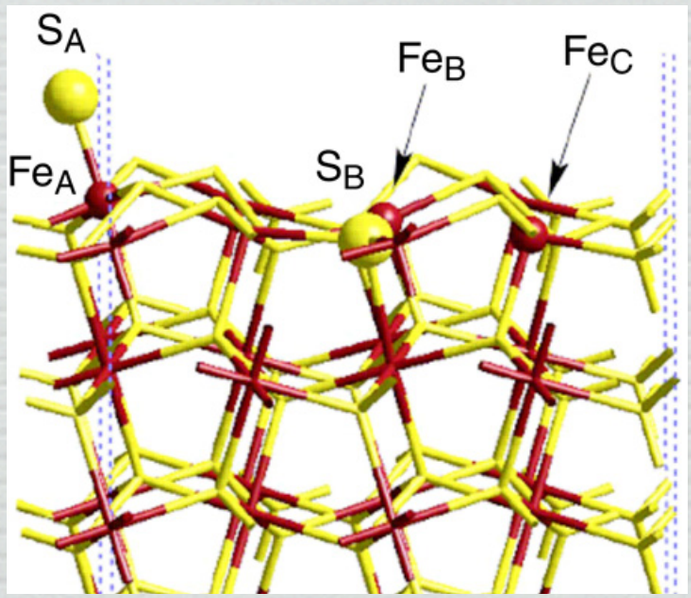
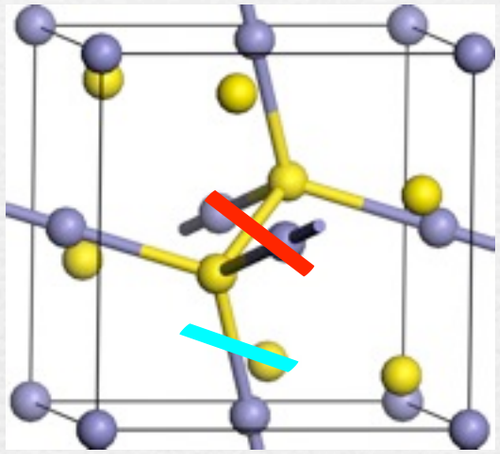
Clean Surfaces of Pyrite: DFT Calculations

Yanning Zhang, Jun Hu, and Ruqian Wu

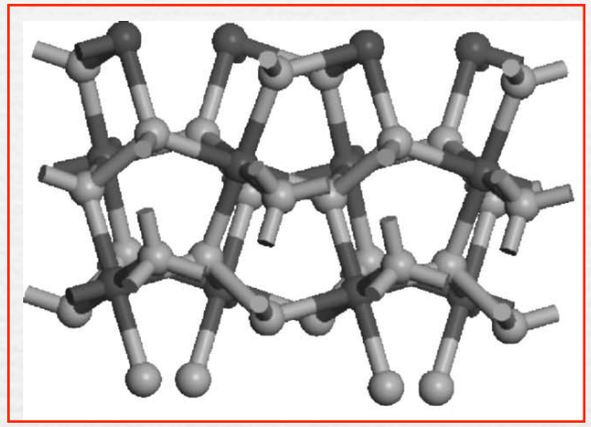
2010.12



Pyrite Surfaces



A



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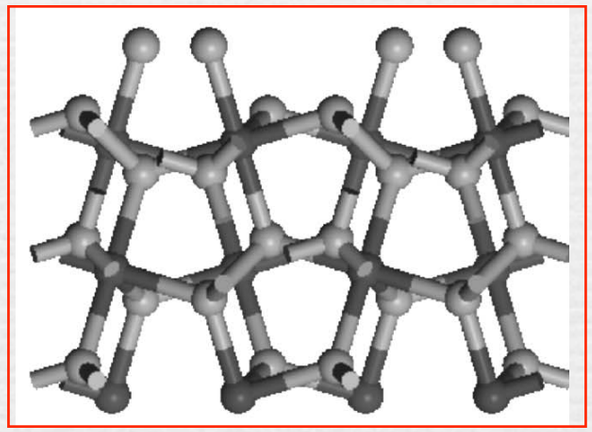
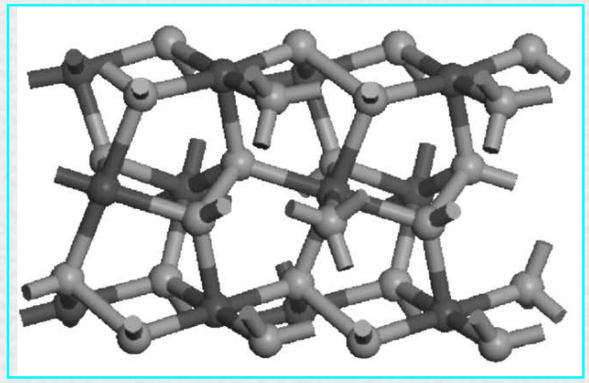
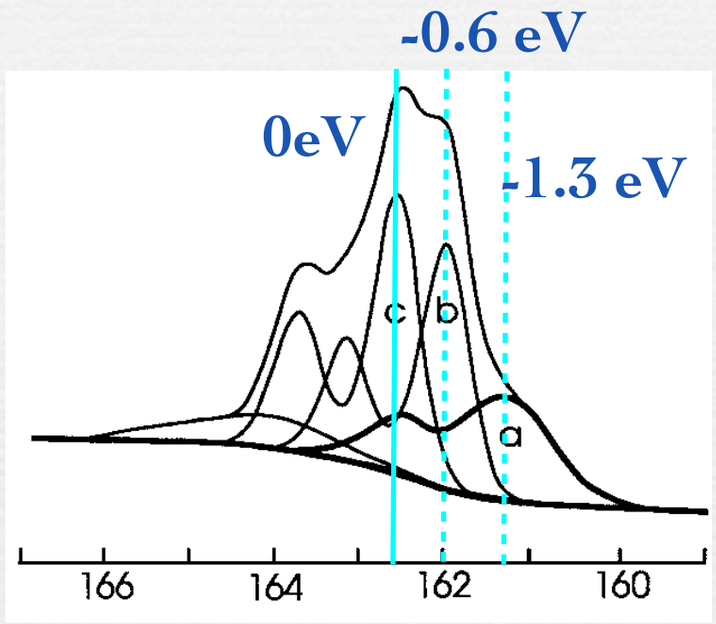
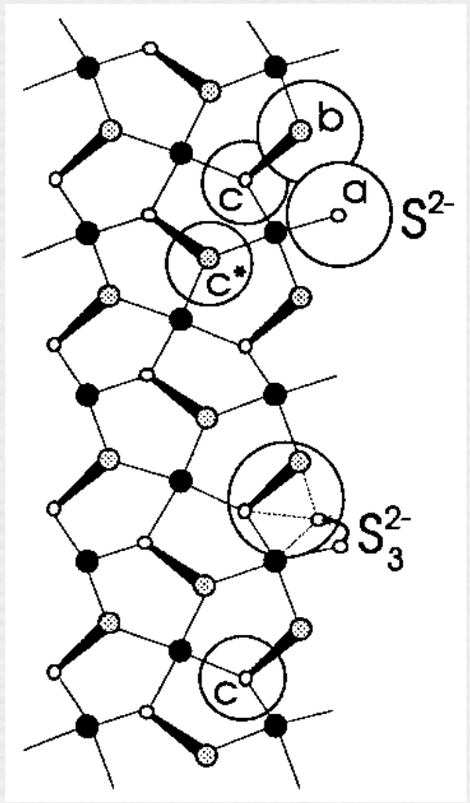


C



S-2p spectrum





American Mineralogist 83 (1998) 1067;
Physical Review B 72 (2005) 235427;
Surface Science Reports 64 (2009) 1–45;
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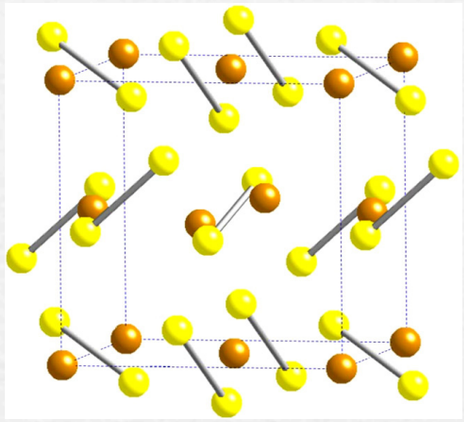
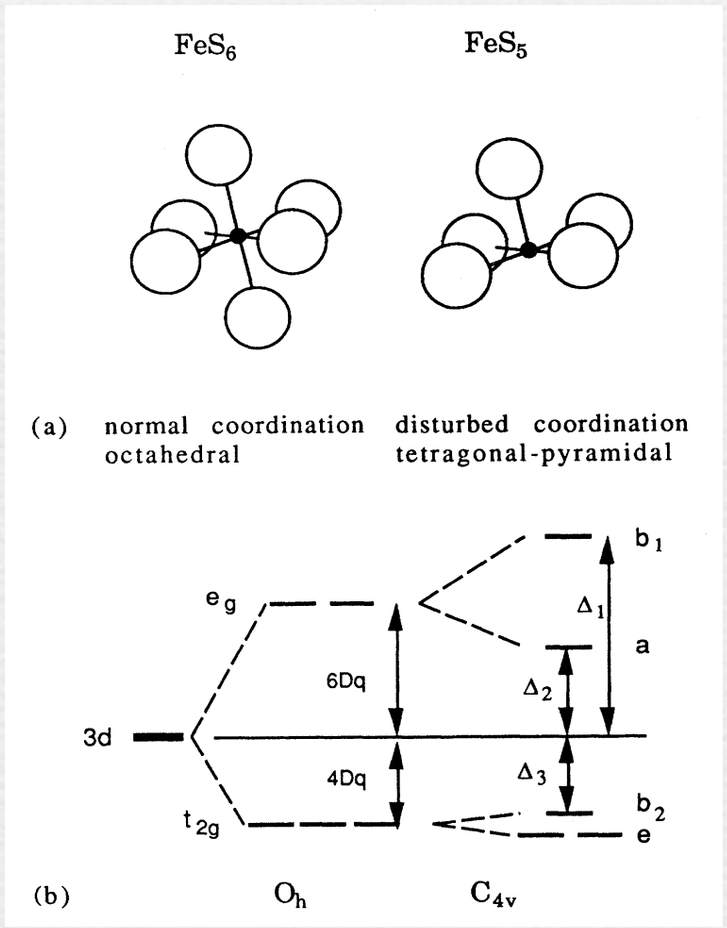
M. Bronold et al., Surf. Sci. Lett. 314 (1994) L931.

Pyrite Surfaces



Studies of various Pyrite surfaces are important to the further development of pyrite: the growth of high-quality films and passivation of under-coordinated iron atoms at the crystal surface.

to improve the photovoltage of pyrite



Start from the **clean surfaces**, state-of-the-art DFT calculations can do:

Structural properties: stability of various surfaces and interfaces, formation energies for different deficiencies…

Electronic Properties: band structure, density of states, defect states, charge rearrangements…

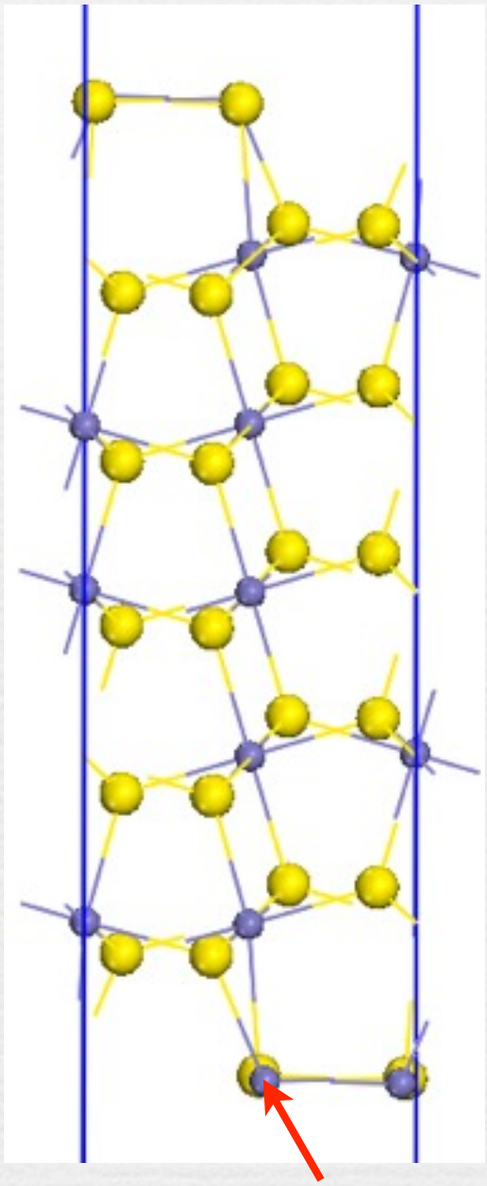
Optical properties: X-ray adsorption spectrum…

Magnetic properties: local magnetization, magnetic ordering, magneto-optical properties...

DFT calculation details

- DFT calculations with the plane-wave-based Vienna Ab initio Simulation Package (VASP)
- Potential: PAW-GGA(PBE)
- Energy cutoff: 300 eV
- Kpoints: 8×8×1 MK
- Atomic model: a seven-layer slab with a vacuum of ~15 Å thick

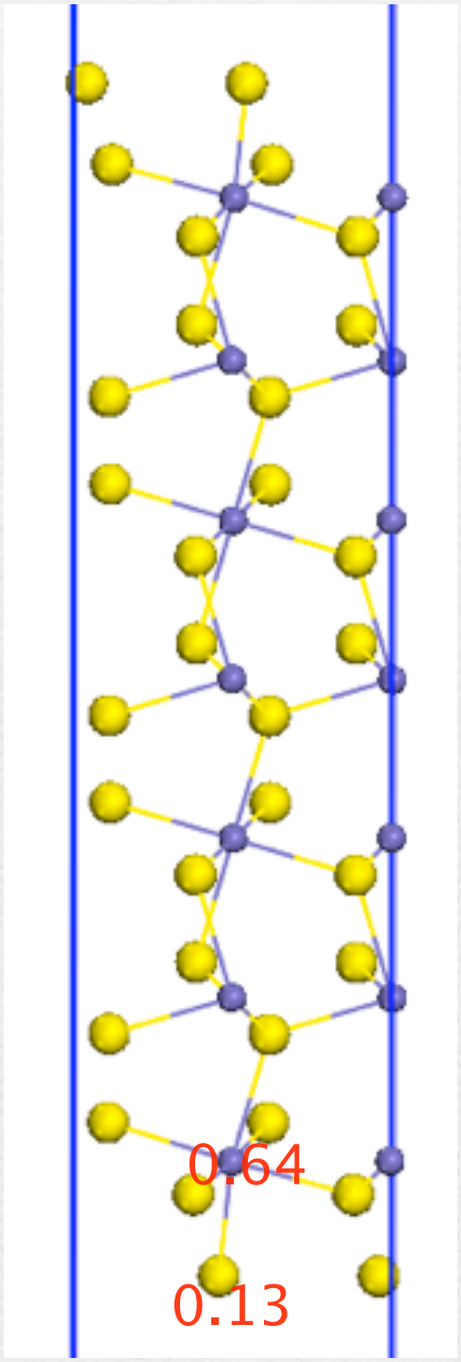
(A)
Fe14S24



$M_{Fe(S)}$ = ~3.5 μ_B

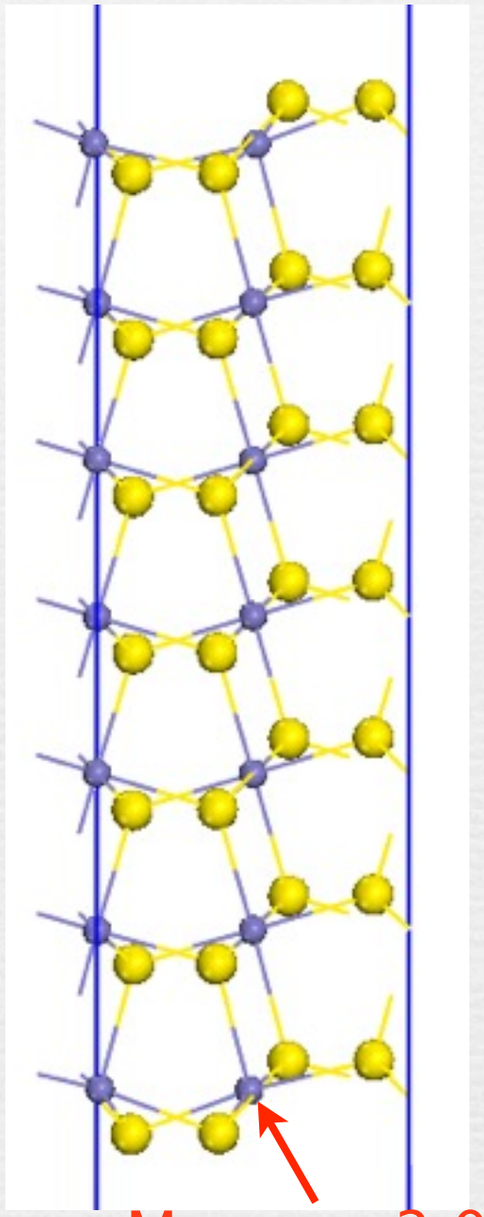
M_{tot} = 16.0 μ_B/cell

(B)
Fe14S32



M_{tot} = 3.05 μ_B/cell

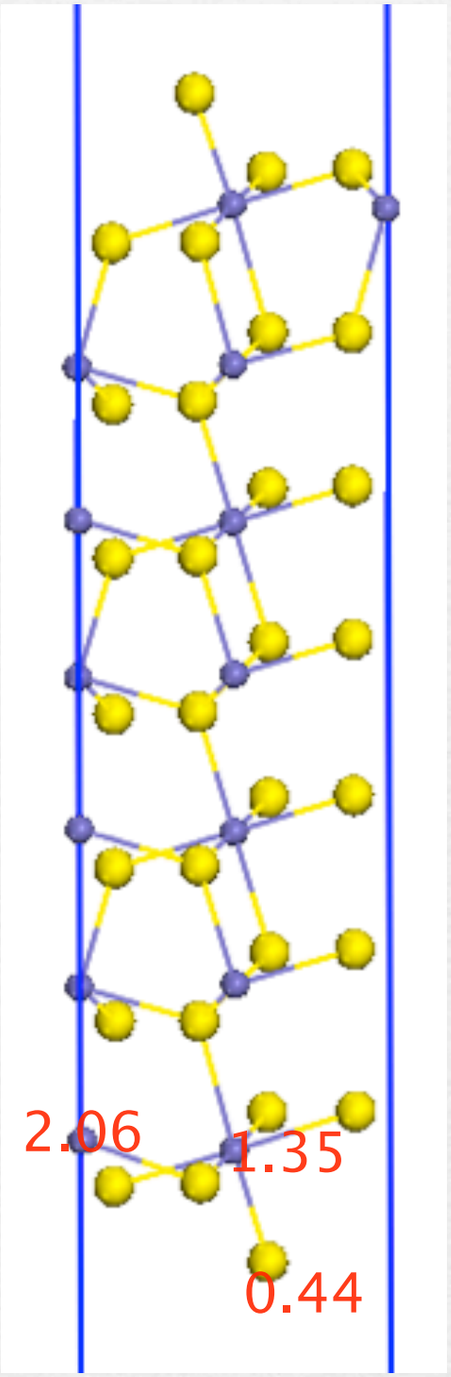
(C)
Fe14S28



$M_{Fe(S)}$ = ~2.0 μ_B

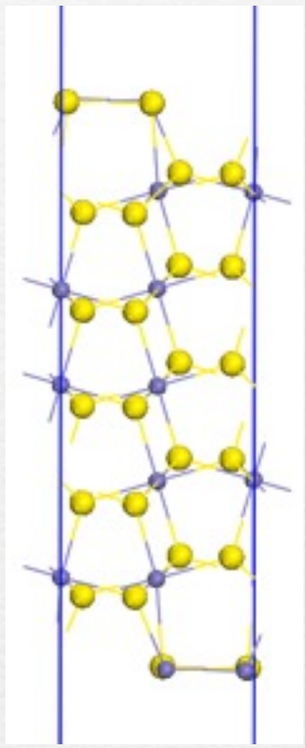
M_{tot} = 8.0 μ_B/cell

(D)
Fe14S30

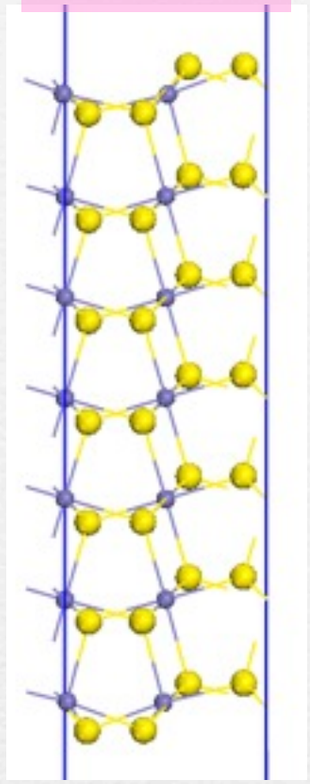


M_{tot} = 8.0 μ_B/cell

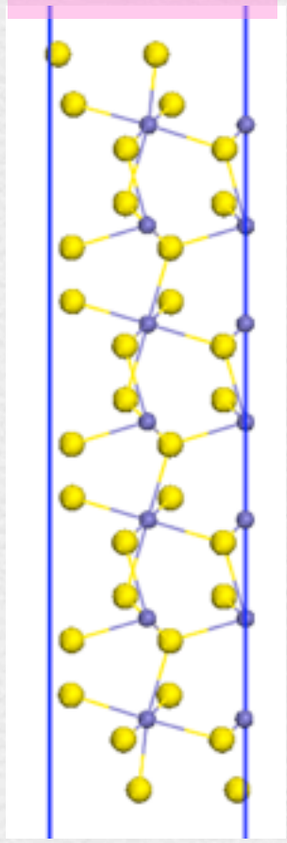
Fe14S24



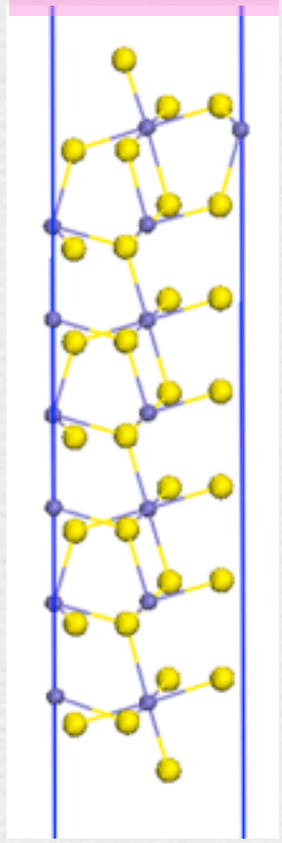
Fe14S28



Fe14S32



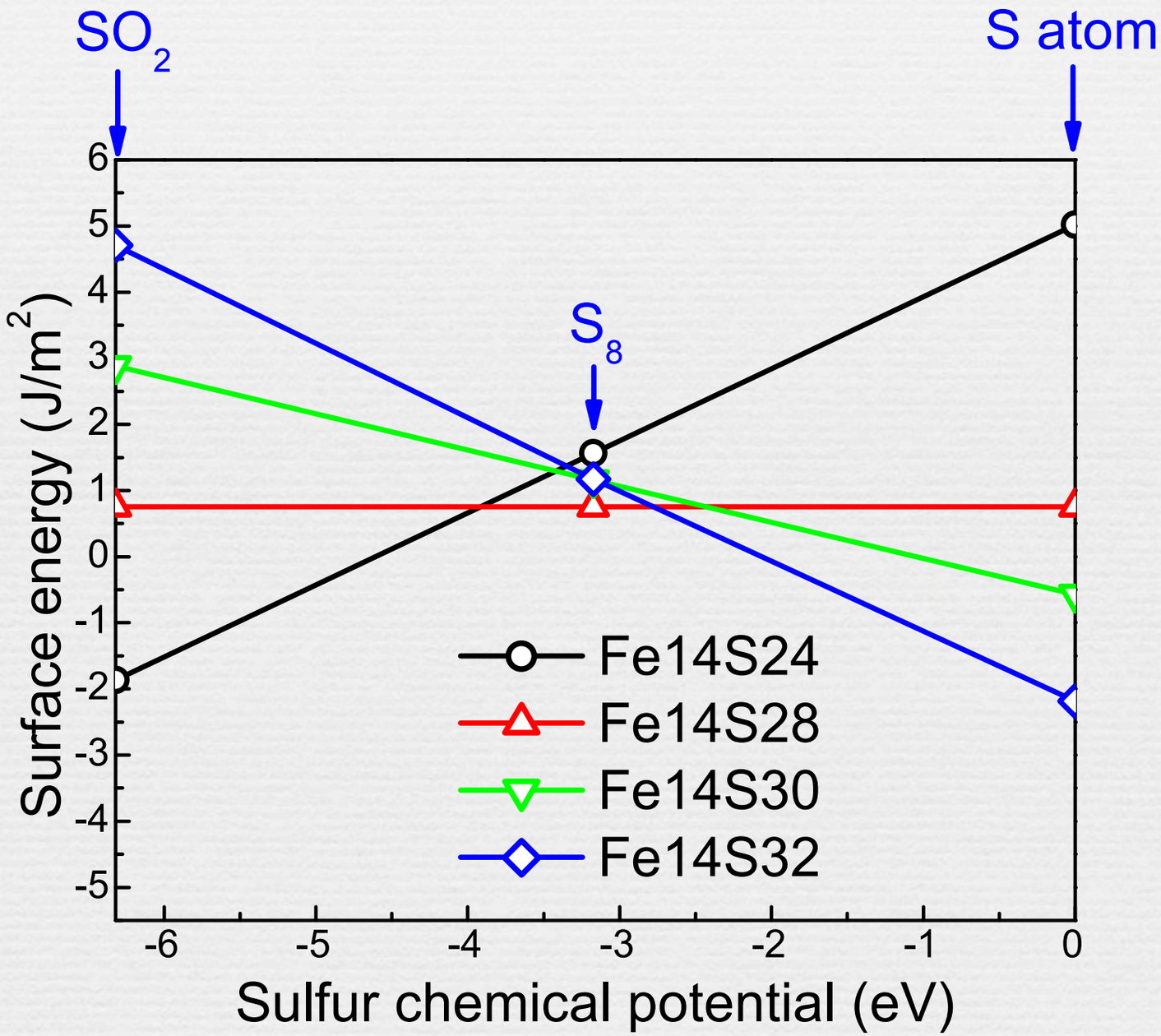
Fe14S30

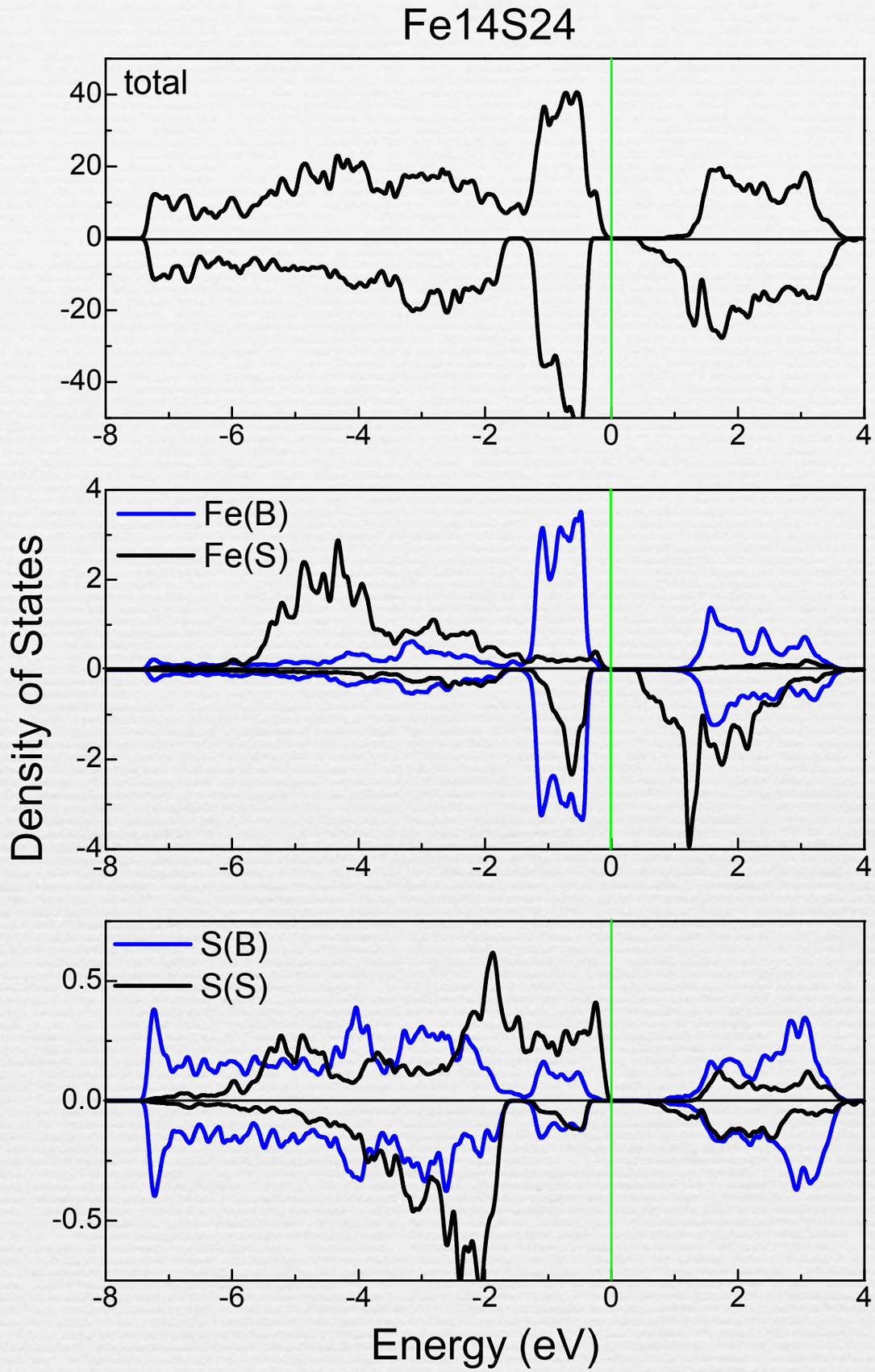


Surface free energy γ(T,p)

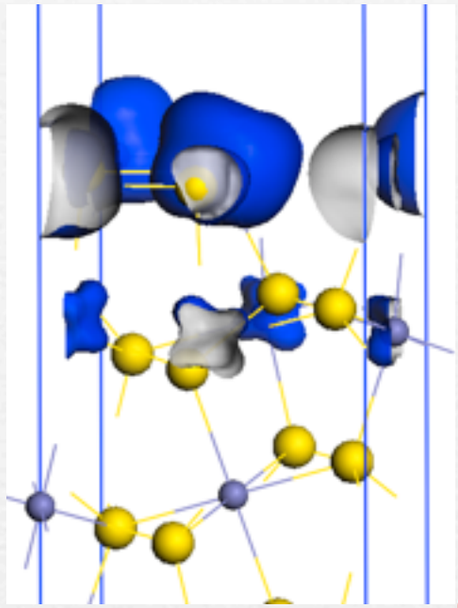
$$\gamma(T,p) = \frac{1}{2A}\left[G(T,p,N_{Fe},N_S) - N_{Fe}\mu_{Fe}(T,p) - N_S\mu_S(T,p)\right]$$

$$\mu_{Fe} + 2\mu_S = \mu_{FeS_2}$$





Density of States (DOS)

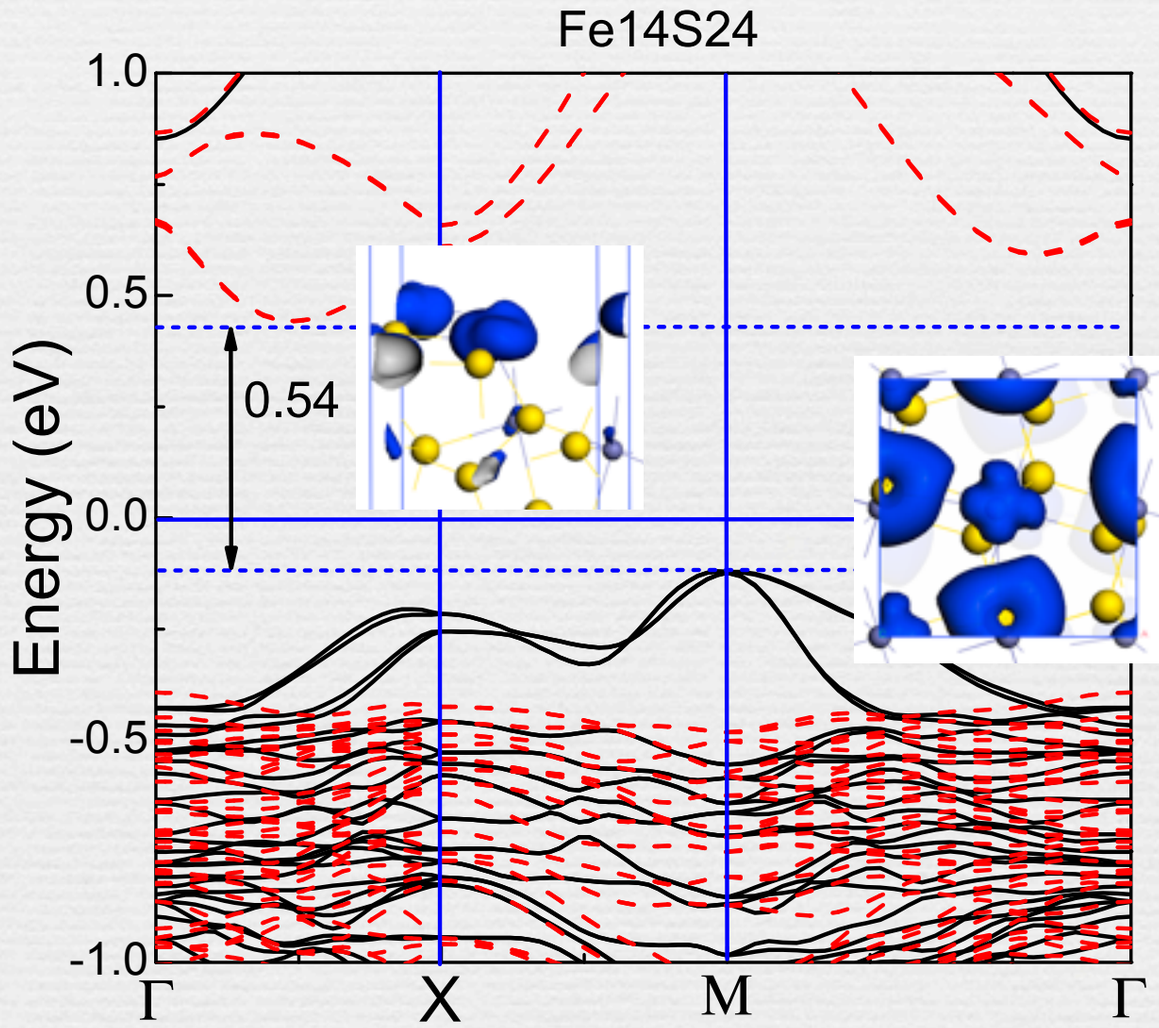


(A)

Spin Density

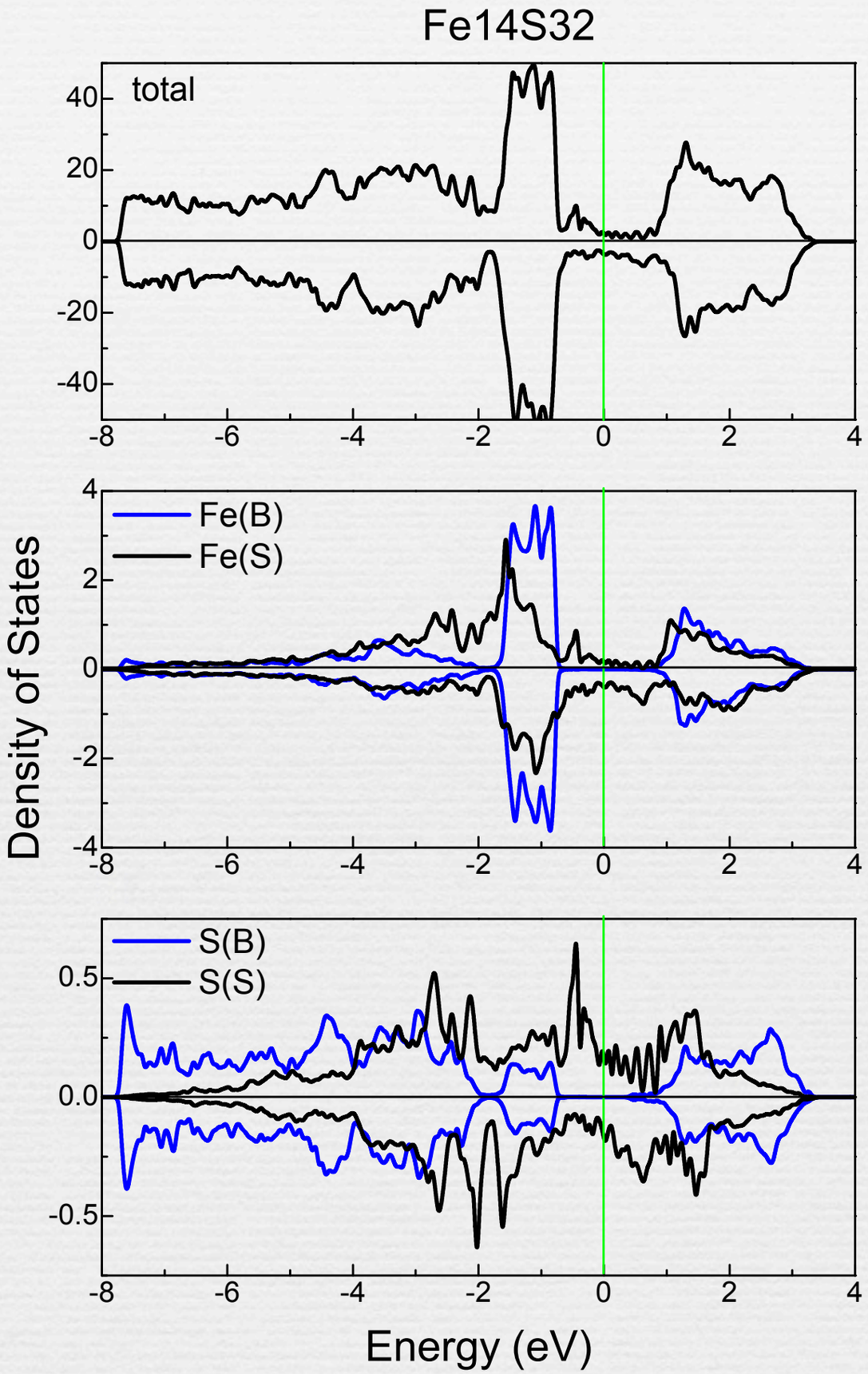
solid -- majority spins

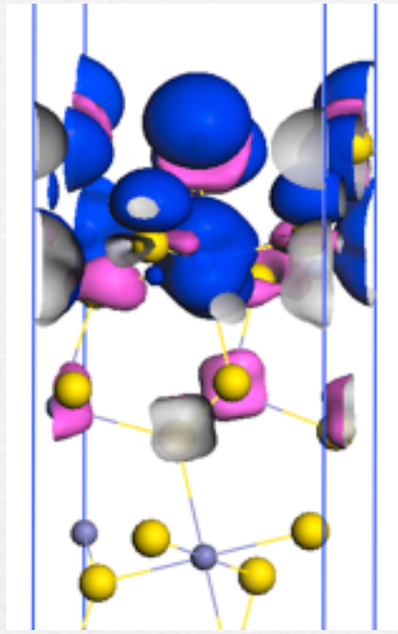
dashed -- minority spins

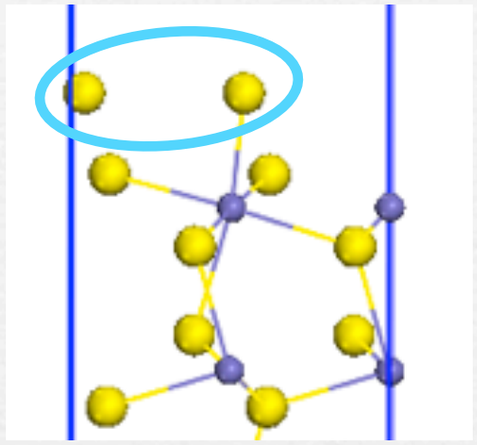


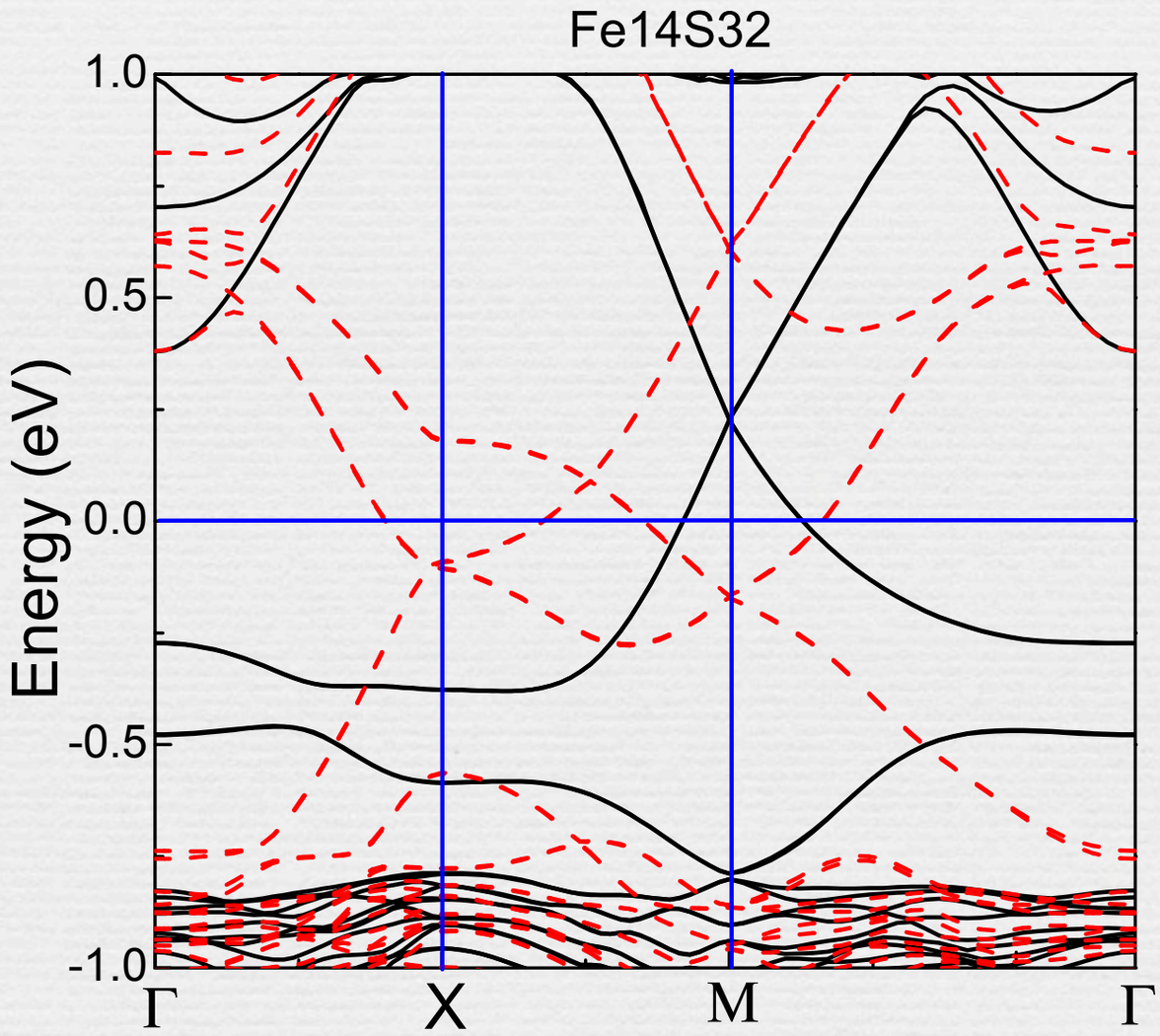
Band Structure

(B)

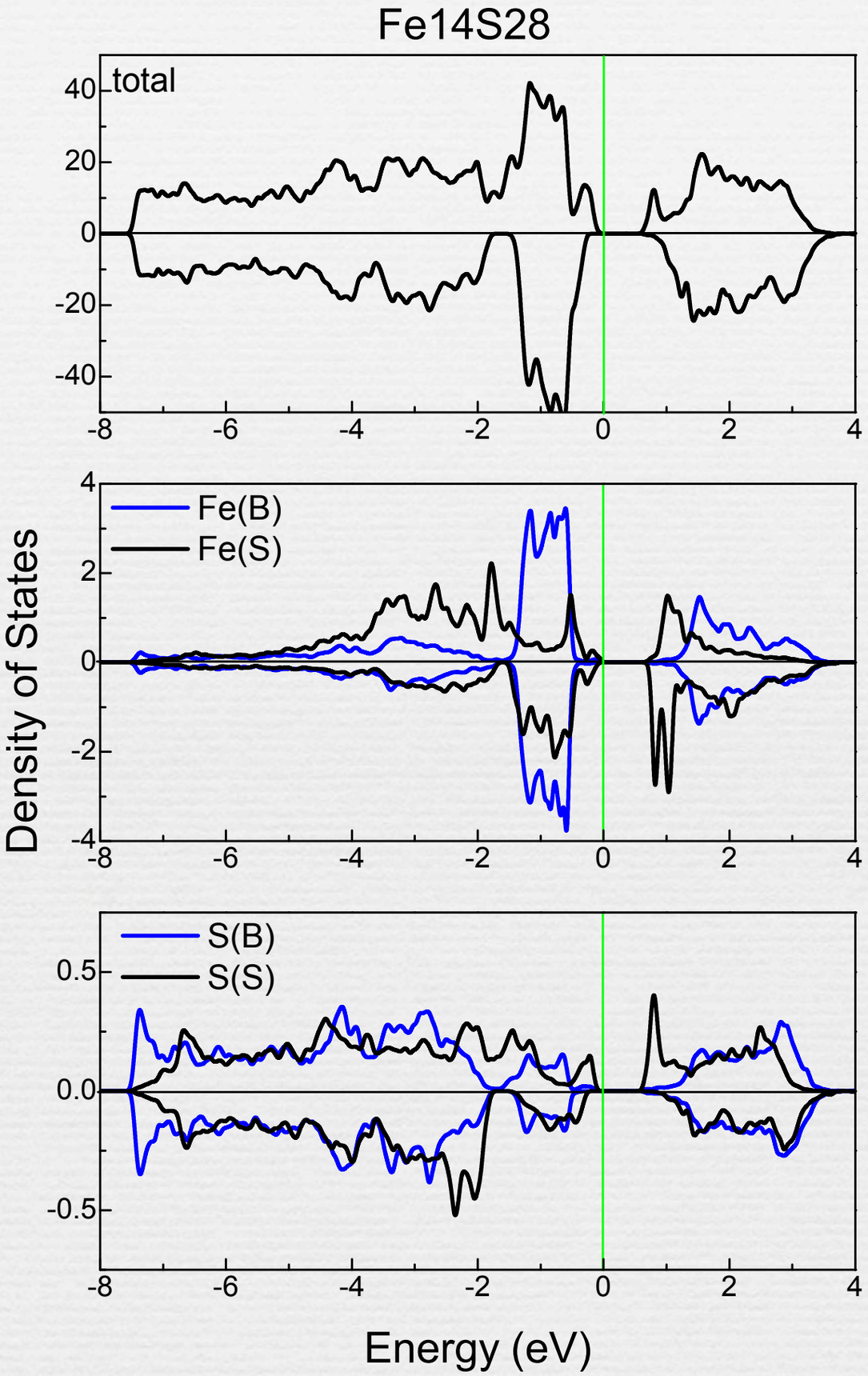

Fe14S32
total
40
20
0
-20
-40
-8
-6
-4
-2
0
2
4
Fe(B)
Fe(S)
Density of States
4
2
0
-2
-4
S(B)
S(S)
0.5
0.0
-0.5
Energy (eV)

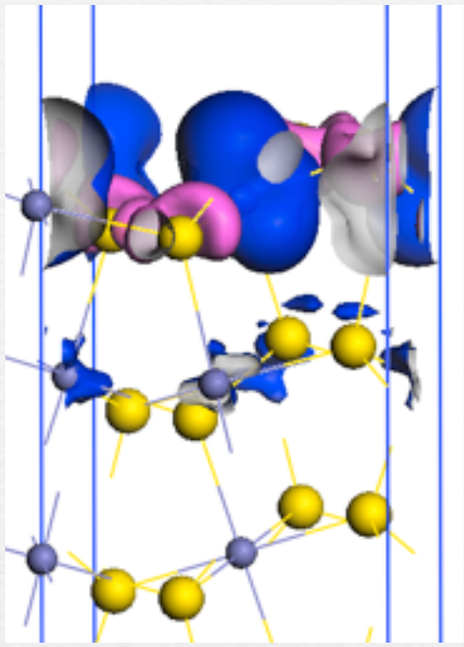


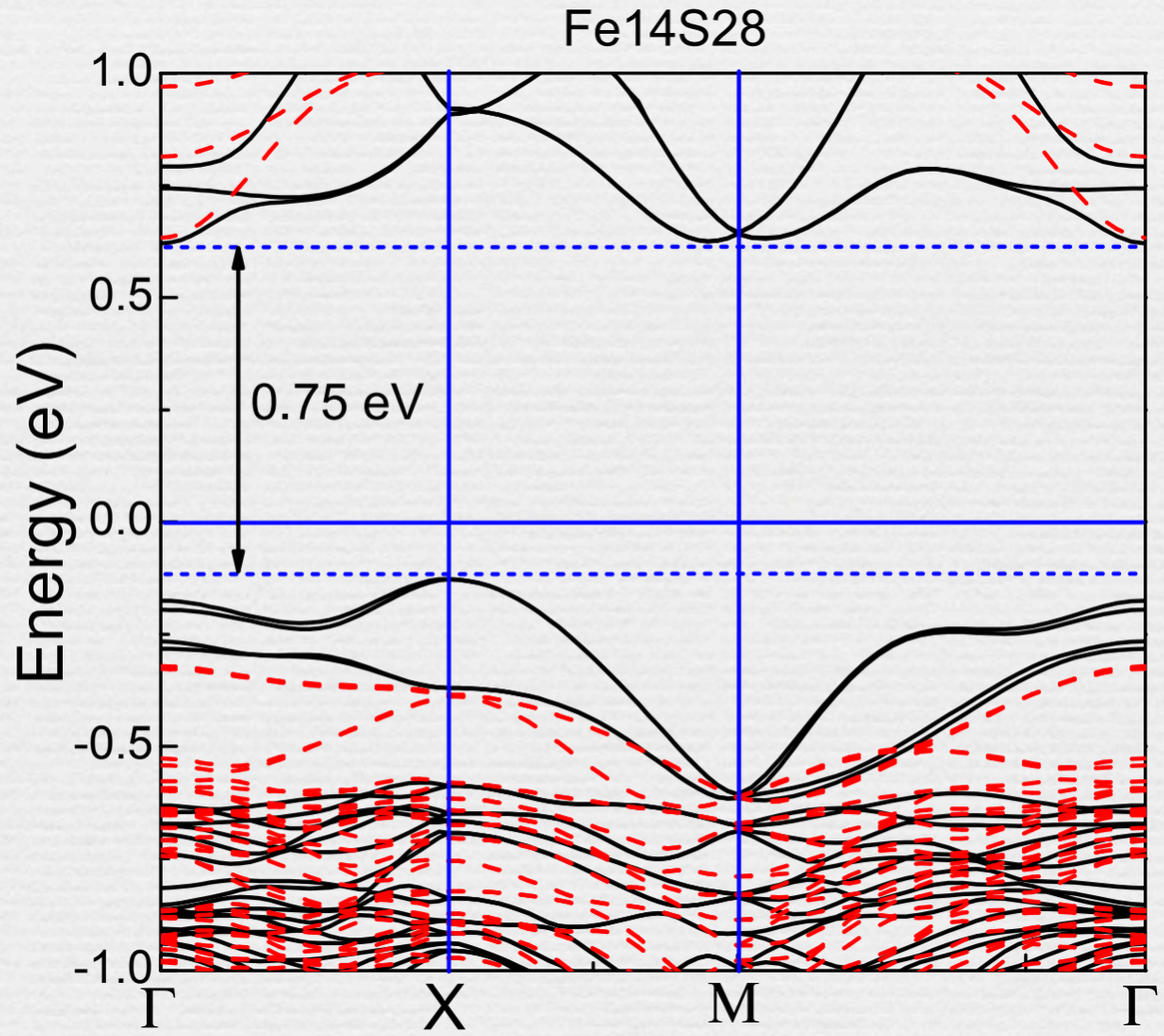



Fe14S32
1.0
0.5
0.0
-0.5
-1.0
Energy (eV)
Γ
X
M
Γ

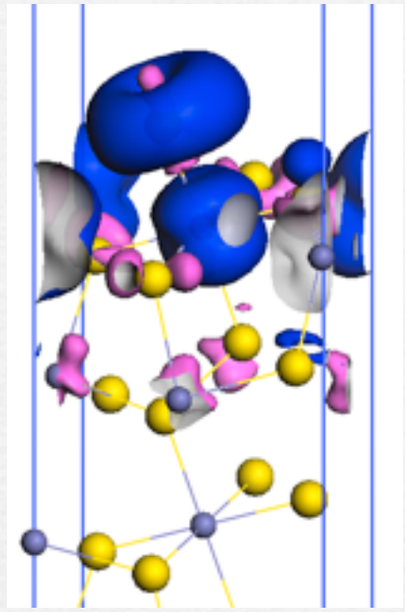
(C)

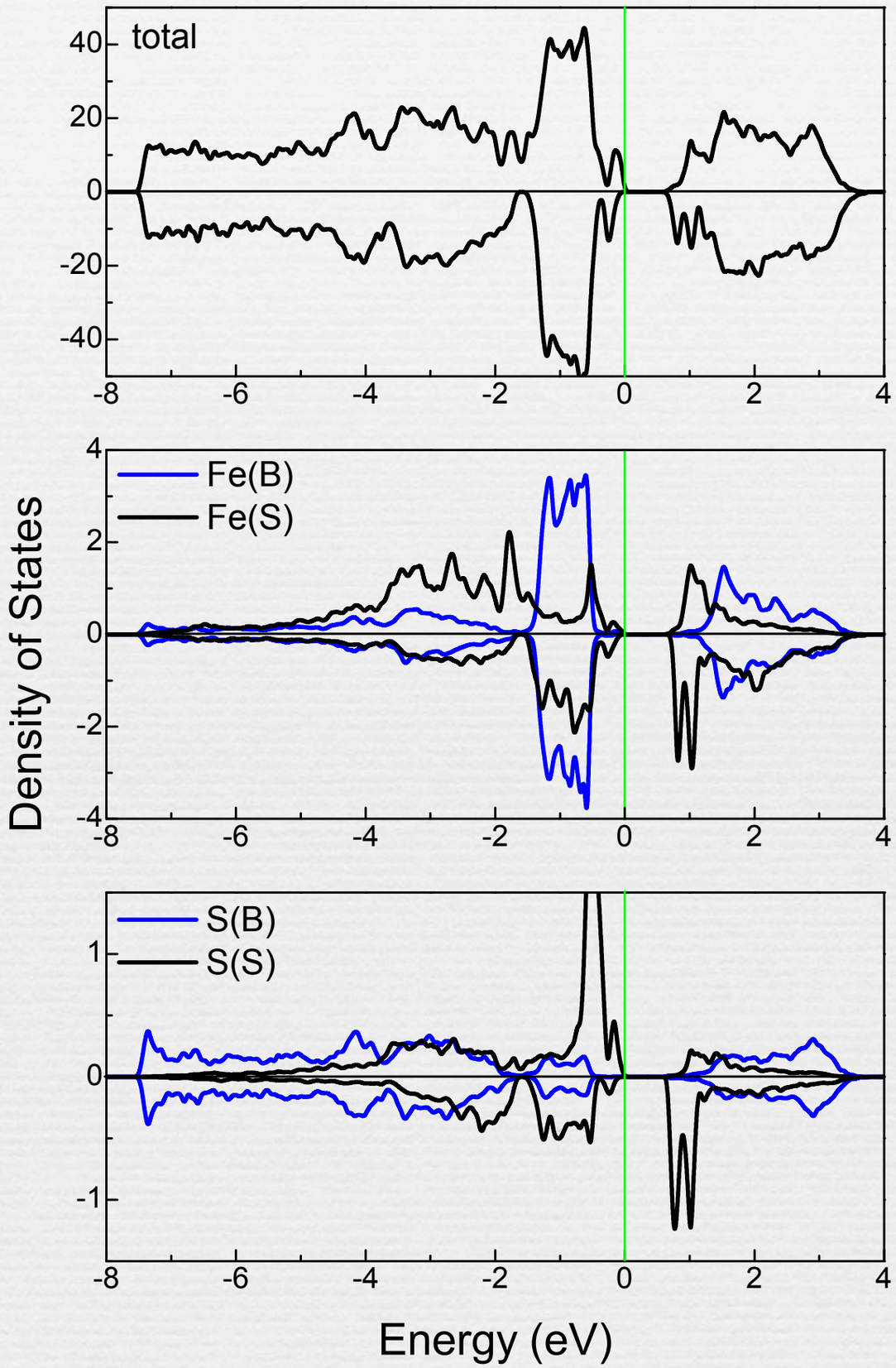

Fe14S28
total
40
20
0
-20
-40
-8
-6
-4
-2
0
2
4
Fe(B)
Fe(S)
Density of States
S(B)
S(S)
Energy (eV)

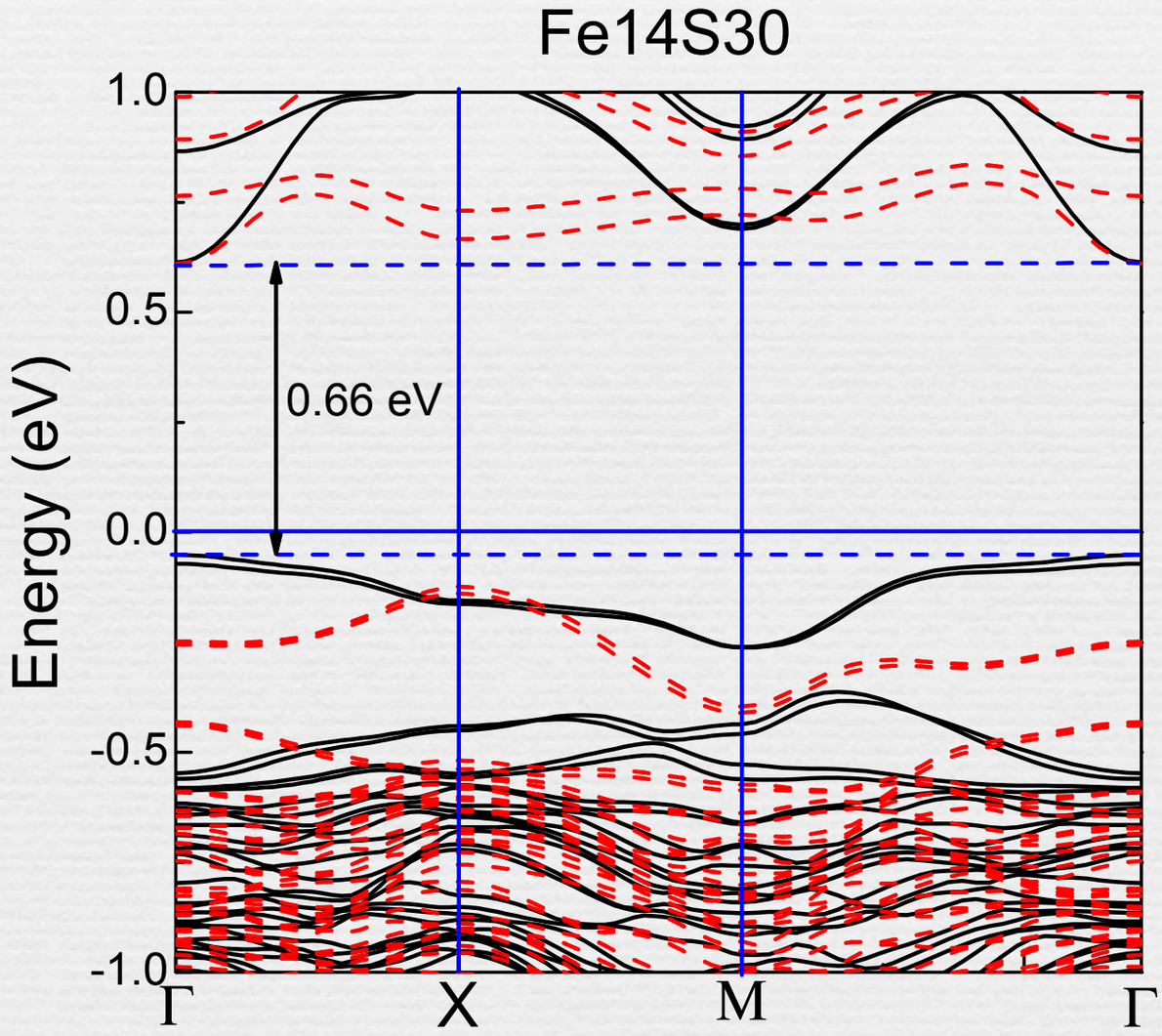



Fe14S28
1.0
0.5
0.0
-0.5
-1.0
0.75 eV
Energy (eV)
Γ
X
M
Γ

(D)

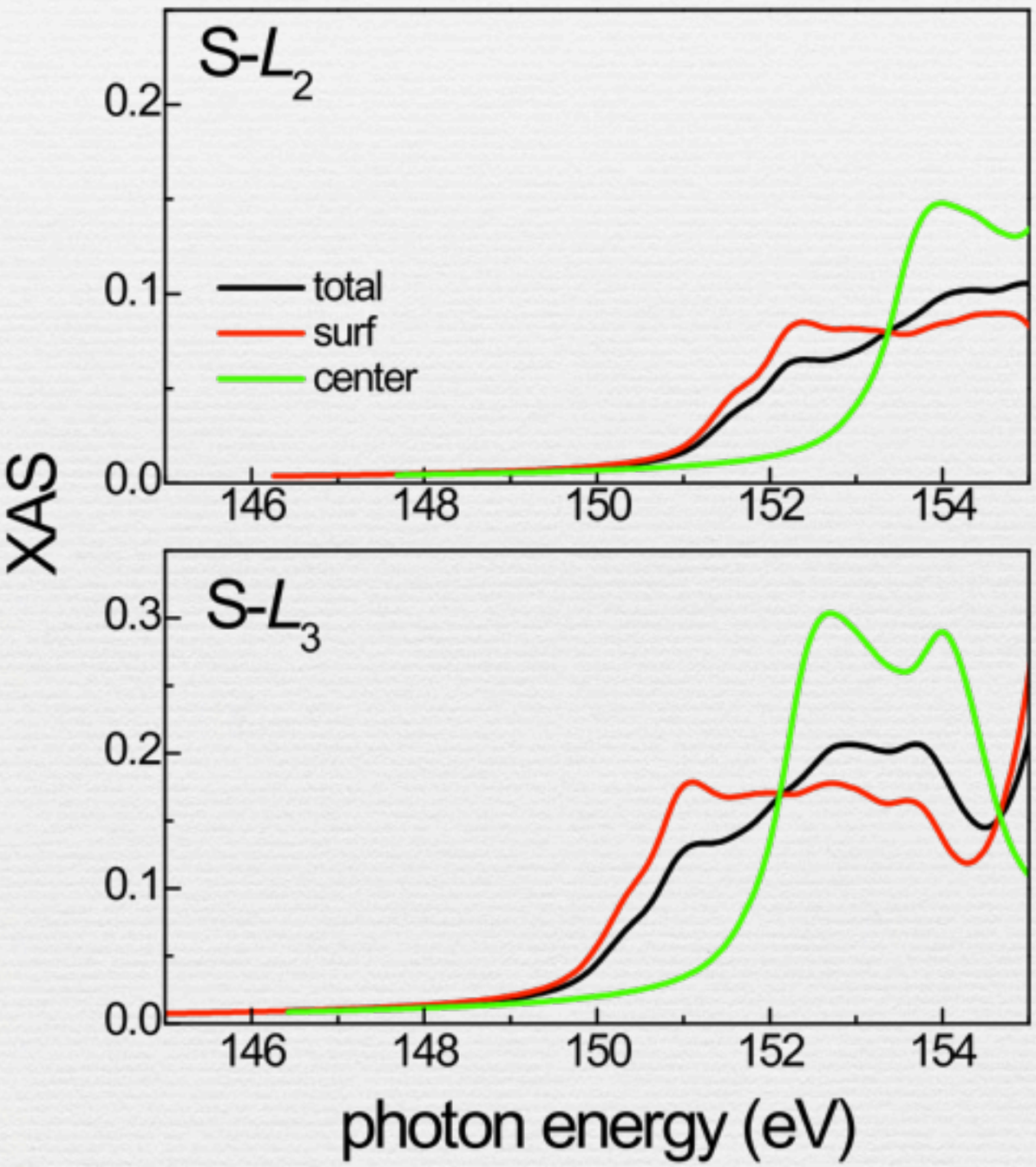



Fe14S30
total
40
20
0
-20
-40
-8
-6
-4
-2
0
2
4
Fe(B)
Fe(S)
Density of States
S(B)
S(S)
Energy (eV)

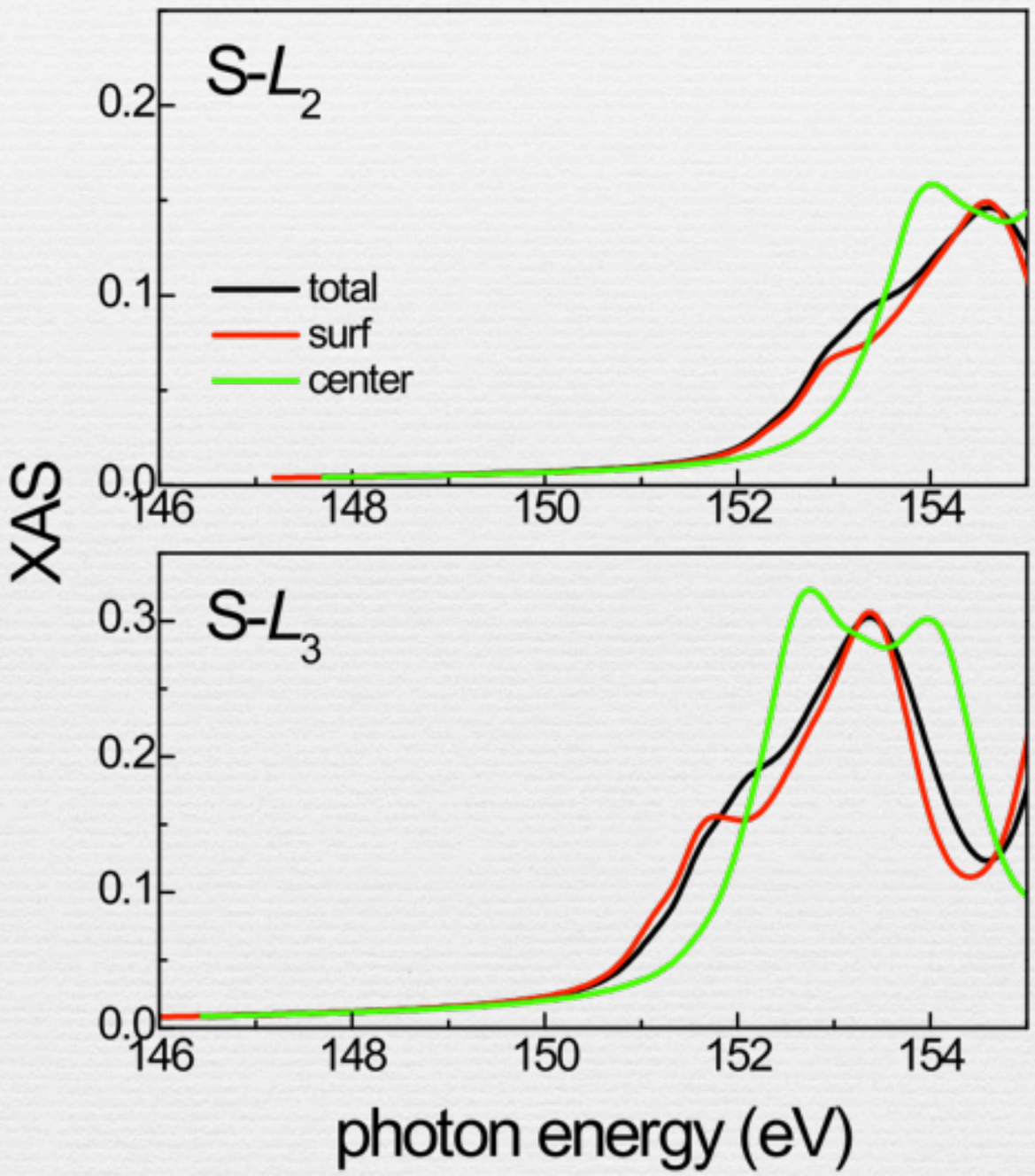

Fe14S30
1.0
0.5
0.0
-0.5
-1.0
0.66 eV
Energy (eV)
Γ
X
M
Γ

X-ray Adsorption Spectrum

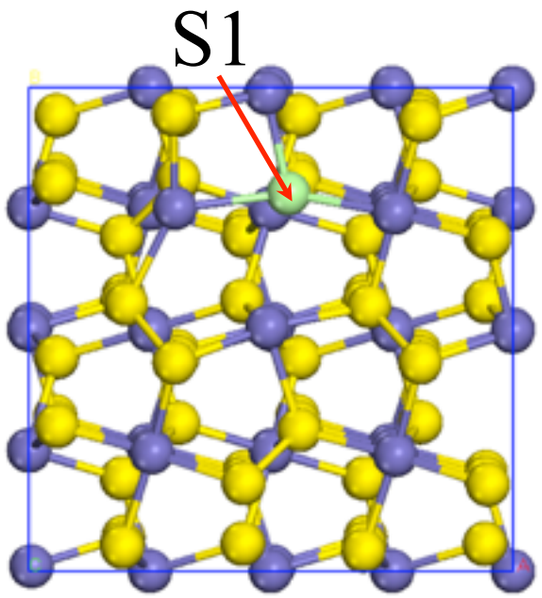
(A) Fe14S24

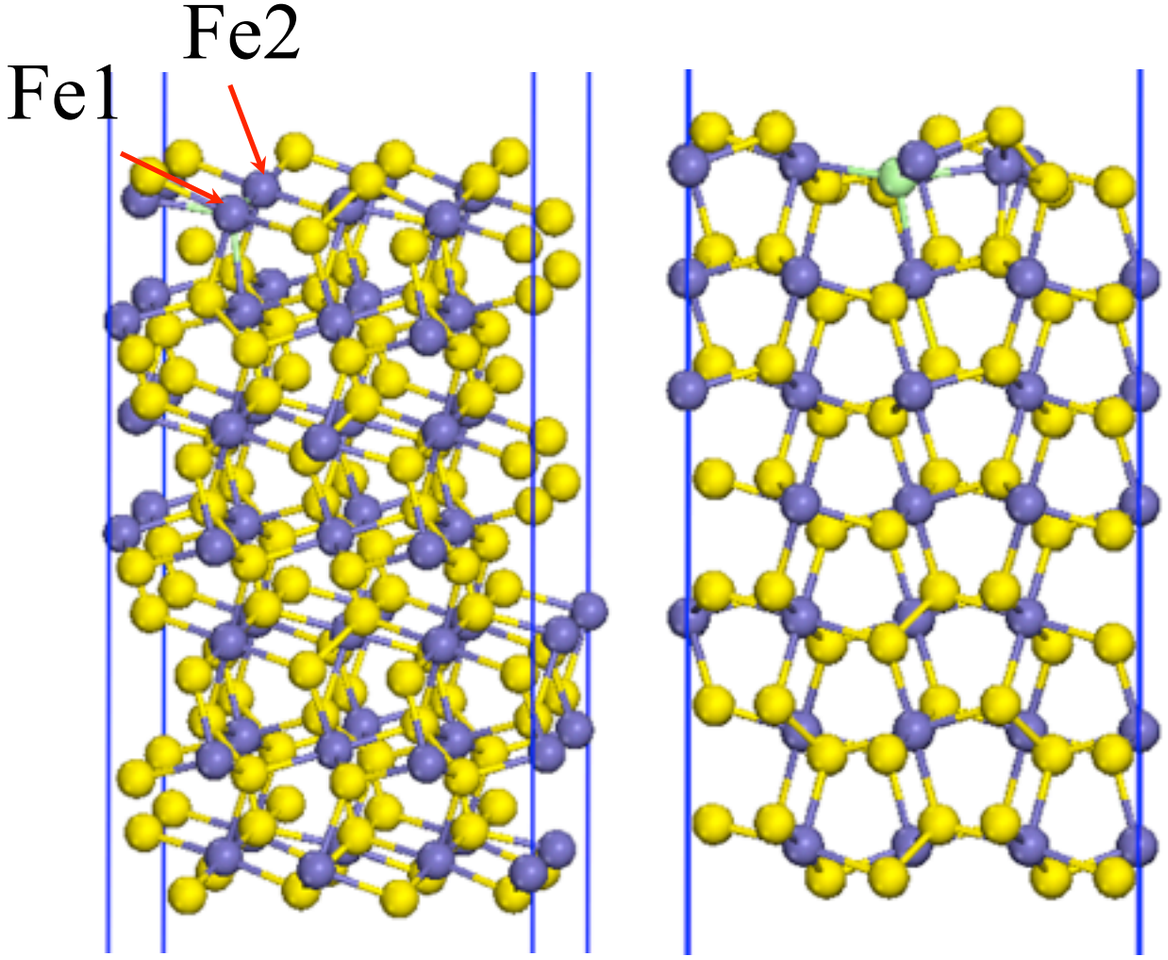


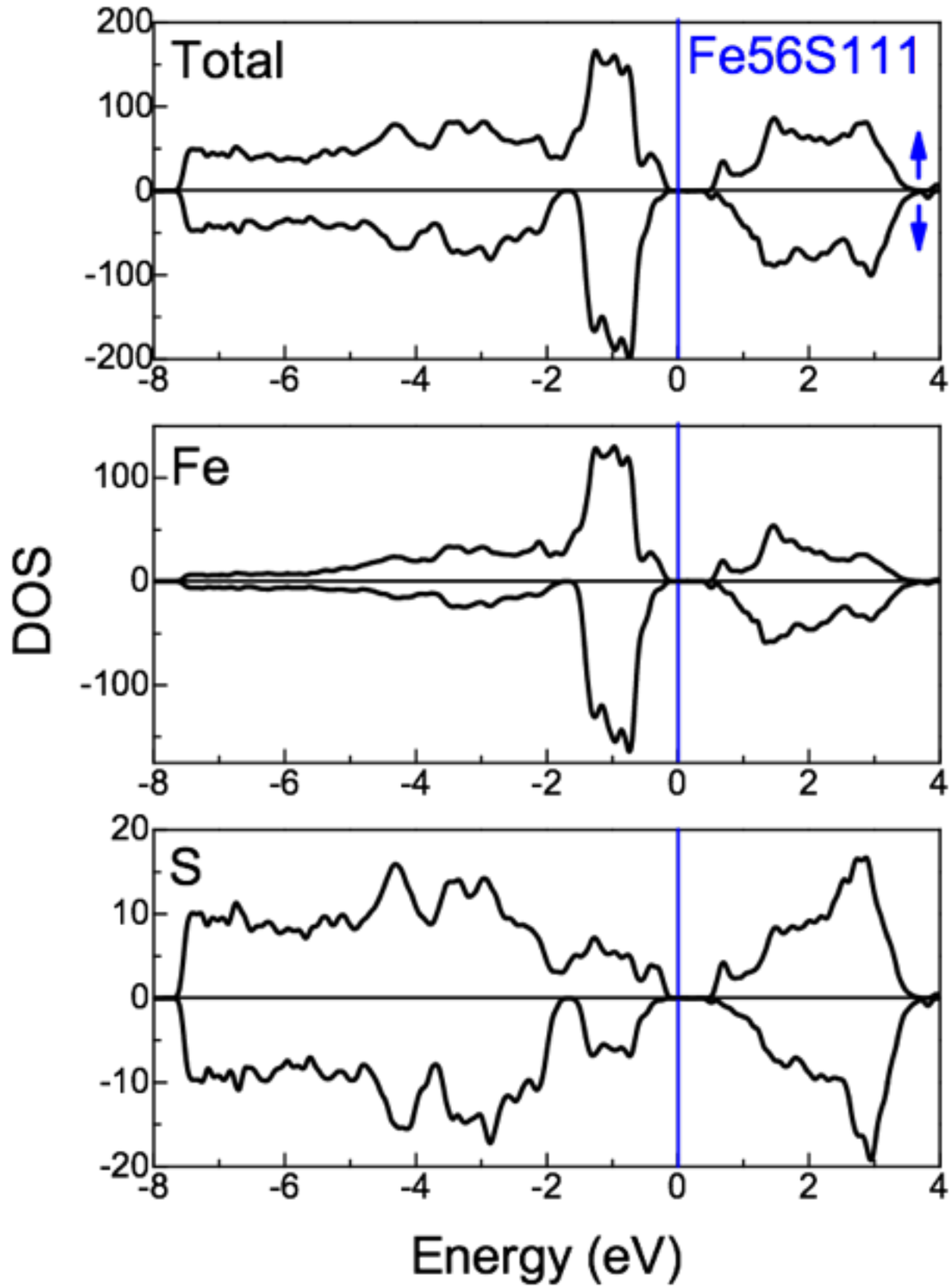
(C) Fe14S28



$Fe_{56}S_{111}$ (C) : one vacancy on surface

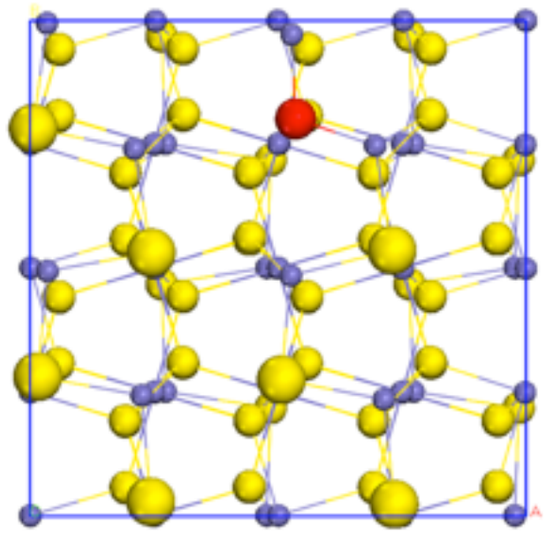






$Fe_{56}S_{96}$ (A)

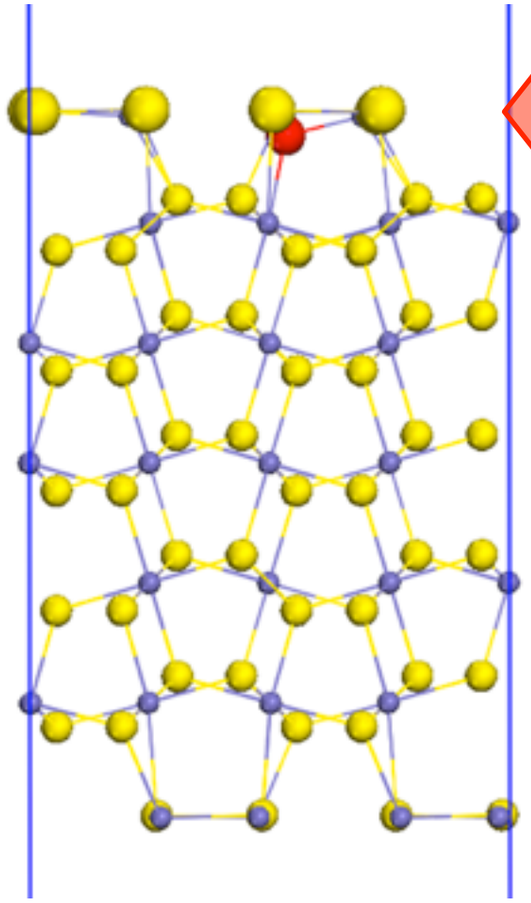
O-substitution for S

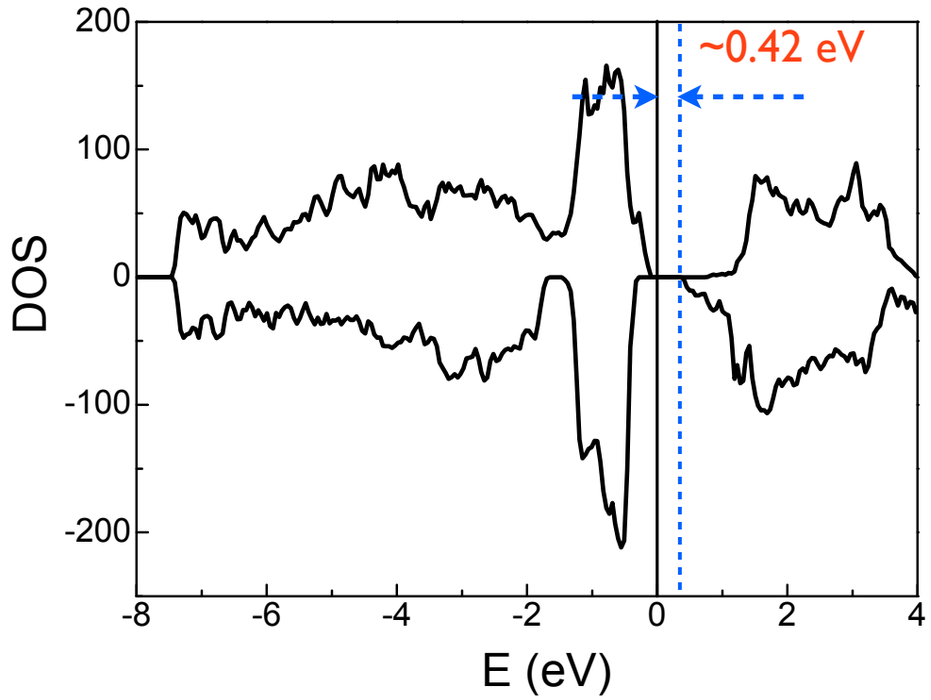


d_{Fe-O} = 1.9, 2.1 Å

d_{Fe-S} = 2.3, 2.6 Å

Δh_{O-S} = -0.57 Å



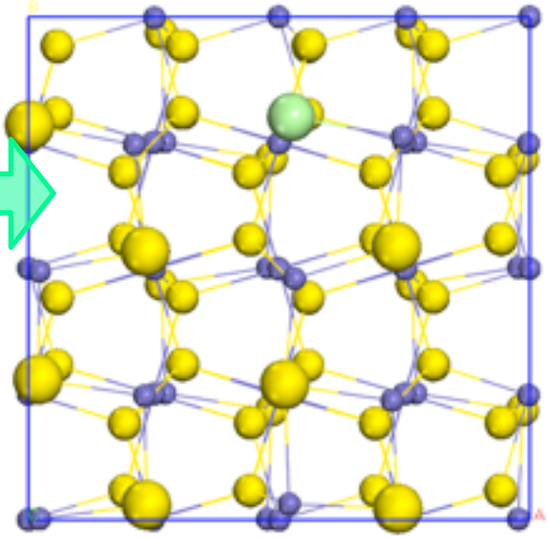


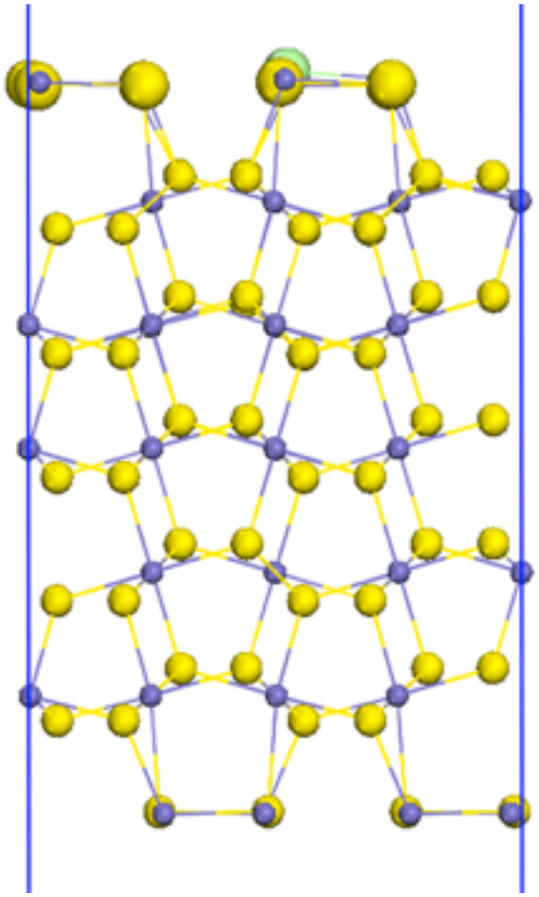
Cl-substitution for S

d_{Fe-Cl} = ~2.44 Å

d_{Fe-S} = ~2.35 Å

Δh_{Cl-S} = +0.26 Å





Summary

- Using density functional calculations, we studied the structural, energy and electronic properties of various Pyrite surfaces.
- The band gap is closely related to the electronic states of surface. Detailed analyses on surface states can provide useful information for the control of surface defects and band gap.
- Surfaces with different vacancies and defects will be studied by DFT calculations through collaborations with experimental and other theoretical efforts.