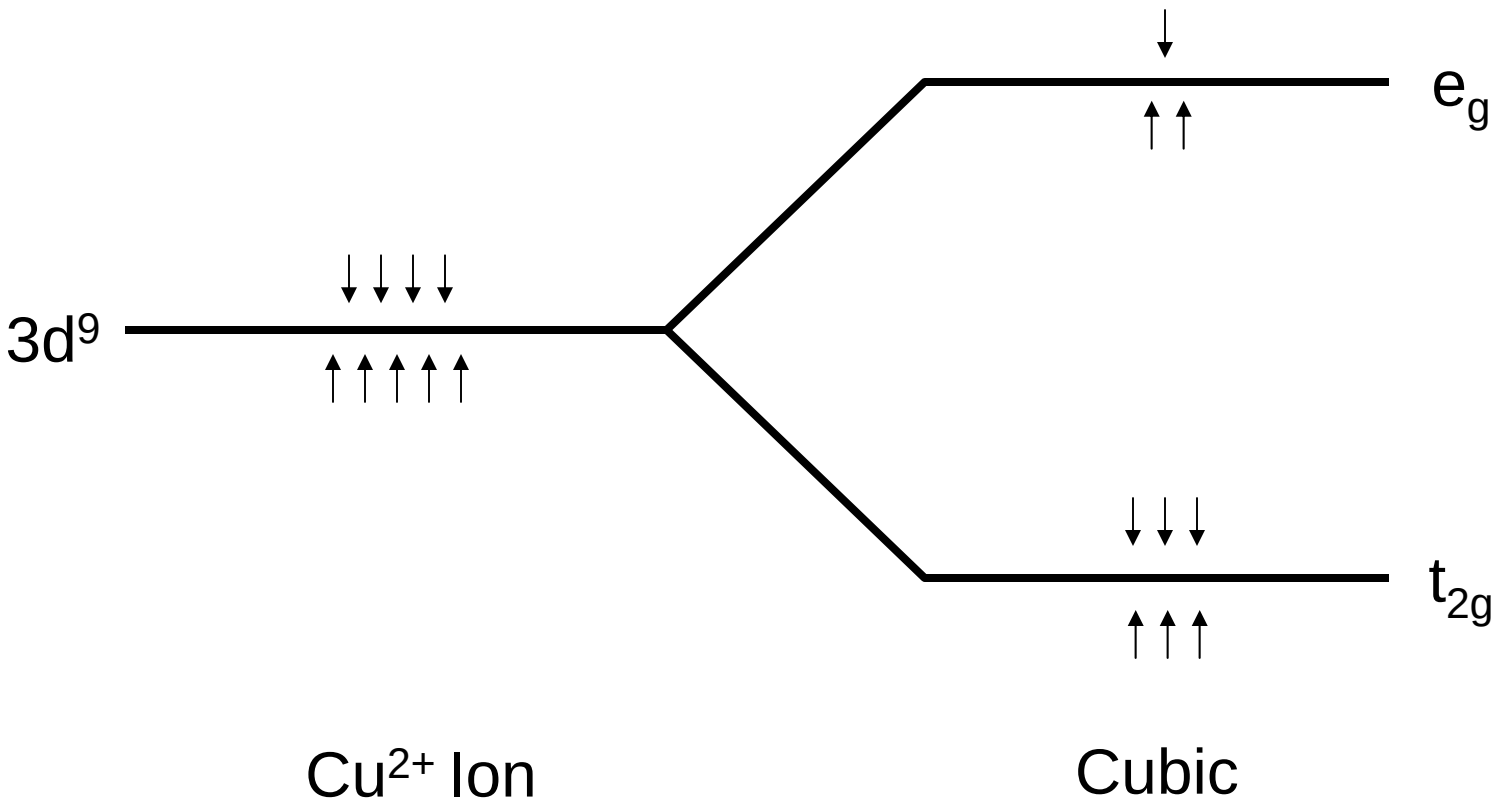


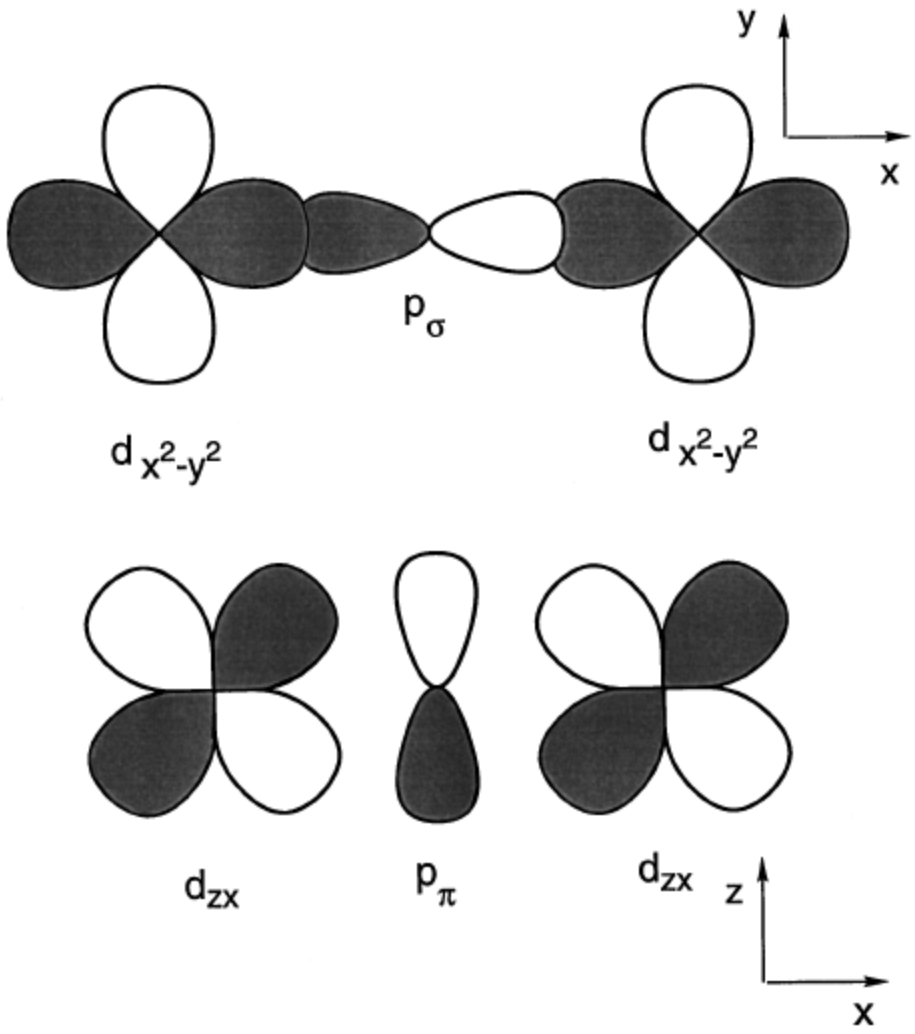
t-CuO Density-of-States




10
4
e_g
6
t_{2g}
2
2
2
2
4
2
2
2
2
$d_{x^2-y^2}$
$d_{3z^2-r^2}$
d_{yz}
d_{zx}
d_{xy}
free atom
cubic
(octahedron type)
tetragonal
orthorhombic

3d Multiplet




y
x
p_σ
$d_{x^2-y^2}$
$d_{x^2-y^2}$
d_{zx}
p_π
d_{zx}
z
x

Extended Hubbard Hamiltonian

Qualitative Description of the Physical Properties of Antiferromagnetic Insulators

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

This is the energy calculated in DFT which describes the physical properties of uncorrelated systems such as semiconductors and metals. This energy depends strongly on the interatomic bond length. "t" is the energy to transfer an electron from atom to atom, and the

This term represents the repulsive force between two electrons on the same ionic site. It tends to separate spins of opposite sign on nearest neighbor ions, thus producing an antiferromagnetic state. "U" is the repelling energy, and "n" is the occupation number (either) or 1) for each spin direction on ion "i". It is

This term is the repulsive energy between two electrons on separate ionic sites and thus dependent on bond length, but not included in the DFT formalism, and thus may play a role in setting the absolute value of the Ground

Return