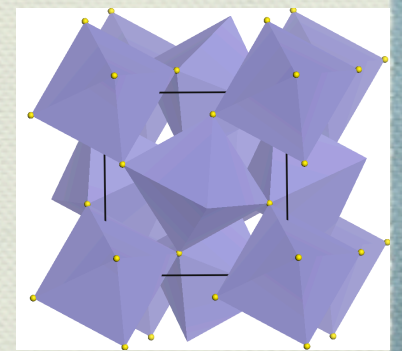


# Density Functional Theory (DFT) Studies for Iron Pyrite



*Yanning Zhang, Jun Hu, and Ruqian Wu*  
2010.9-2011.8



# What we can do for studies of Pyrite

$$\left[-\frac{1}{2}\nabla^2 + V(r)\right]\Psi_i(r) = \varepsilon_i\Psi_i(r)$$

## **Structural properties**

Elastic constants, formation energies for vacancies and other deficiencies , stability of nanostructures, surfaces and interfaces ...

## **Electronic Properties**

Band structure, density of states, defect states, charge rearrangements, wave function of local or non-local states, transport ...

## **Optical properties**

Dielectric function, x-ray adsorption, phonon ...

## **Magnetic properties**

Local magnetization, magnetic ordering, magneto-optical properties ...

# What we have done for studies of Pyrite

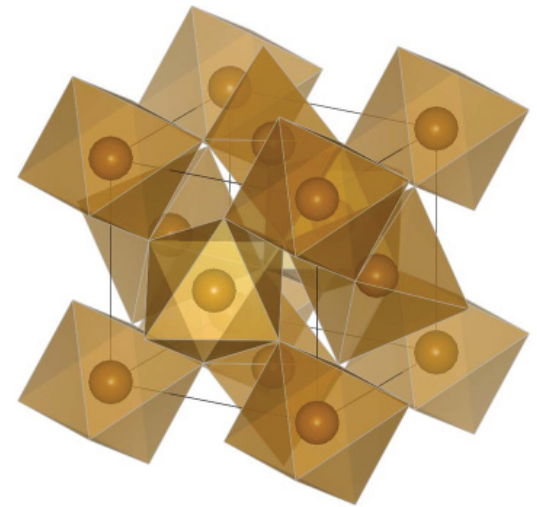
## Bulk FeS<sub>2</sub>

- ☑ Various *vacancies* (S monomer and dimer, Fe);
- ☑ Different *dopants* (O, N, P, Se, F, Cl and Br);
- ☑ Different *metal substituents* (Sc, V, Cr, Mn, Co, Ni, Cu and Zn) on the electronic, optical and magnetic properties of the bulk FeS<sub>2</sub>.

## FeS<sub>2</sub>(001) surfaces

- ☑ The influence of the surface *stoichiometry* and *morphology* on the band gap of FeS<sub>2</sub>(001) surfaces;
- ☑ The *segregation* of S vacancy and atom between surface and interior sites under different surface conditions;
- ☑ X-ray absorption spectroscopy (*XAS*);
- ☑ The *surface energies* of Fe-S pair potentials of the bulk FeS<sub>2</sub> and the FeS<sub>2</sub>(001) surface.

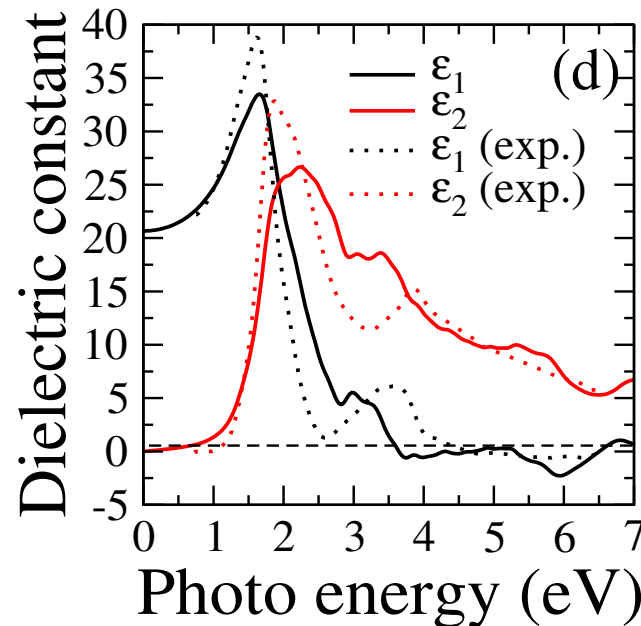
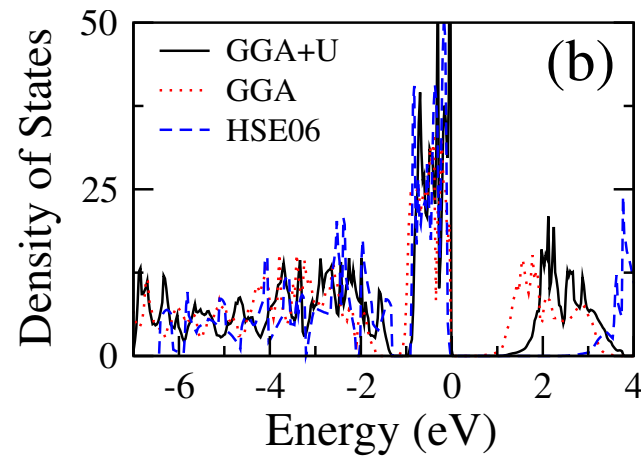
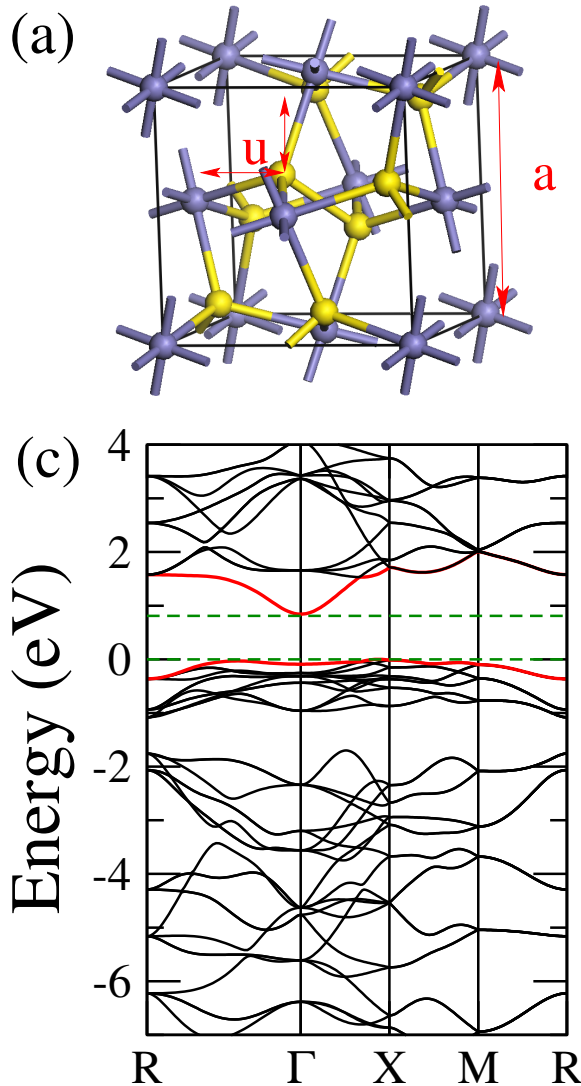
# Bulk FeS<sub>2</sub>



# Computational Details

- DFT calculations with the plane-wave-based *Vienna Ab initio Simulation Package* (VASP)
- Projector augmented wave (PAW) method
- Generalized-gradient approximation (GGA)
- The Hubbard U correlation ( $U = 2.0$  eV)
- Energy cutoff (350 eV), cell-size dependent  $k$ -points
- Atomic model: up to  $3 \times 3 \times 3$  supercell for bulk simulations; a seven-layer slab with a vacuum of  $\sim 15$  Å thick for surface calculations.

# Structure, band gap and dielectric functions of bulk FeS<sub>2</sub>



**Lattice constant,  $a$ :**

calc.: 5.422 Å

exp.: 5.419 Å

**Internal coordinate,  $u$ :**

calc.: 0.385

exp.: 0.385

**Band gap:**

calc.: 0.81 eV from GGA+U

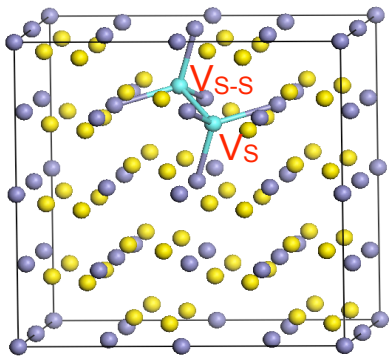
0.50 eV from GGA

2.66 eV from HSE06

exp.: 0.95 eV

**Effect masses:**

$m_h=1.23$ ;  $m_n=0.49$



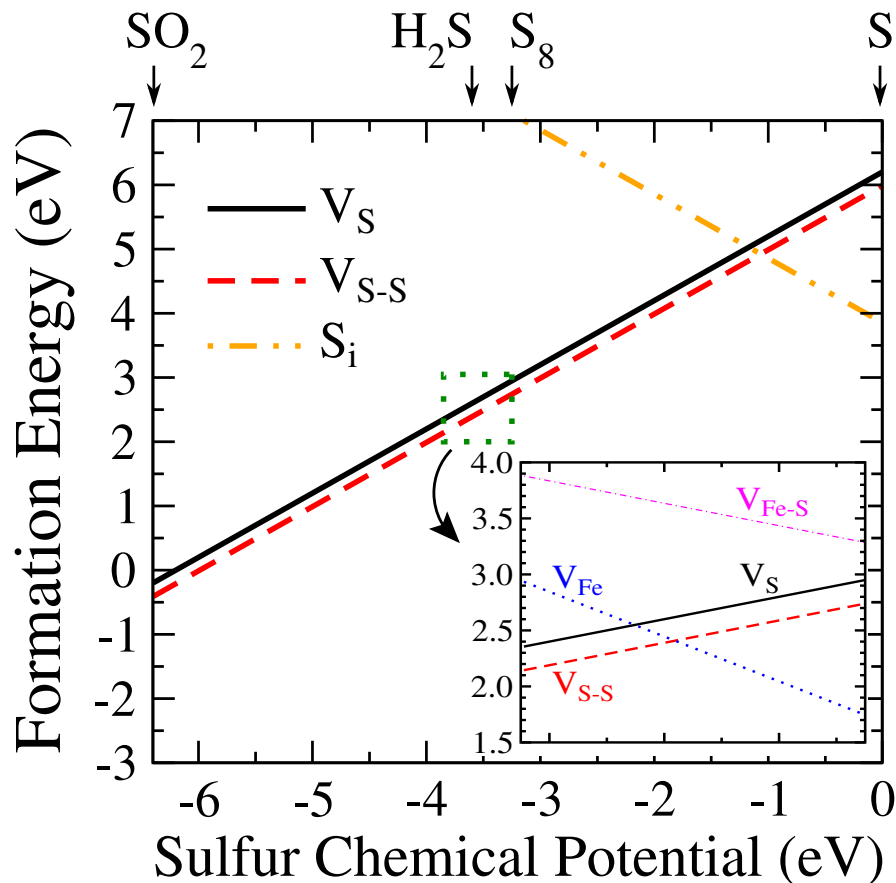
# Vacancies: S monomer ( $V_S$ ), S dimer ( $V_{S-S}$ ), and Fe

$$\Delta H_f = [E(V) - E(FeS_2) + n_S \mu_S] / n_S$$

$E(V)$  -- the total energy of a  $FeS_2$  cell *with* sulfur vacancies.

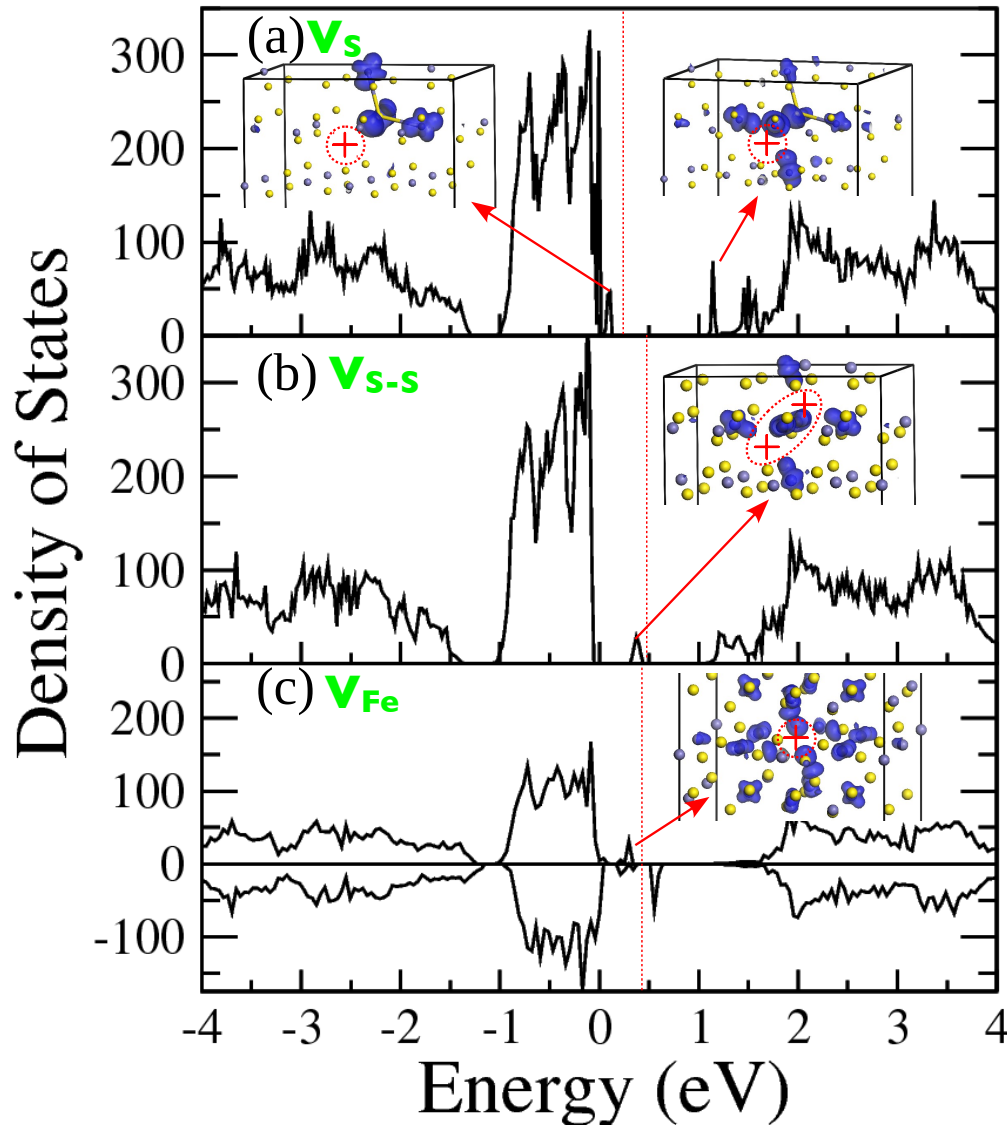
$E(FeS_2)$  -- the total energy of  $FeS_2$  *without* sulfur vacancies.

$\mu_S$  -- the chemical potential of a S atom



- ❖  $V_S$  and  $V_{S-S}$  can form easily in the O-rich condition;
- ❖ It's relatively easy to remove an additional S once  $V_S$  is formed;
- ❖ In the S-rich environments, the removal of a S-Fe pair costs high energy and  $V_{Fe-S}$  is hence unlikely to develop in samples.
- ❖ The presence of S interstitial is excluded, because of the high formation energy.

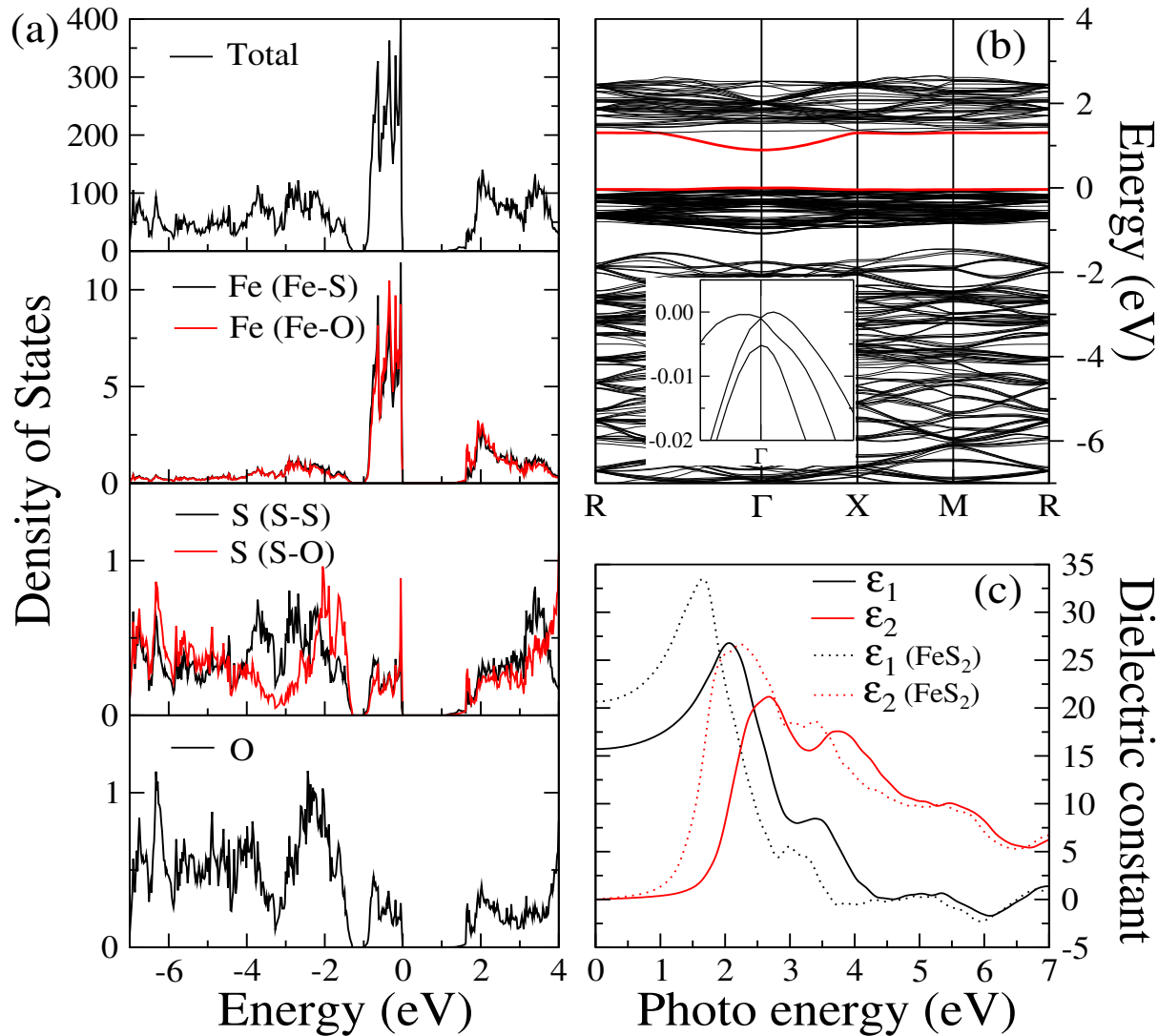
# The effect of vacancies on the electronic properties of bulk FeS<sub>2</sub>



- ❖  $V_S$  induces defect states near VBM ( $S-p_z$  and  $Fe-t_{2g}$ ) and CBM ( $S-p_z$  and  $Fe-e_g$ );
- ❖  $V_{S-S}$  produces a nonbonding state ( $Fe-e_g$ ) right below the Fermi level;
- ❖ Both  $V_S$  and  $V_{S-S}$  do **not** reduce the band gap;
- ❖  $V_{Fe}$  triggers spin polarization, with a magnetic moment  $2.0 \mu_B/\text{cell}$ , suggesting possible long range magnetic ordering in Fe-deficient pyrite;
- ❖ Several states appear in the band gap; they may trap electrons in the minority spin channel or holes in the majority spin channel.

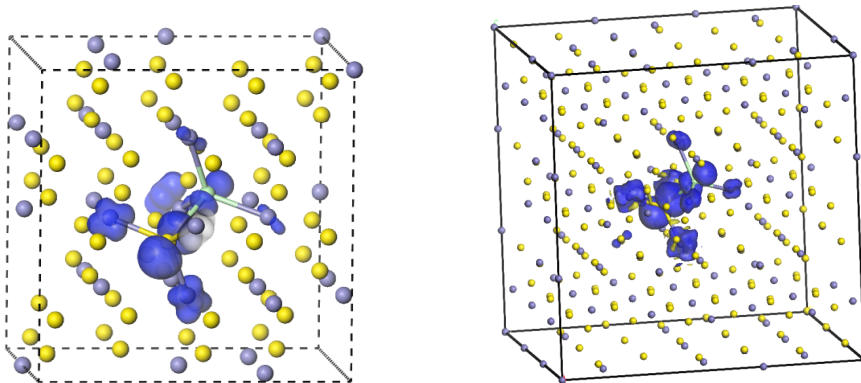
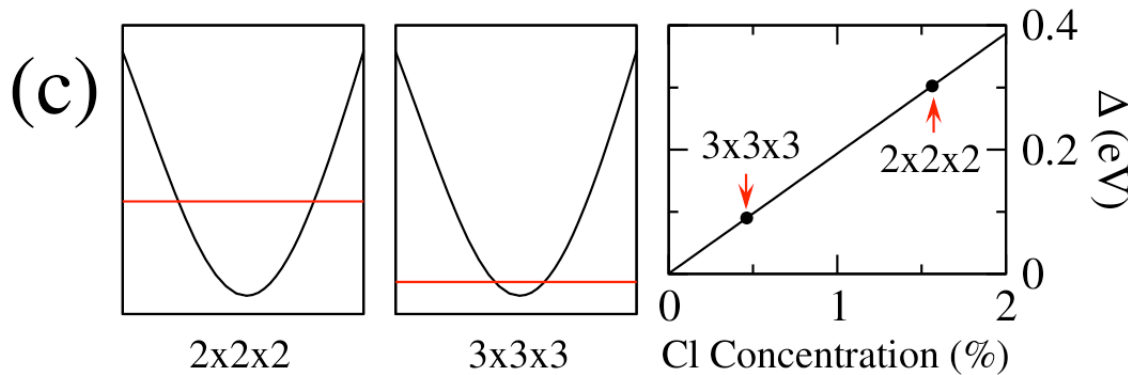
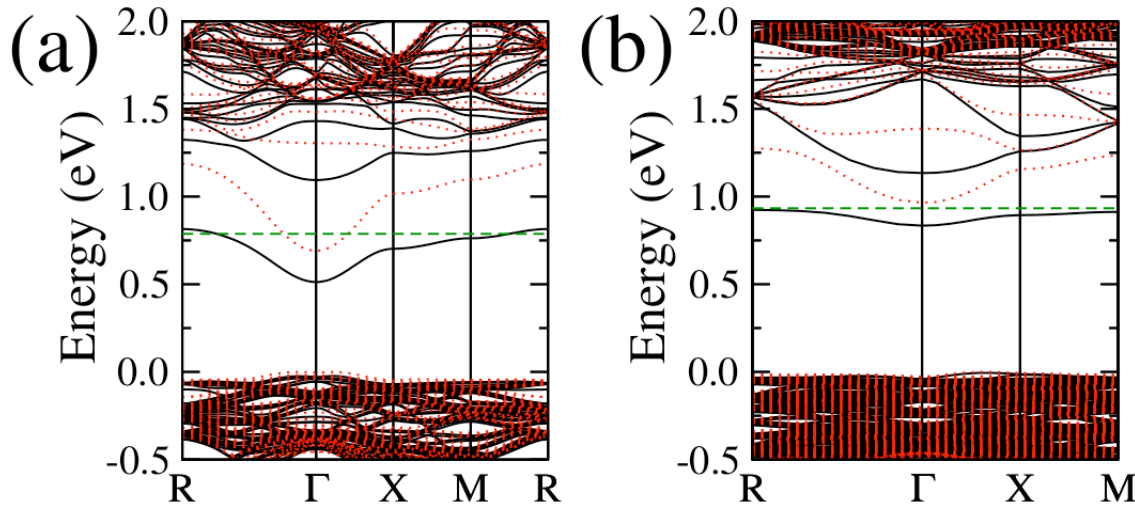


# Oxygen substitution of S



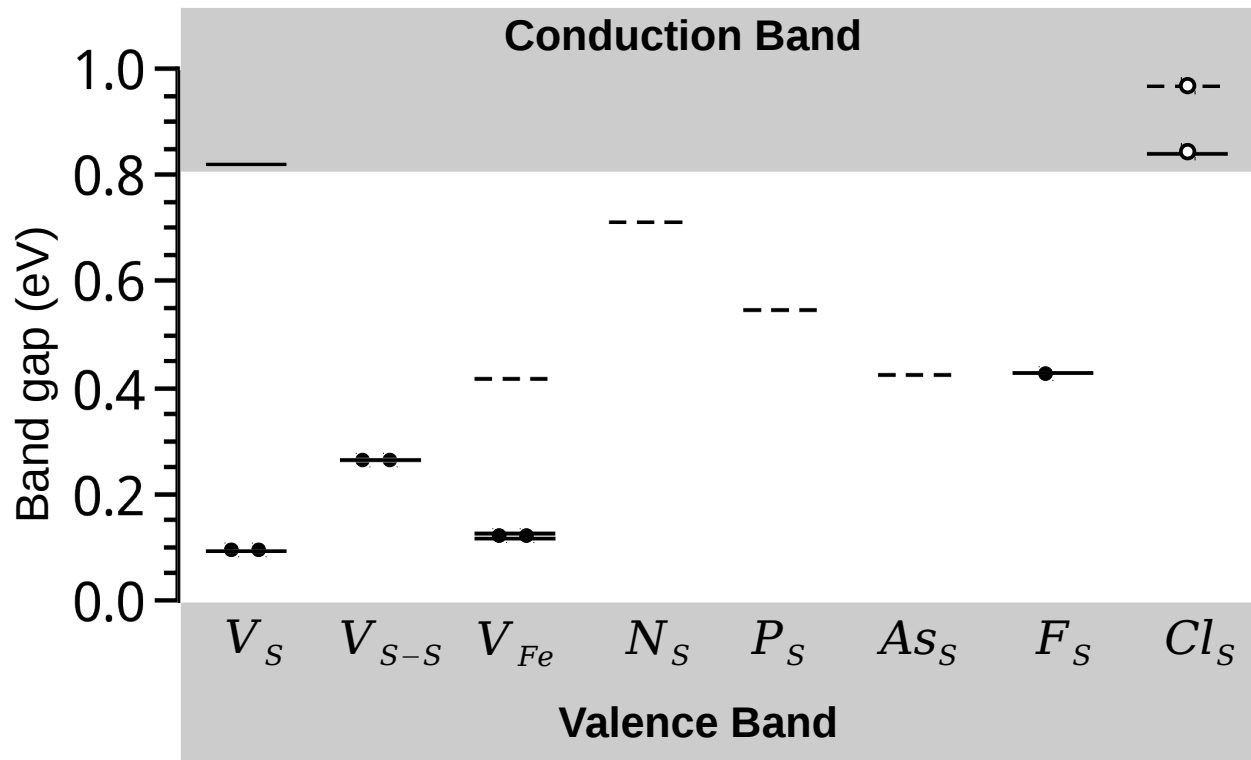
- ✿ No gap state is induced;
- ✿ S 3p states shift upwards due to the hybridization with O;
- ✿ Charge states:
  - O (-1.65);
  - S in O-S bond (0.62);
  - other S (-0.43)
- ✿ Band gap: 0.89 eV
- ✿ Effective masses:  $m_h=2.05$ ,  $m_n=0.54$

# Chlorine substitution of S



- ❖  $\text{Cl}_s$  has a long-range effect, which makes the  $\text{FeS}_2\text{Cl}$  (1.6%) a compound and results in a metallic feature due to the partially occupied new conduction band;
- ❖ At concentration of 0.5%, Cl can be regarded as impurity, although the impurity band is dispersive.
- ❖ The impurity bandwidth is linearly dependent on the Cl concentration.
- ❖ The  $m_n$  of spin majority channel is larger than that of spin minority channel: 0.79 vs 0.57; while the trend of  $m_n$  are opposite: 1.70 vs 2.61.

# The defect levels alignment ( $\Gamma$ point)

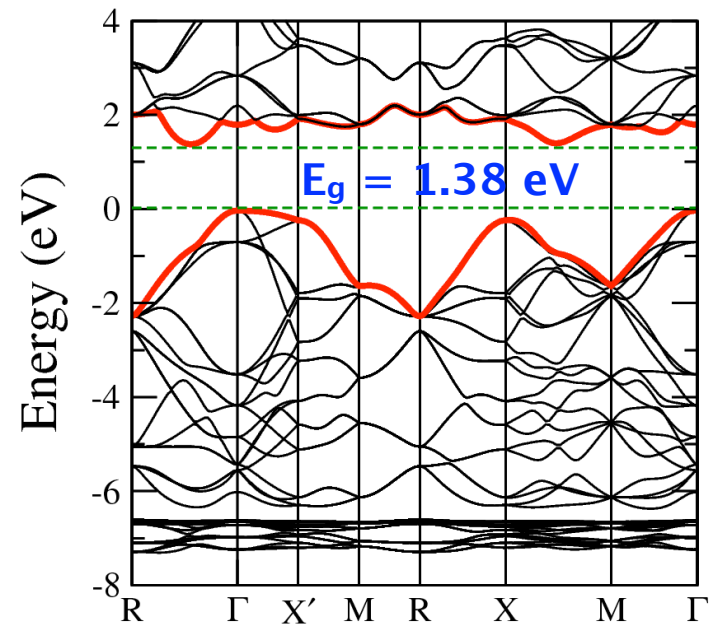
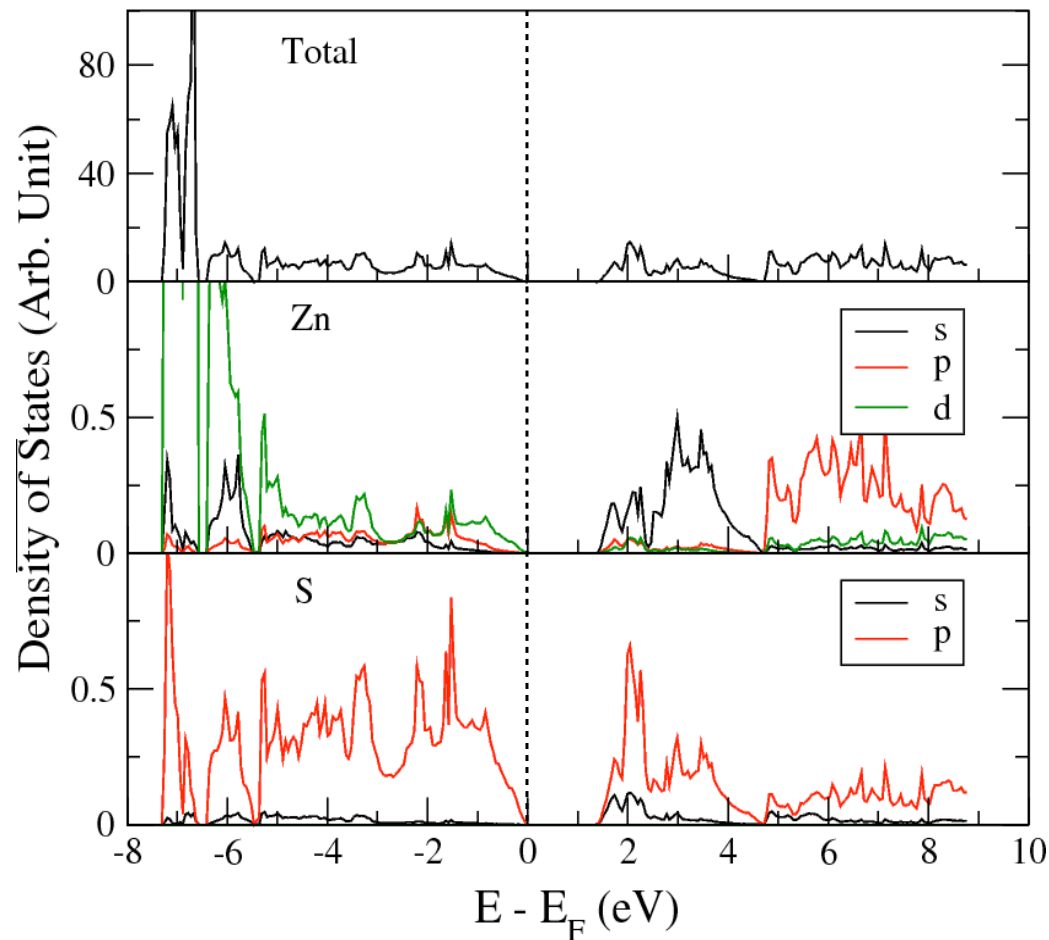


- Vacancies can't produce carriers since both the donor level ( $V_S$  or  $V_{S-S}$ ) and acceptor level ( $V_{Fe}$ ) are deep. So  $V_{Fe}$  could not be the source of p-type semi-conducting in pyrite sample.
- Doping Cl in  $\text{FeS}_2$  may produces resonant donor state. The same as Br, but Br induces larger structure distortion due to the large ionic size.
- Doping Group-V elements may not obtain shallow acceptors.

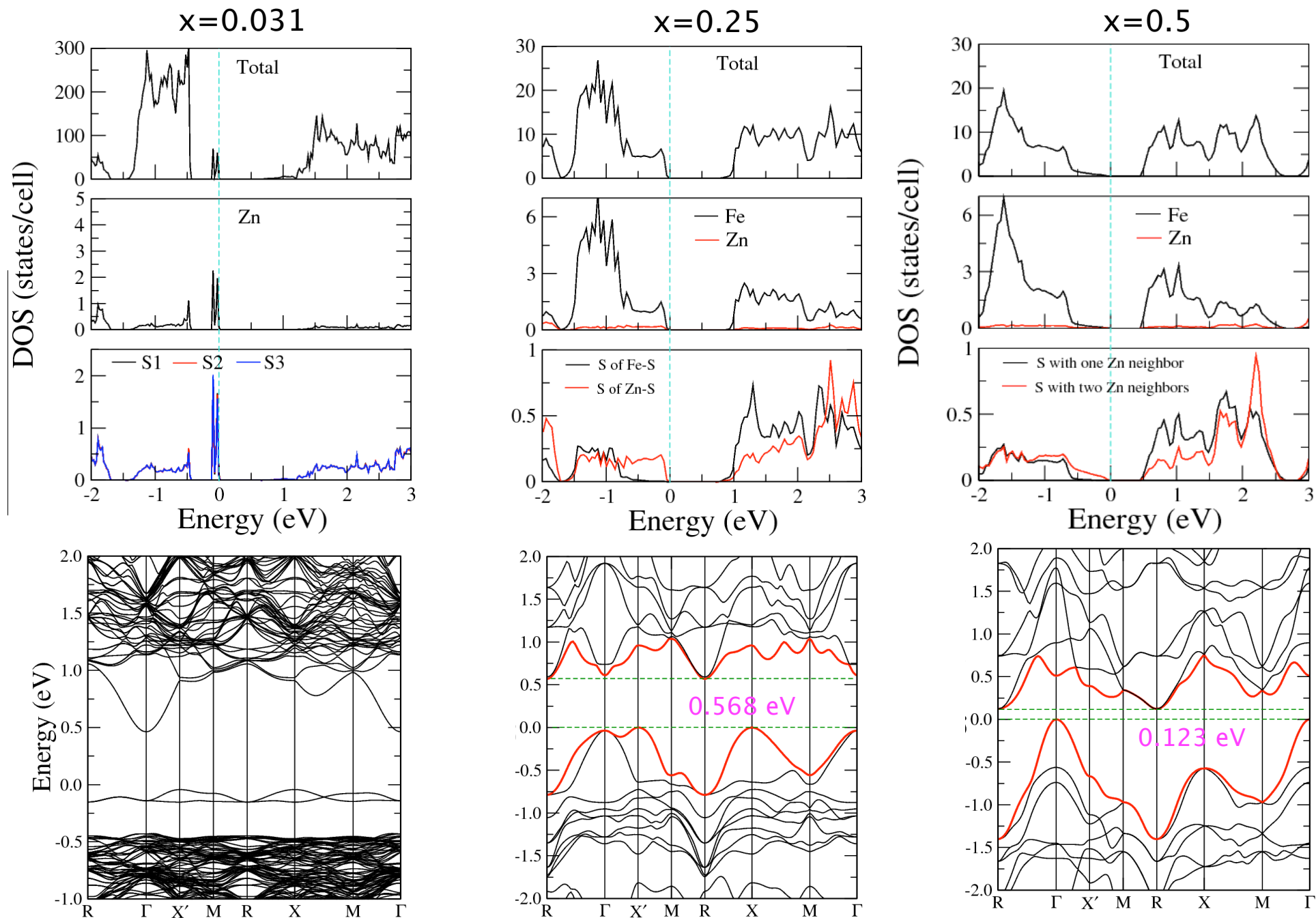
# The effect of different metal substituents on the electronic properties of bulk FeS<sub>2</sub>

21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn

**Bulk ZnS<sub>2</sub>**



# Fe<sub>1-x</sub>Zn<sub>x</sub>S<sub>2</sub> alloys

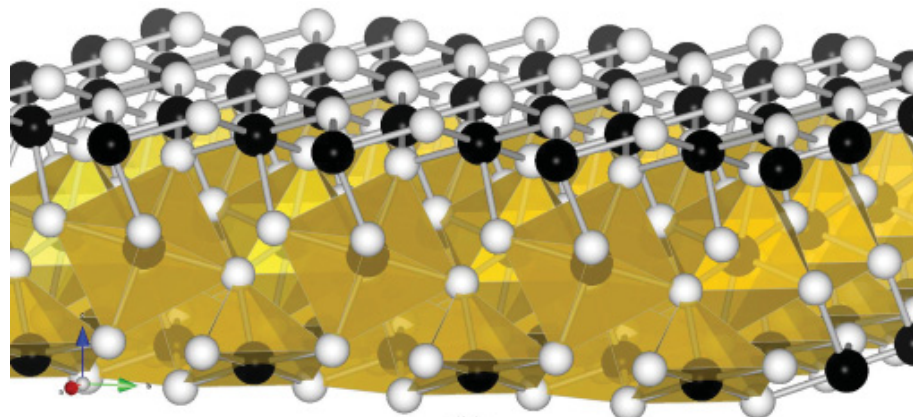


# Summary

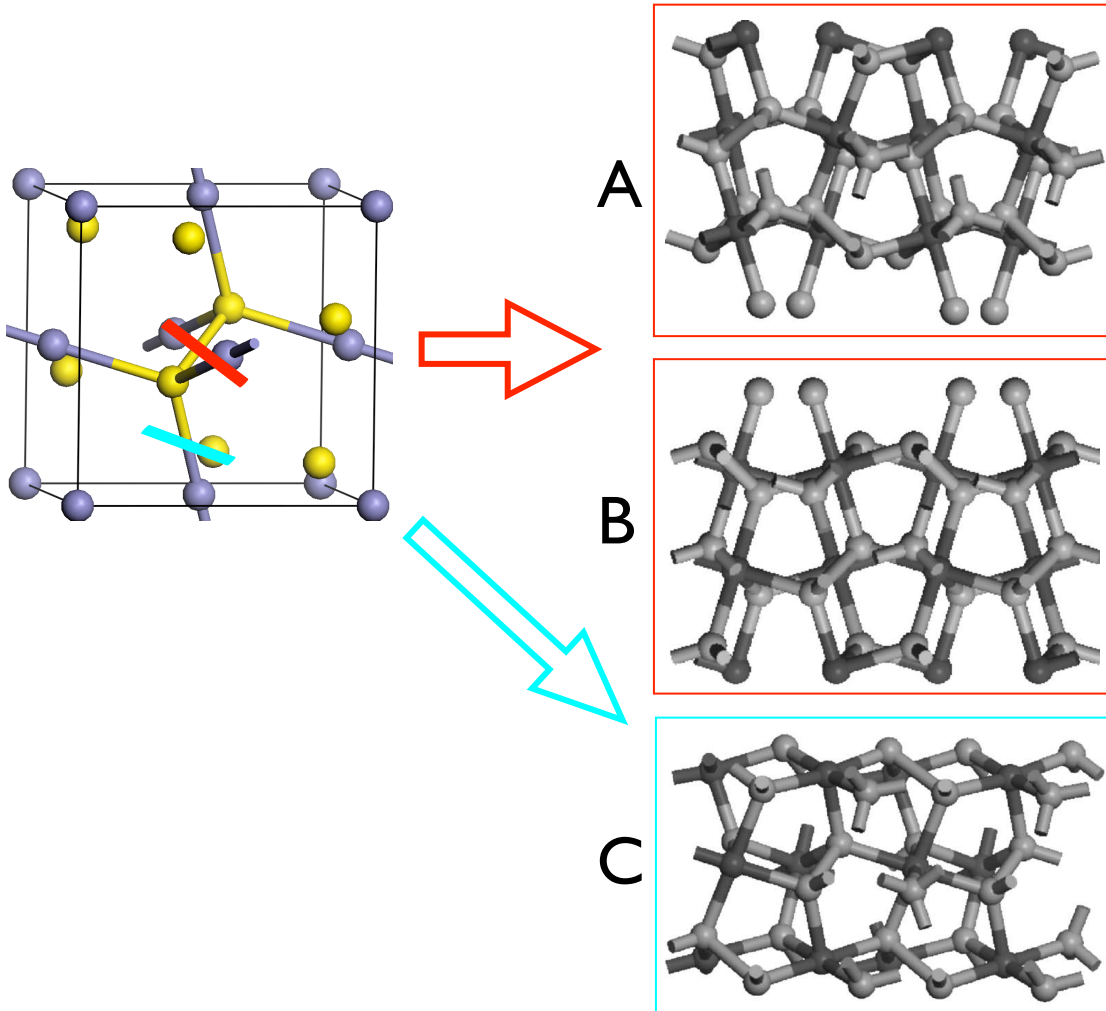
- We have studied various native defects
- We have doped various Group-V, -VI and -VII elements in principle.
- We'll pay our attention to cation doping with 3d transition metal elements in the future.
- We'll study the optical properties of  $\text{Fe}_{1-x}\text{Zn}_x\text{S}_2$  to see if it deserves further studies.

J. Hu, Y.N. Zhang, M. Law and R.Q. Wu, “*First-principles study on electronic properties of anion defects in iron pyrite*”, Phys. Rev. B, to be submitted.

# FeS<sub>2</sub>(100) surfaces

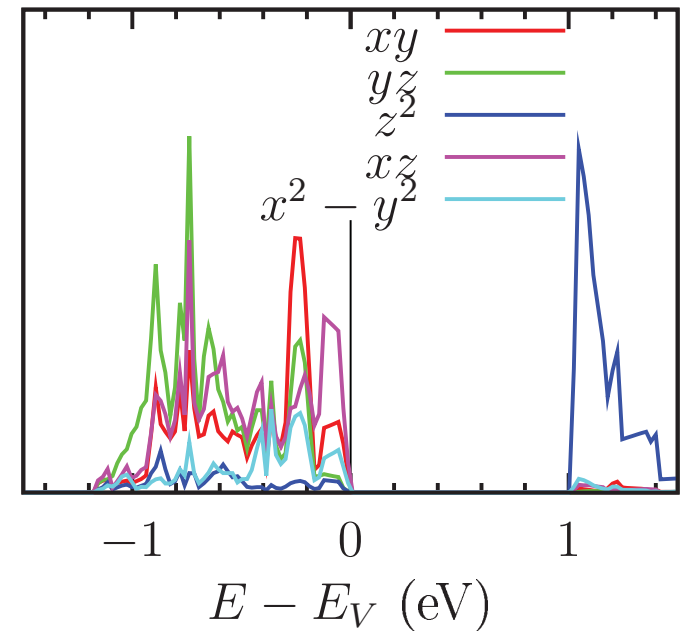


# Pyrite (100) Surfaces



R. Sun et al., PRB 83, 235311 (2011)

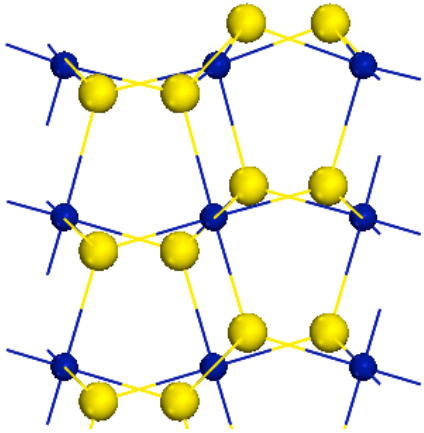
- *low-spin* ground state
- The  $d_z^2$  surface states are located at the CB edge
- no gap state



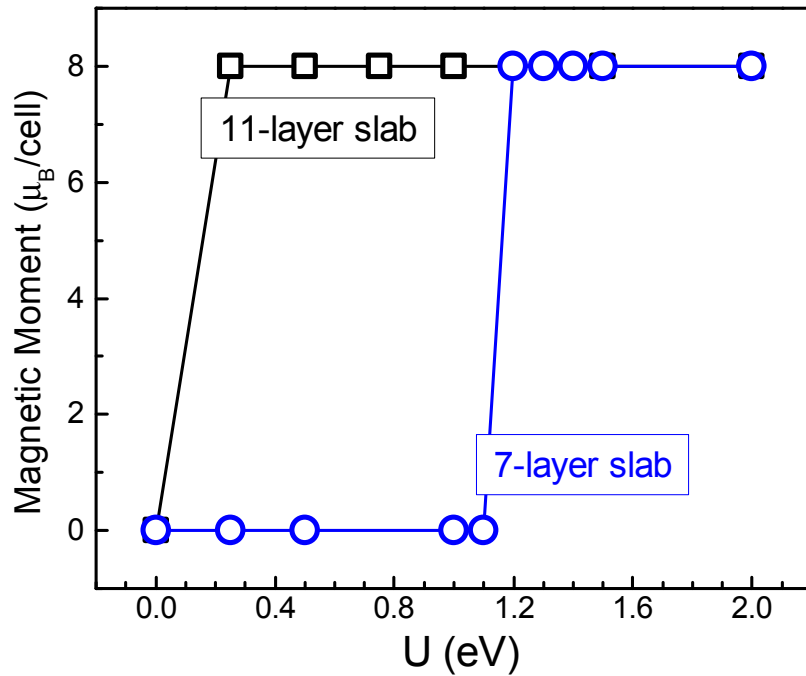
American Mineralogist 83 (1998) 1067;  
Physical Review B 72 (2005) 235427;  
Surface Science Reports 64 (2009) 1–45;

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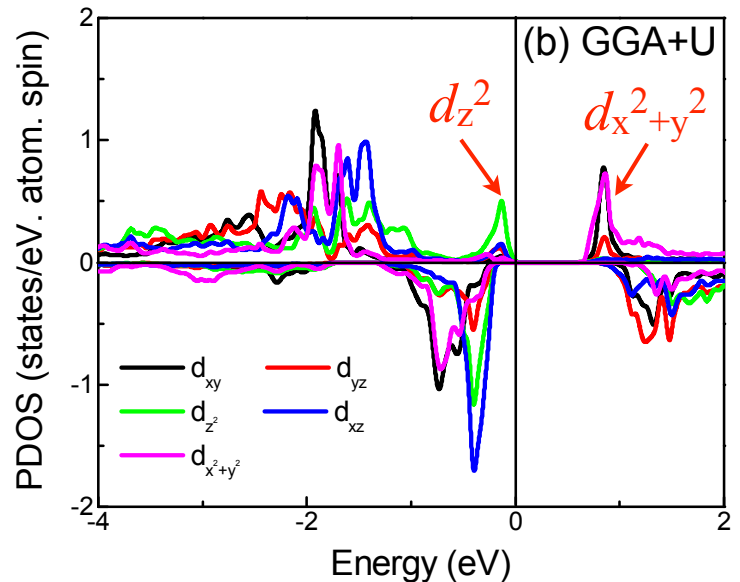
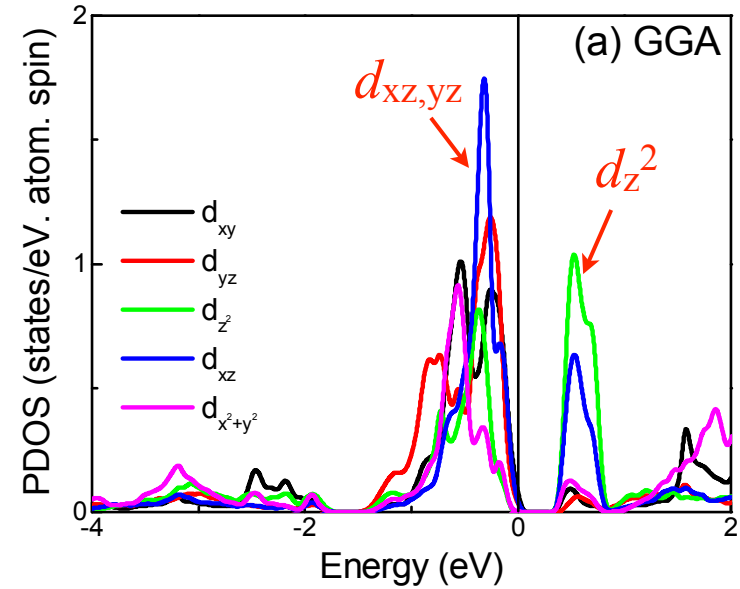




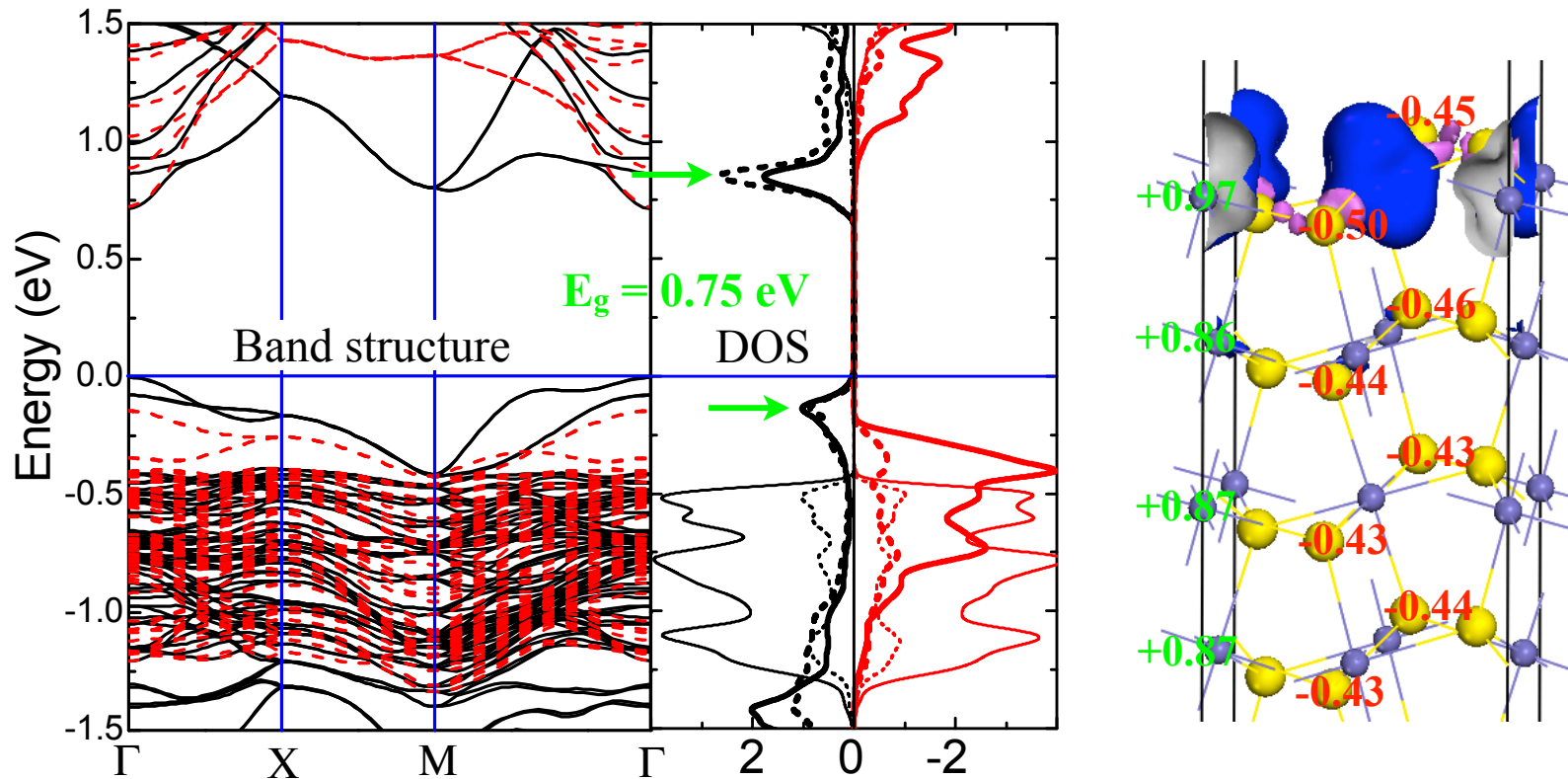
# DFT tests on the spin configuration of stoichiometric FeS<sub>2</sub>(100) surface



- The high-spin state of stoichiometric FeS<sub>2</sub>(001) surface is stable in a wide range of U values.
- The Hubbard U correlation greatly changes the electronic properties of surface.



# Electronic structure of stoichiometric surface



- ✓ The gap is determined by the energy separation between two surface states in the *majority* spin channel: one with the Fe- $d_z^2$  feature atop the valance band (VB) and one has the Fe- $d_{x^2+y^2}$  feature at the bottom of the conduction band (CB);
- ✓ The magnetization mainly occurs in the *outermost* layer, whereas the interior layers remain in the low-spin status;
- ✓ Each surface Fe atom losses 0.1 more electrons, mainly from the dangled Fe-S bond to their sulfur neighbors.

# Structure and surface energy with a varying stoichiometry

$$\gamma = \frac{1}{2A} [E_{slab} - N_{Fe}\mu_{Fe} - N_S\mu_S]$$

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

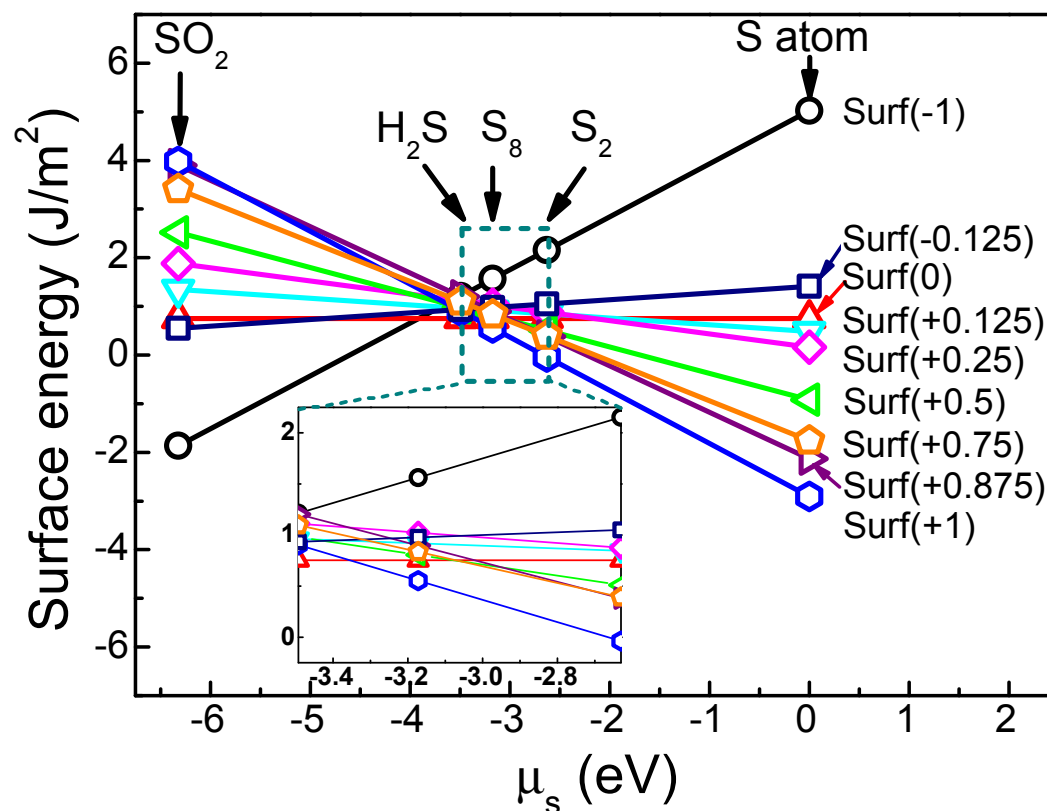
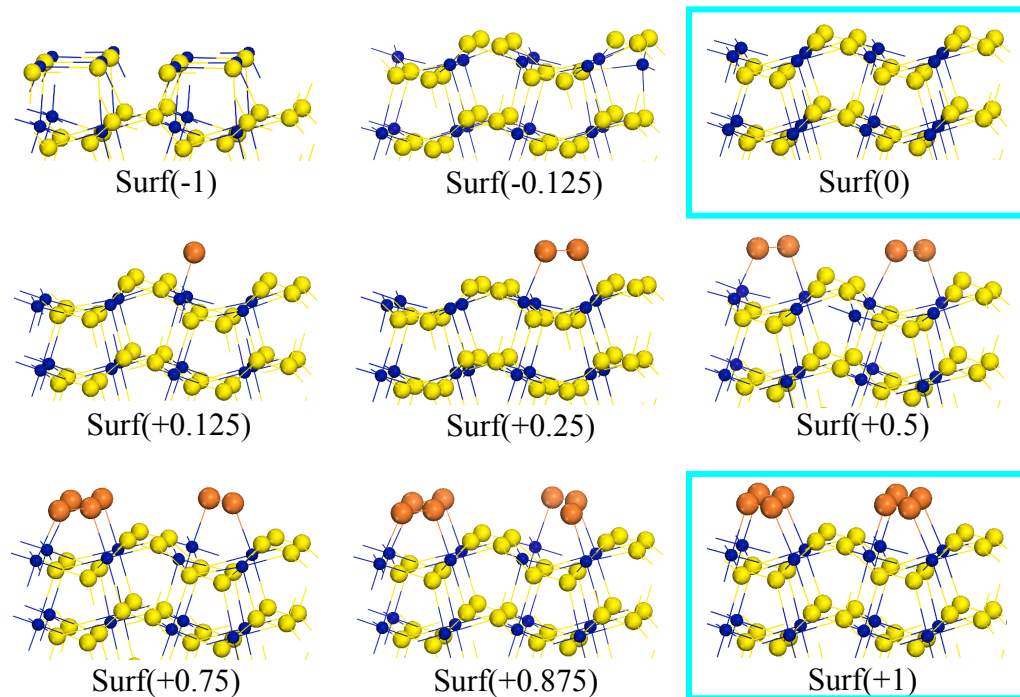
$E_{slab}$  -- the total energy of FeS<sub>2</sub> surface;

$N_{Fe} / N_S$  -- the numbers of Fe / S atoms;

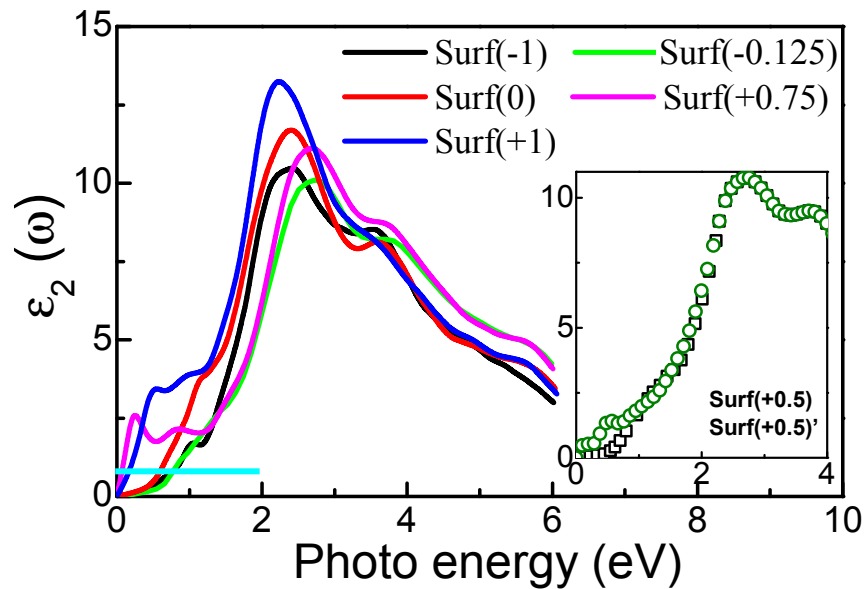
$\mu_{Fe} / \mu_S$  -- the chemical potential of Fe / S atom;

$A$  -- the surface area.

- ✓ Addition of sulfur atoms to Surf(0) forms dimers on the Surf(n) surfaces;
- ✓ The Surf(0) is stable only in a narrow window,  $-3.92 \text{ eV} < \mu_S < -3.36 \text{ eV}$ ;
- ✓ In a typical annealing environment, Surf(+1) is more preferential except at the end of H<sub>2</sub>S.



# Band gap as a dependence of surface sulfur stoichiometry

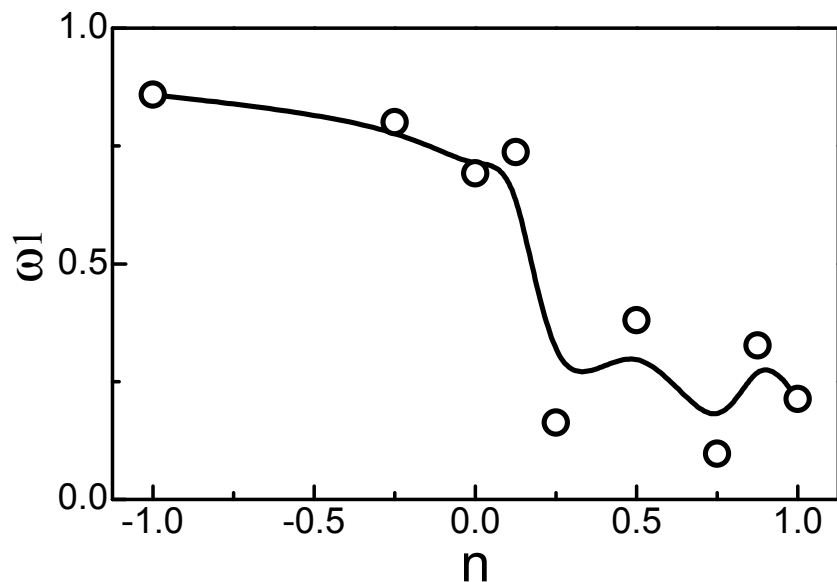


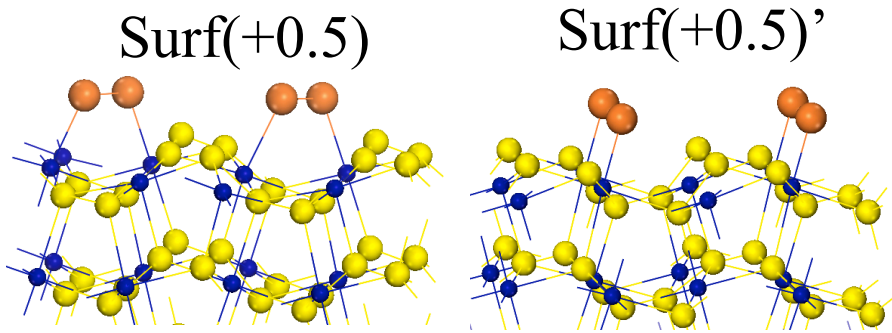
❖  $\epsilon_2(\omega)$  curves keep the main features of bulk pyrite for  $\omega > 1$  eV;

❖ For  $n < 0.25$ ,  $\epsilon_2(\omega)$  curves drops quickly for  $\omega < 1$  eV;

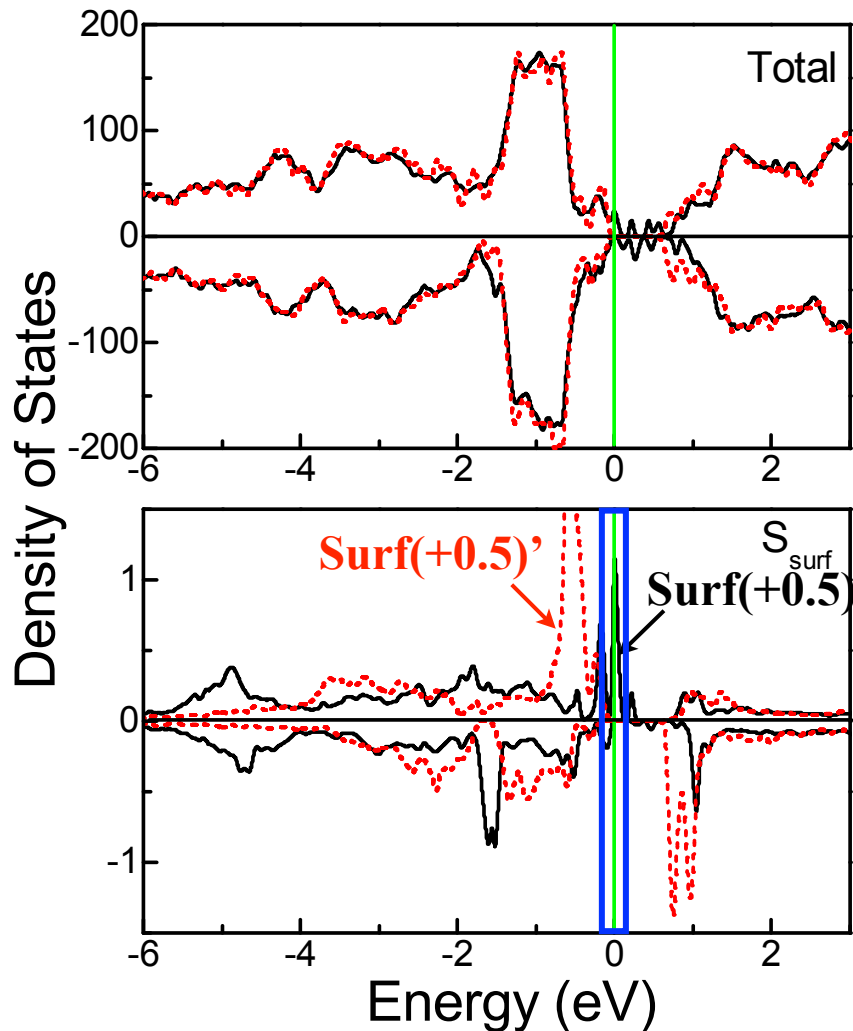
❖ For  $n > 0.25$ , side peaks appear at  $\omega < 0.5$  eV, demonstrating a decrease in band gap;

❖ The “band gap” shrinks with increasing surface sulfur: from  $\sim 0.75$  eV to metallic feature.

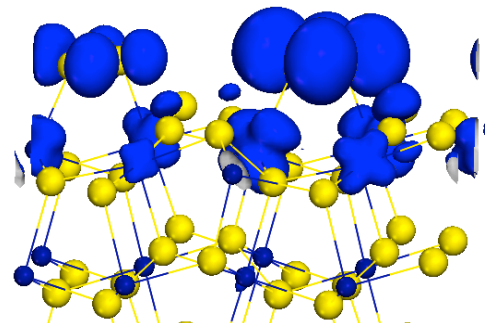




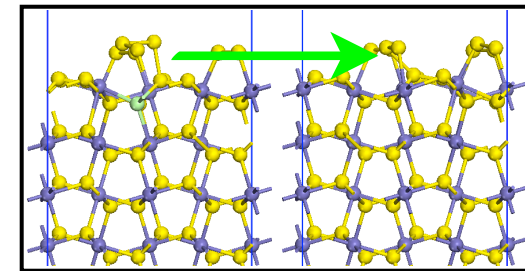
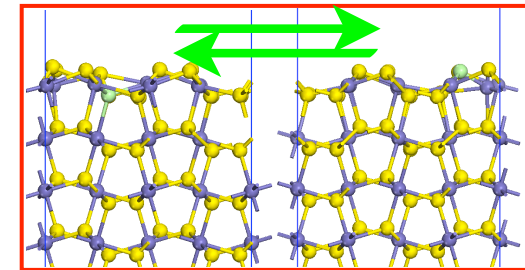
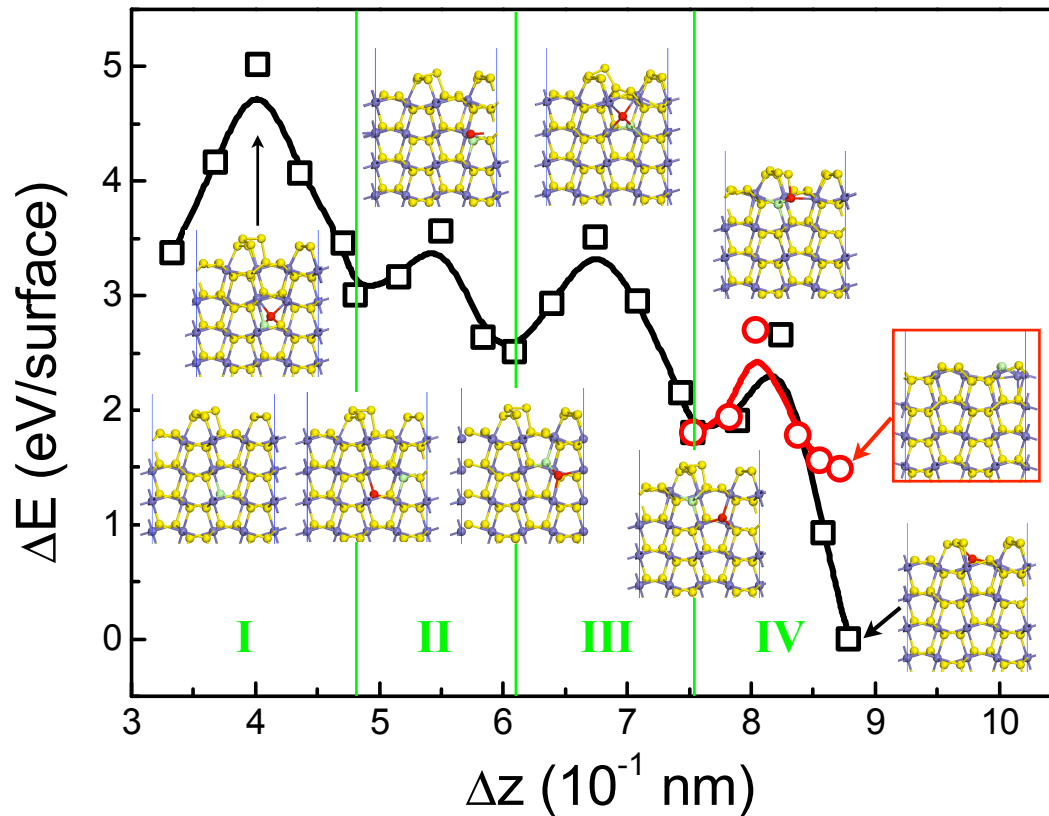
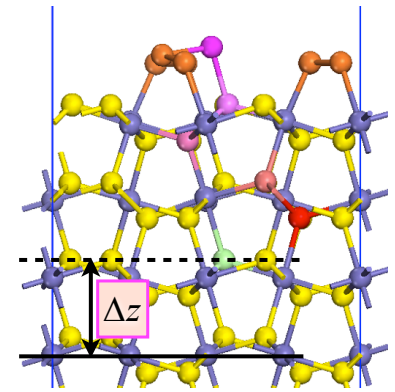
## The effect of surface sulfur morphology on the band gap



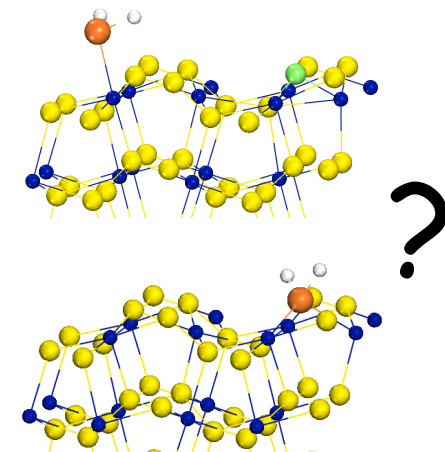
- ❖  $S_{0.5}'$  is unstable with an energy loss of 2.62 eV/surface against the  $S_{0.5}$ ;
- ❖ The band gap for  $S_{0.5}'$  is 0.65 eV, with large  $S-p_x, p_y$  peaks located at the edge of VB and CB.
- ❖ For  $S_{0.5}$  surface, several sharp peaks appear within the gap region, mainly with  $Fe-d_{xz, yz}$  and  $S-p_x, p_y$  features.



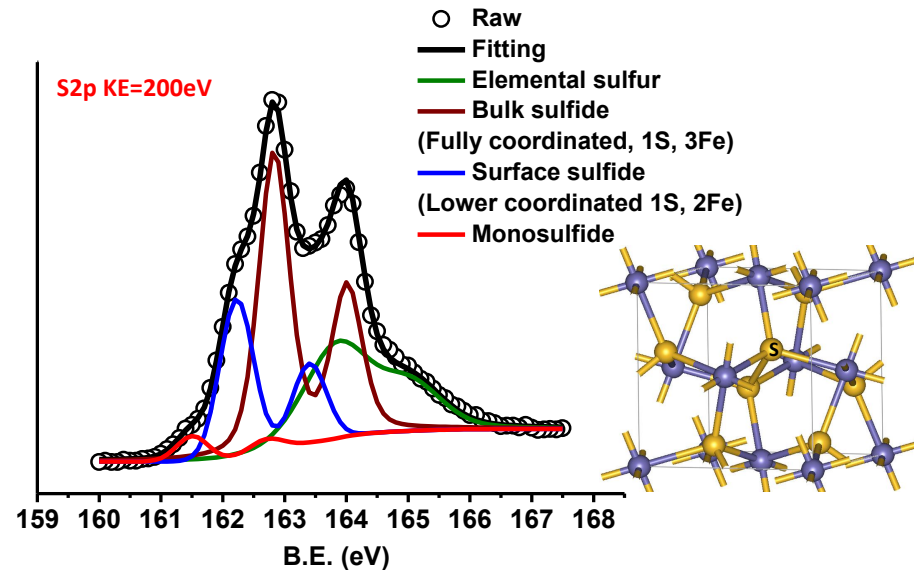
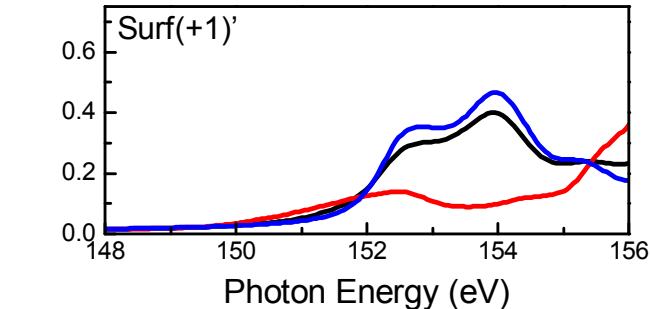
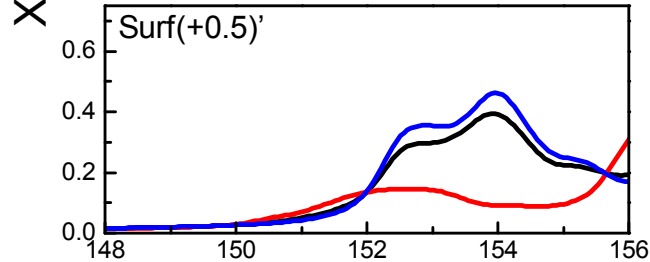
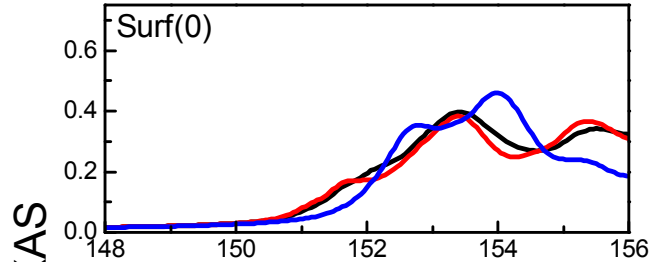
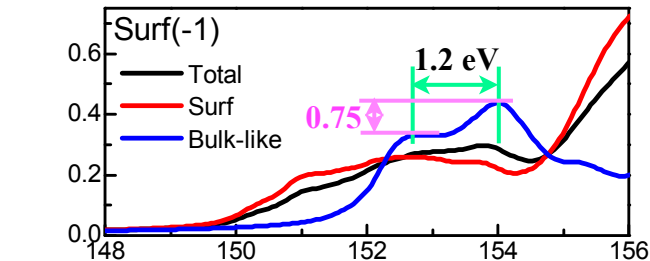
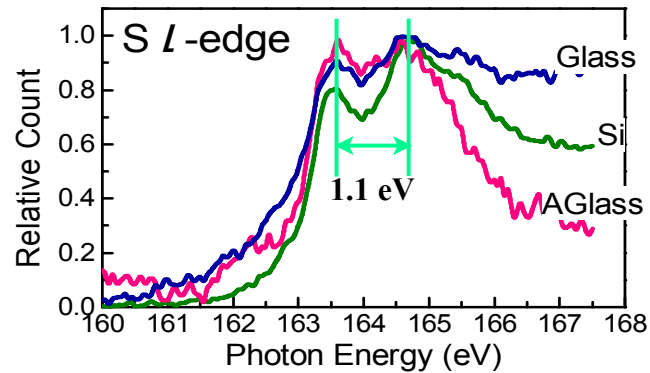
# The segregation of S vacancy and atom



- ❖ The segregation of S vacancy from the interior layer to the outermost layer is energetically preferred;
- ❖ The surface conditions may affect the segregation of S vacancy.



# X-ray absorption spectroscopy (XAS)



❖ XAS spectrum of pyrite is very useful for studies of the surface structure and valance states.

# Summary

Systematic spin-polarized DFT calculations were performed for studies of pyrite  $\text{FeS}_2(100)$  surfaces of different stoichiometry.

The stoichiometric  $S_0$  surface is magnetic, semiconducting, and shows high stability in the annealing conditions typically used in experiments.

While S-deficient surfaces still remain semiconductive feature, Excess sulfur dimers may easily form on the stoichiometric surface under S-rich conditions, leading to metallic behavior.

**Y.N. Zhang, J. Hu, M. Law and R.Q. Wu, “*The influence of surface sulfur stoichiometry and morphology on the band gap of pyrite  $\text{FeS}_2(100)$  surfaces*”, *Phys. Rev. Lett*, to be submitted.**



# What we will do soon

- ✿ Segregation of S vacancy under different surface conditions:  
S, H<sub>2</sub>S, and/or Oxygen;
- ✿ Studies of related clean sulfide surfaces: Marcasite, Pyrrhotite  
and troilite;
- ✿ Interface and interfacial states;
- ✿ Optical properties of more complex surfaces/interfaces;
- ✿ .....

- ◆ Density functional calculations can provide various useful information for studies of Pyrite bulk, surface, and nanostructures.
- ◆ It is essential that our calculations are conducted through collaborations with experimental and other theoretical efforts.