First-principles studies of impurity states in bulk iron pyrite

Jun Hu, Yanning Zhang and Ruqian Wu

Department of Physics & Astronomy

University of California, Irvine

Outline

i. Background

ii. Method

iii. Results and discussions

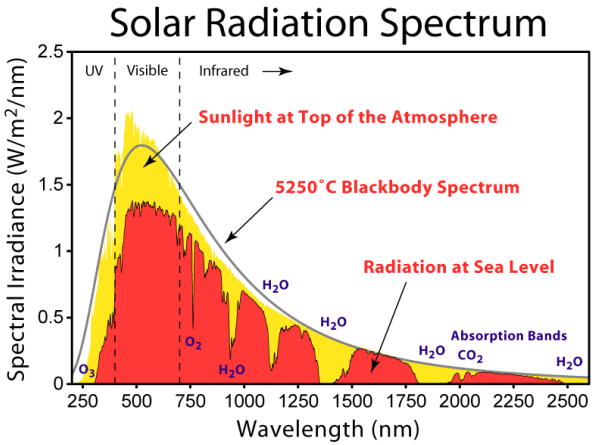
iv. Conclusions and perspective

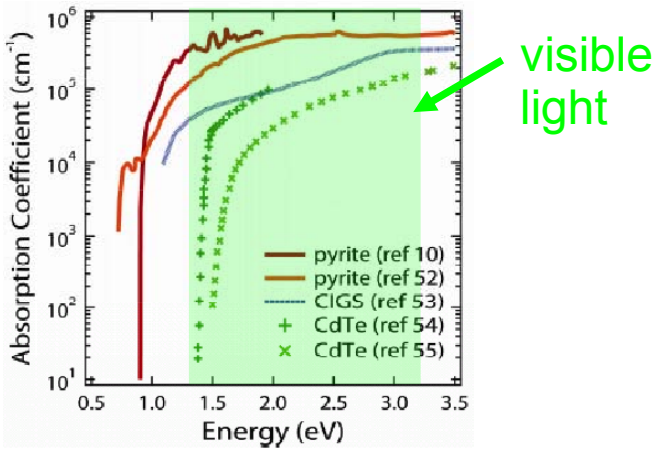
I. Background

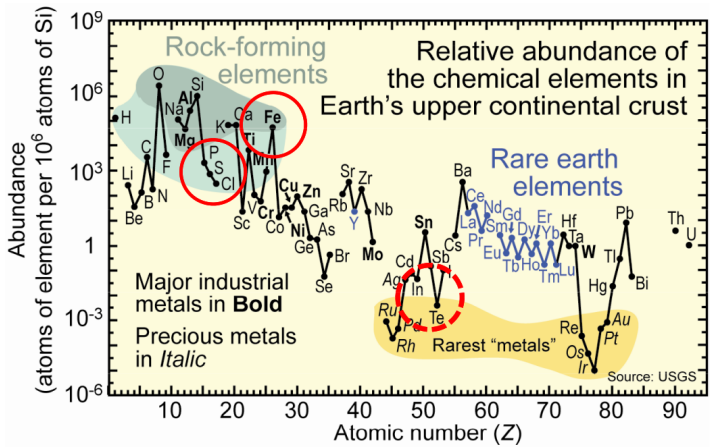
Iron pyrite (FeS_2) is a promising semiconductor for use in solar photovoltaic and photoelectrochemical cells, because of:

i) high absorption coefficient of visible light which stores most part of solar energy

ii) relative abundance in Earth







However, the sulfur deficiency in the as-grown FeS_2 leads to low mobility of carriers and thus low free carrier density.

The aim of our work is to find out effective ways to:

i) suppress formation of sulfur vacancies

ii) engineer the band gap and density of free carriers

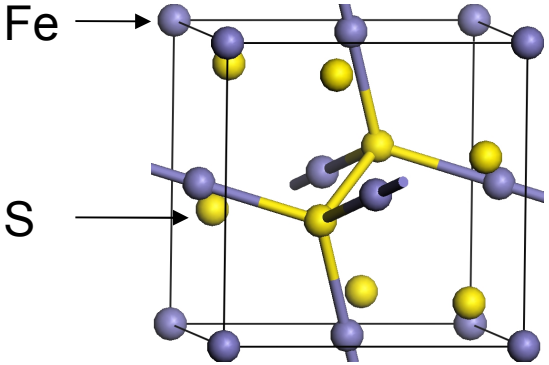
These may be achieved by exotic doping.

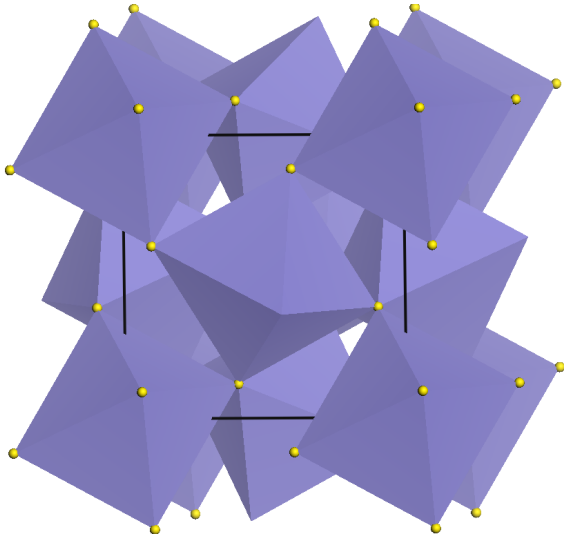
II. Methodology

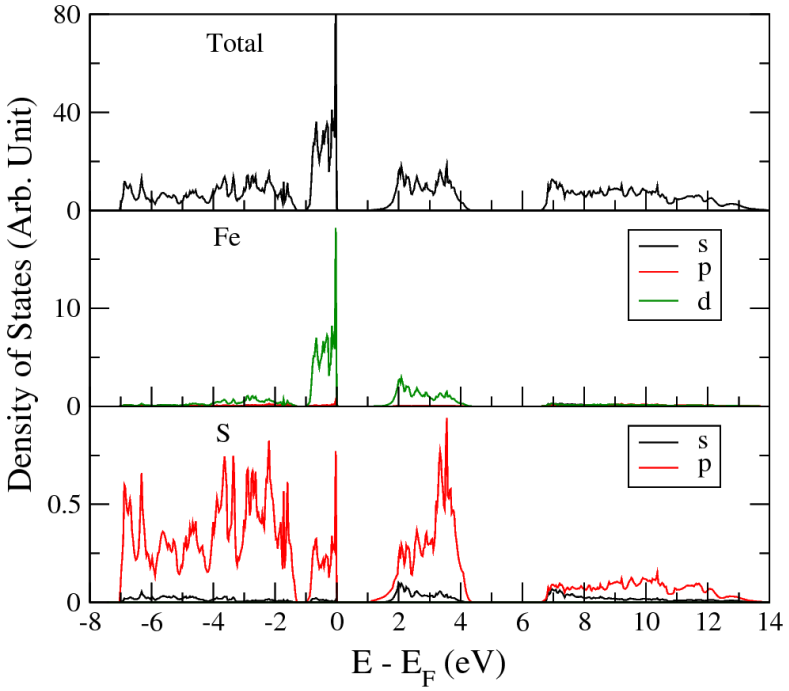
We performed first-principles calculations based on density functional theory (DFT).

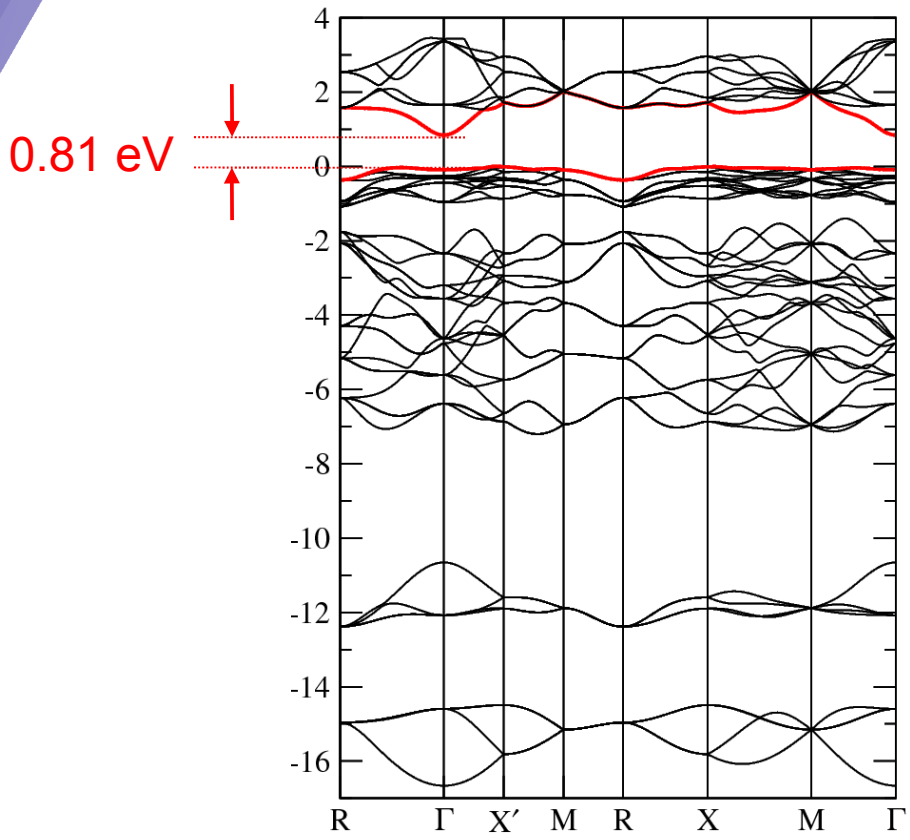
- Code: Vienna Ab-initio Simulation Package (VASP)
- Exchange-correlation functional: generalized-gradient approximation plus Hubbard U (GGA+U)
- Potential: Projector Augmented Wave (PAW)
- Supercell: 2x2x2
- K-grid mesh: 5x5x5

Basic properties of iron pyrite

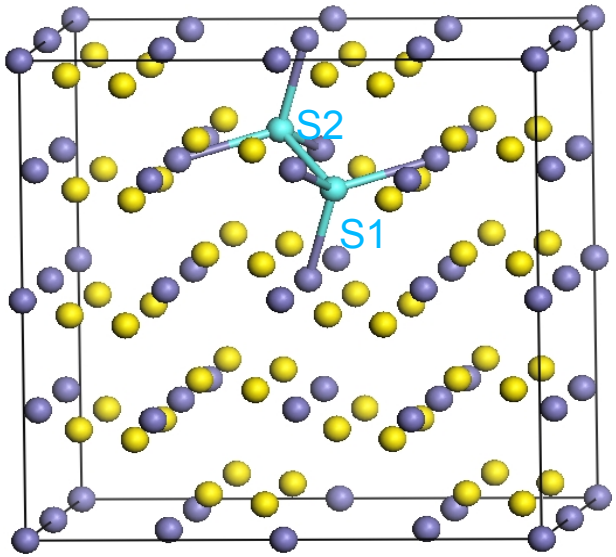


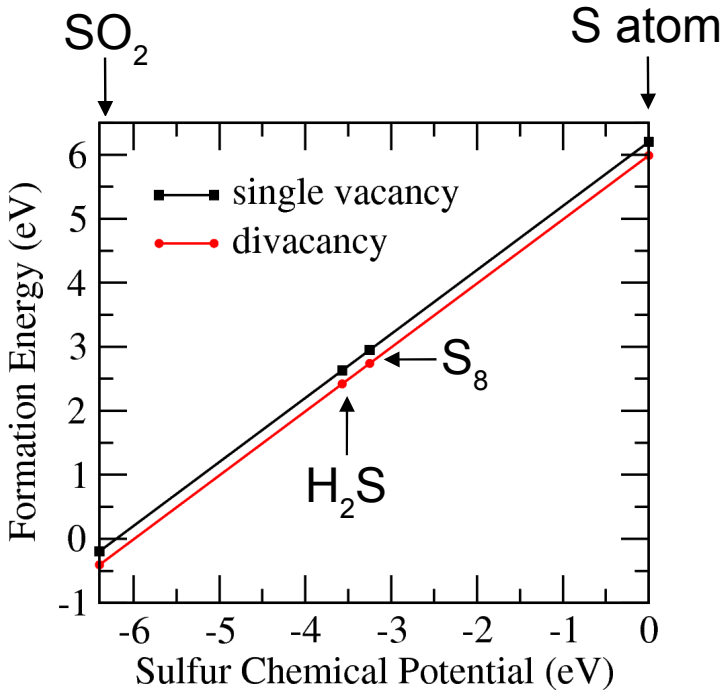




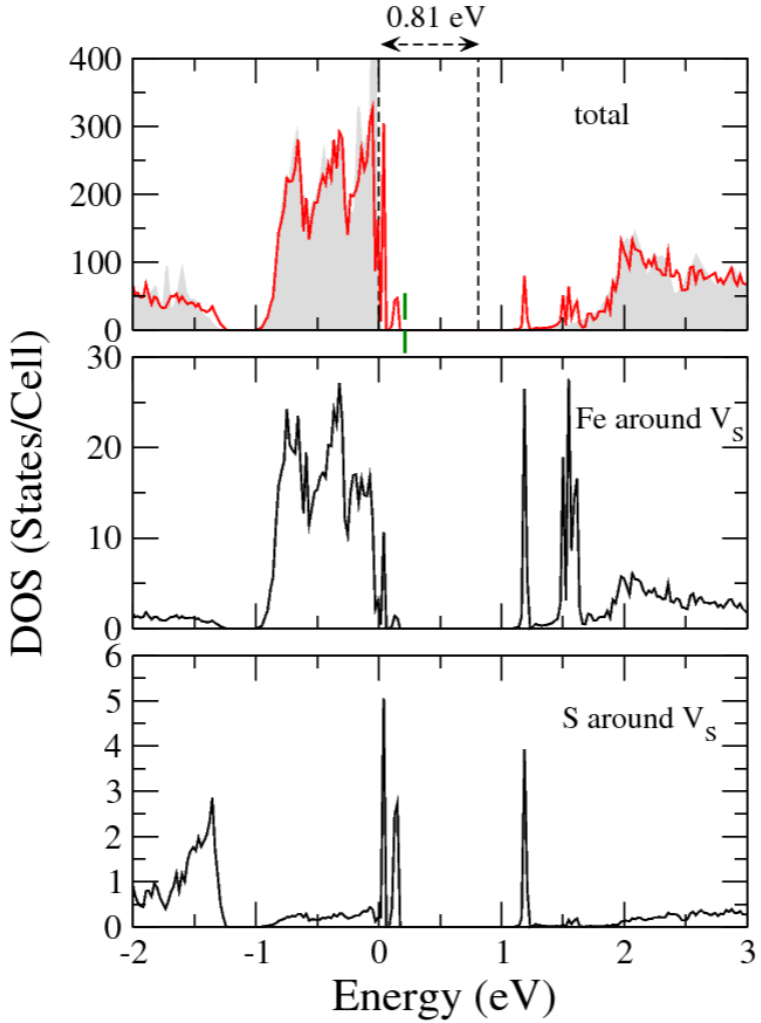


Formation of single and pair S-vacancies in Pyrite





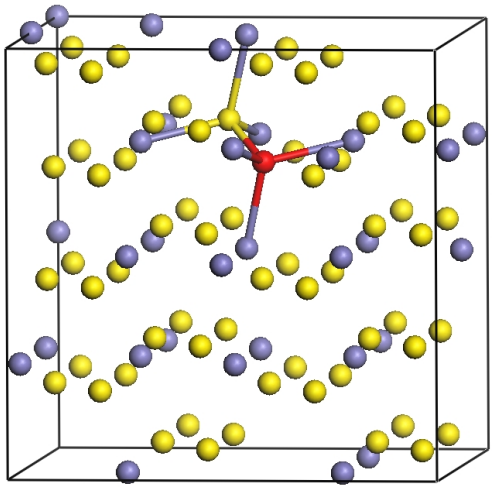
DOS for single sulfur vacancy



The sulfur vacancy induces trap states near valence band maximum (VBM) and conduction band minimum (CBM), suppressing the mobility of carriers.

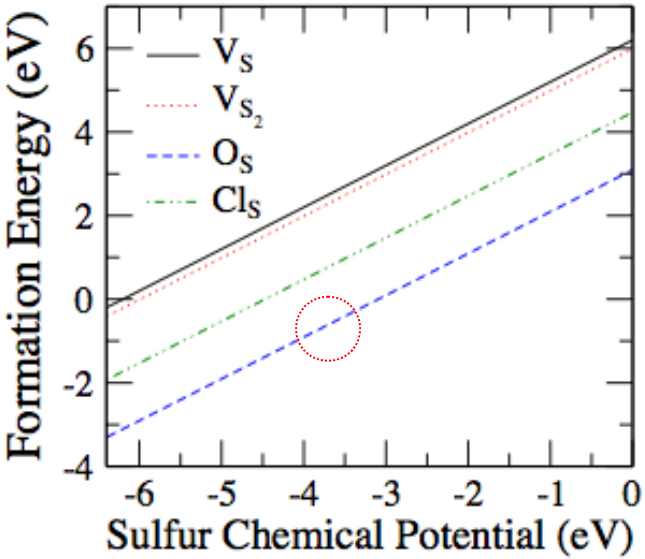
III. Results and discussions

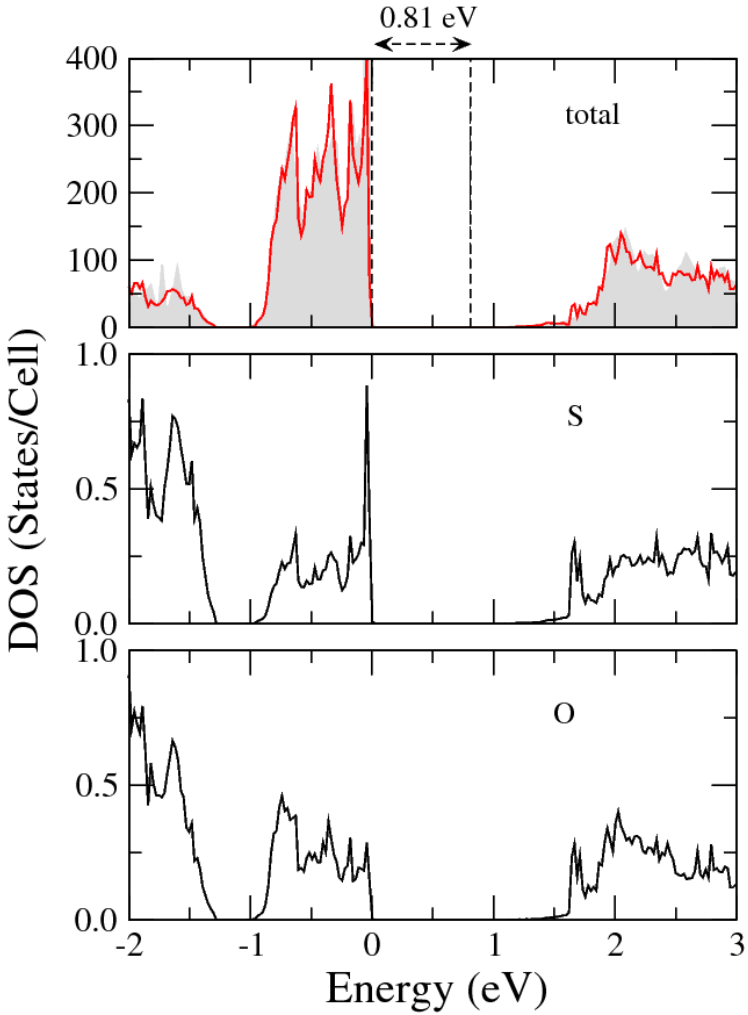
O-substitution for S



$d_{S\text{-}Fe}$ = 2.29 Å
$d_{S\text{-}O}$ = 1.73 Å
$d_{O\text{-}Fe}$ = 2.32 Å

$d_{S\text{-}Fe}$ = 2.27 Å (in bulk)
$d_{S\text{-}S}$ = 2.16 Å (in bulk)

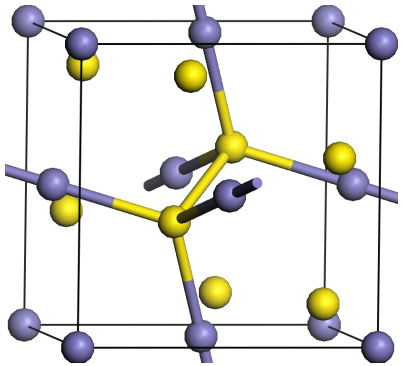




The oxygen may incorporate into FeS_2 effectively in oxygen rich condition.
The gap states from sulfur vacancies are also removed.

Can we doping holes or electrons?

In principle, group-V elements substitution of S are acceptors and group-VII elements substitution of S are donors; similar cases for cation elements substitution of Fe.



7	8	9
N	O	F
15	16	17
P	S	Cl

acceptor donor

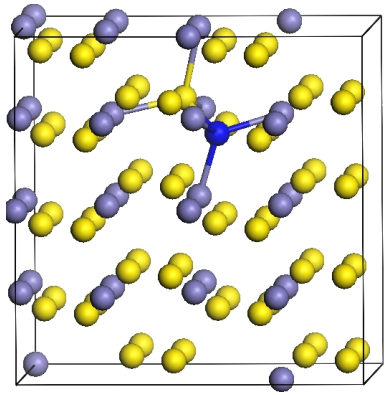
24	25	26	27	28
Cr	Mn	Fe	Co	Ni

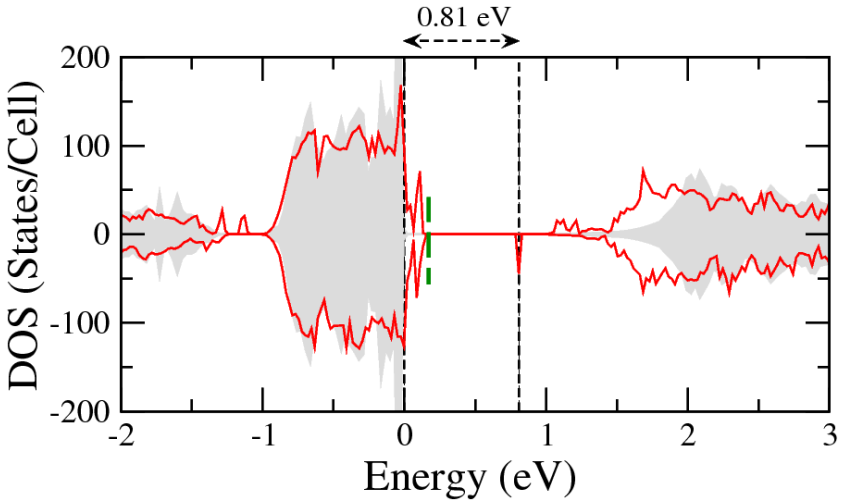
acceptor donor

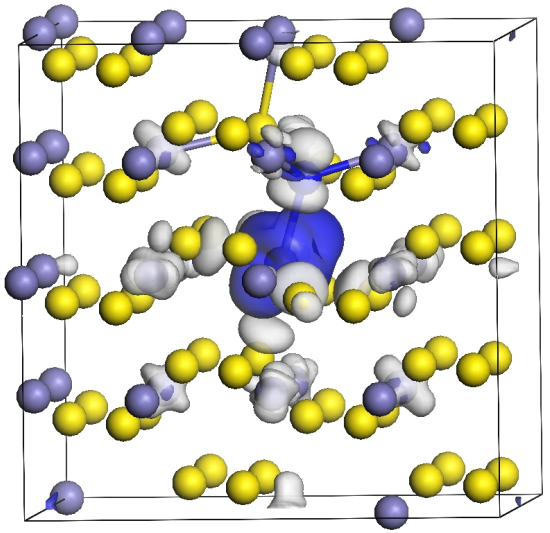
III. Results and discussions

Anion doping: N and P

N_S

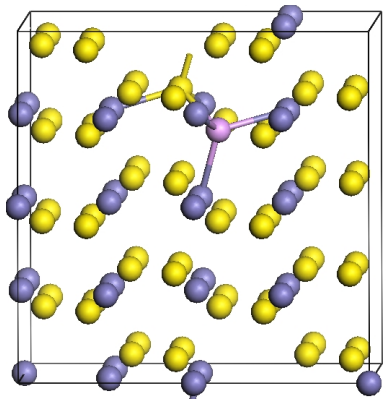


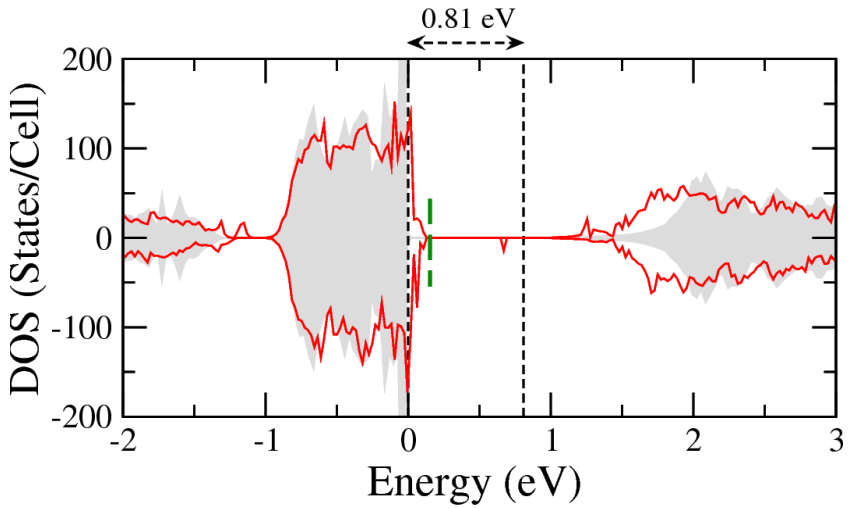


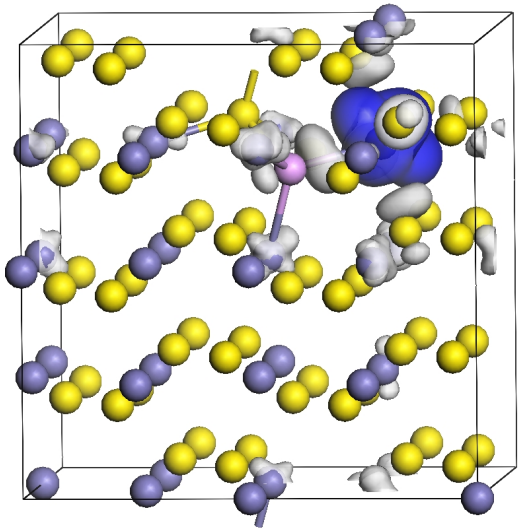


Spin density

P_S





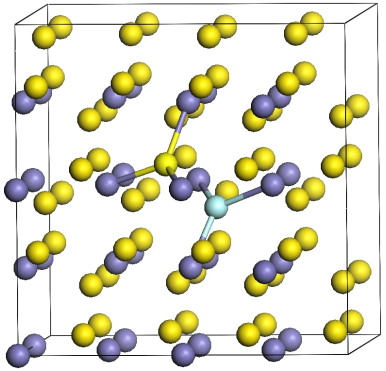


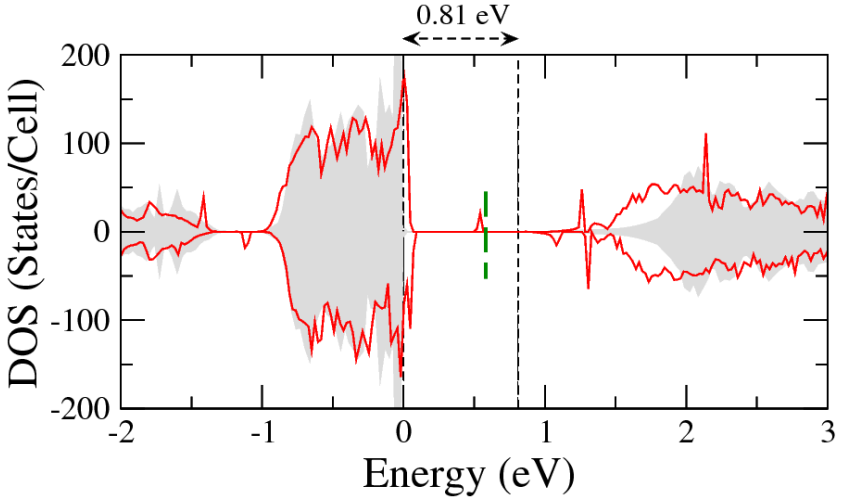
Spin density

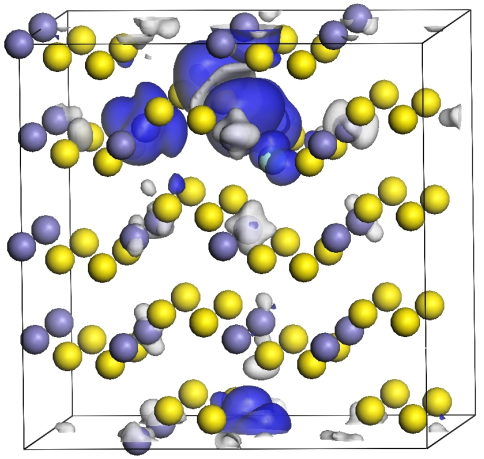
Doping with N or P only induces deep and localized gap state, so they are not good candidates to doping holes in iron pyrite.

Anion doping: F and Cl

F_s

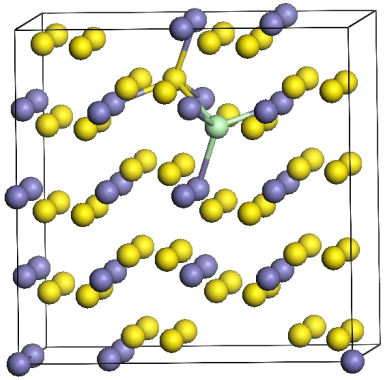


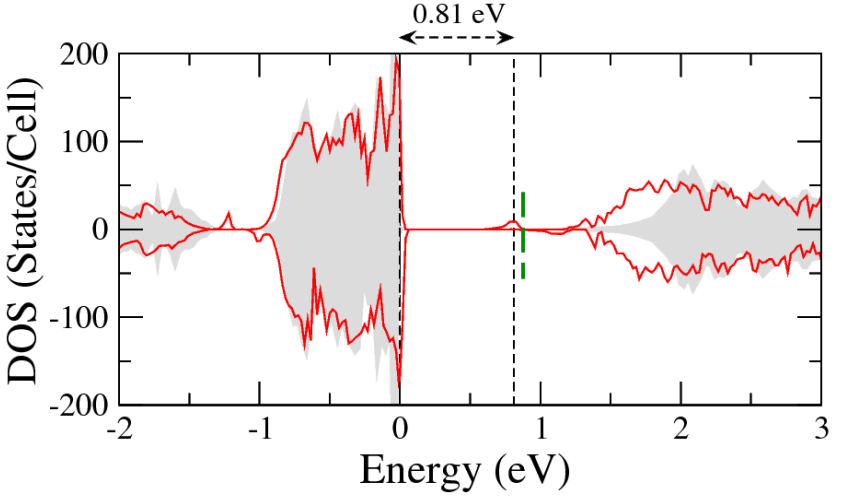


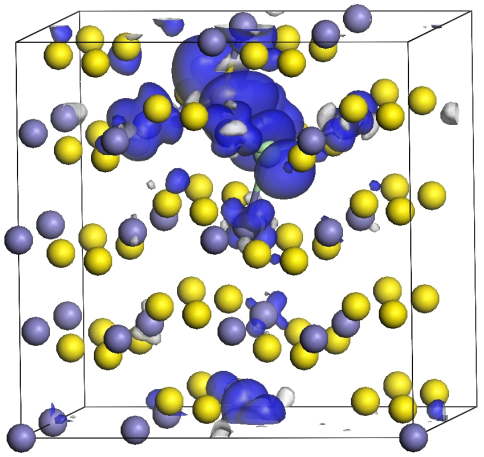


Spin density

Cl_s





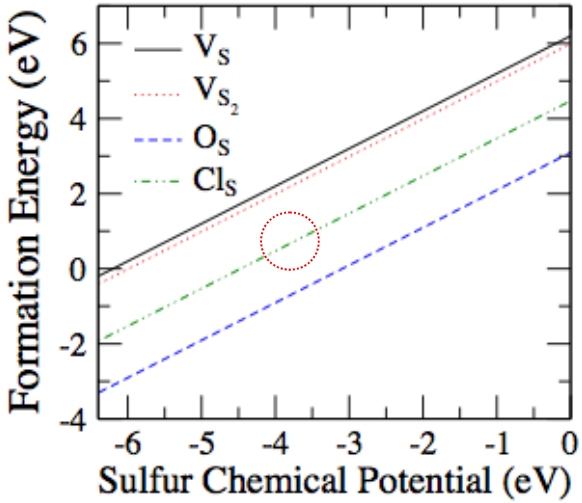


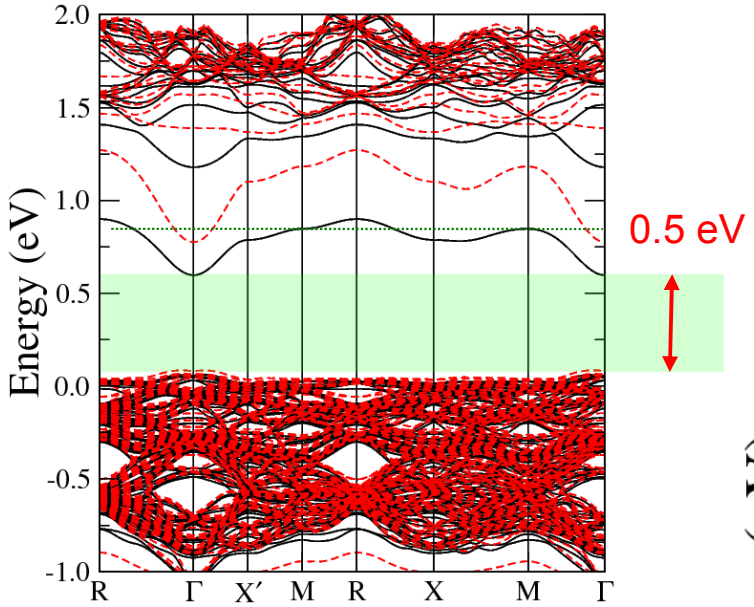
Spin density

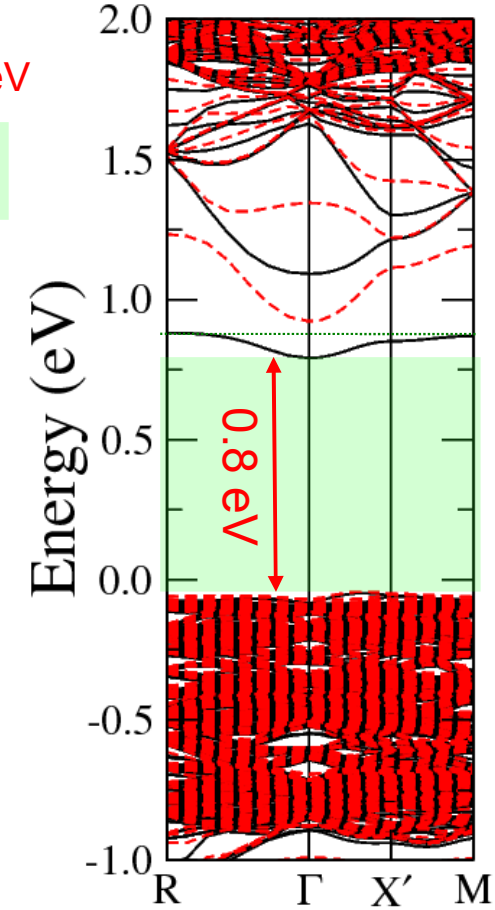
Doping with F also induces deep and localized gap state, but Cl appears to be a good dopant.

III. Results and discussions

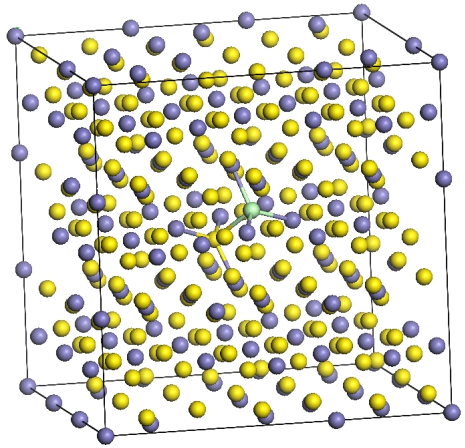
Anion doping: Cl

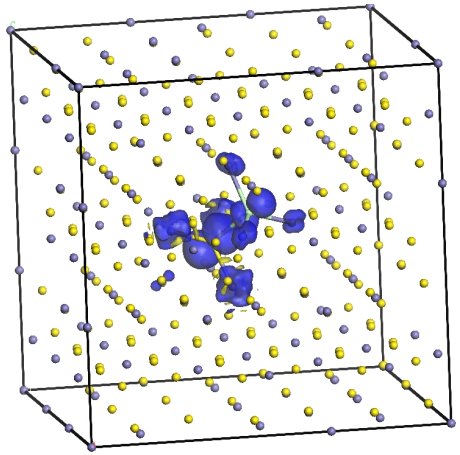






3x3x3 supercell





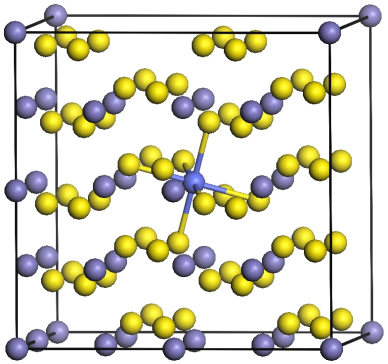
spin density

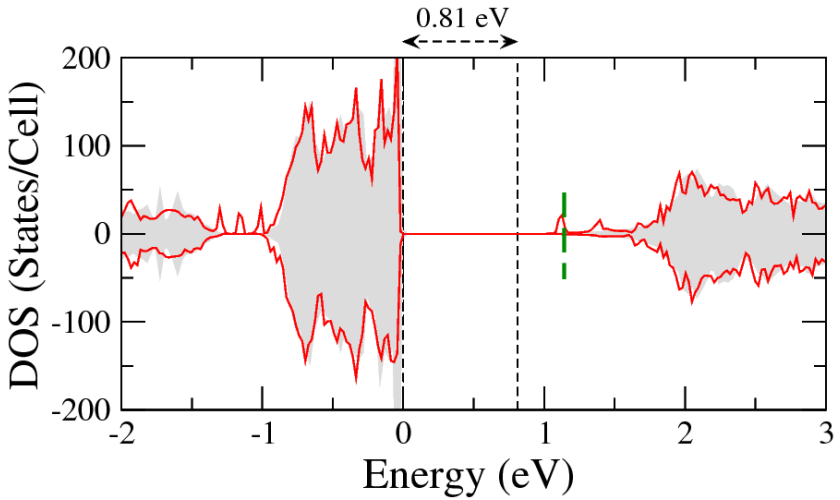
Doping with Cl at level of 1.6% provides a 0.996 μ_B local magnetic moment, and produces $3x10^{18}/cm^3$ delocalized electrons for transport; it also narrows band gap from 0.8 eV to 0.5 eV.

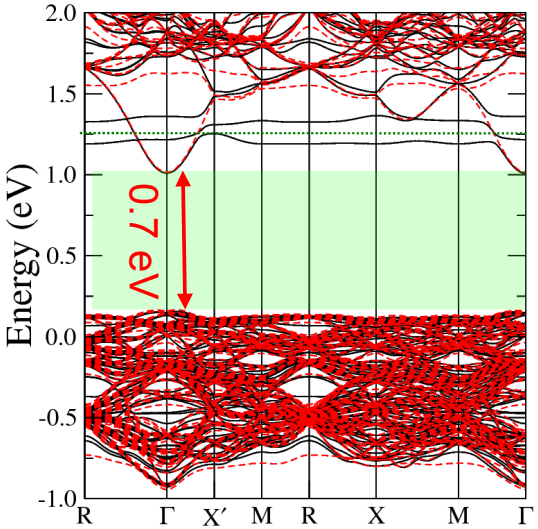
III. Results and discussions

Cation doping: Co and Ni

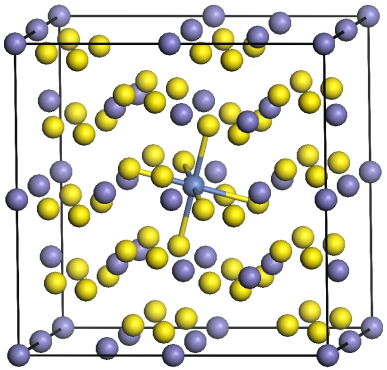
Co_{Fe}

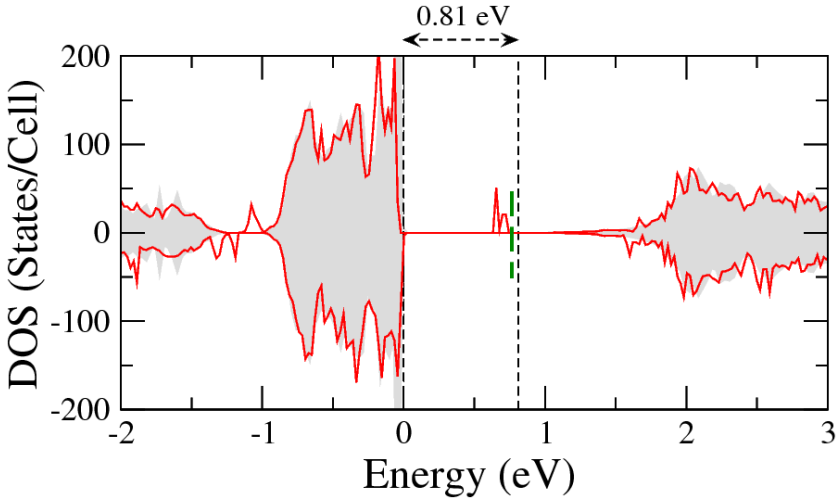


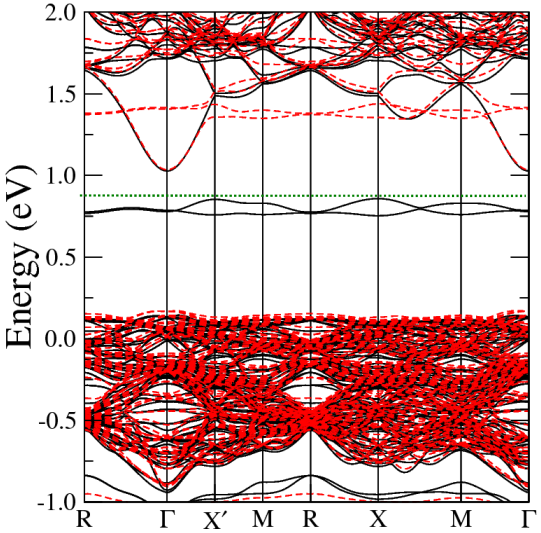




Ni_{Fe}



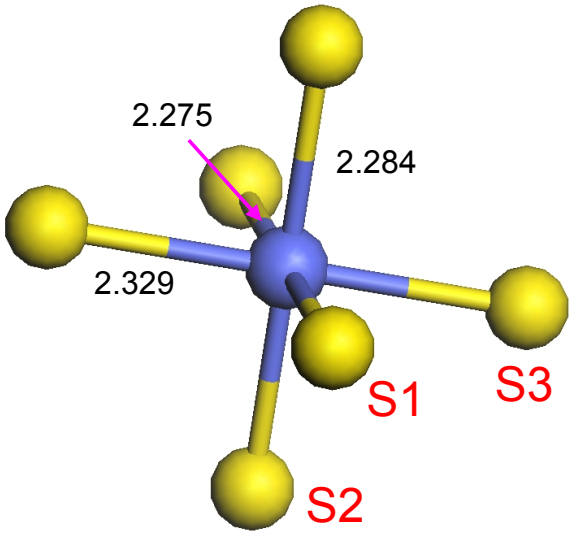




The defect states of Co_{Fe} mix with conduction bands of bulk iron pyrite, so it may be an effective impurity to donate electron carriers.

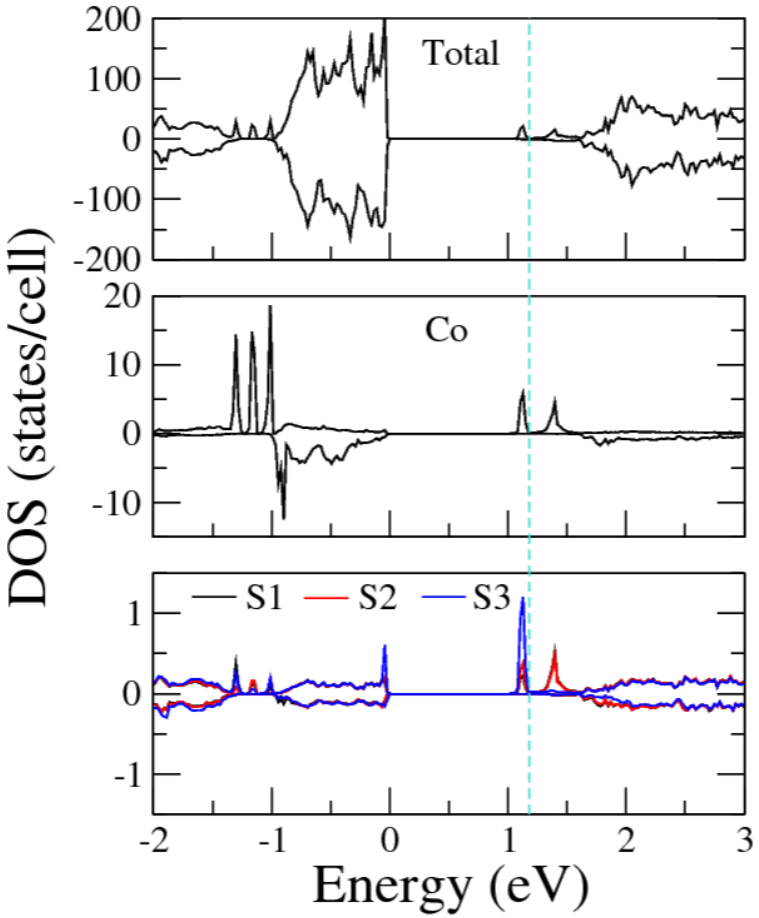
III. Results and discussions

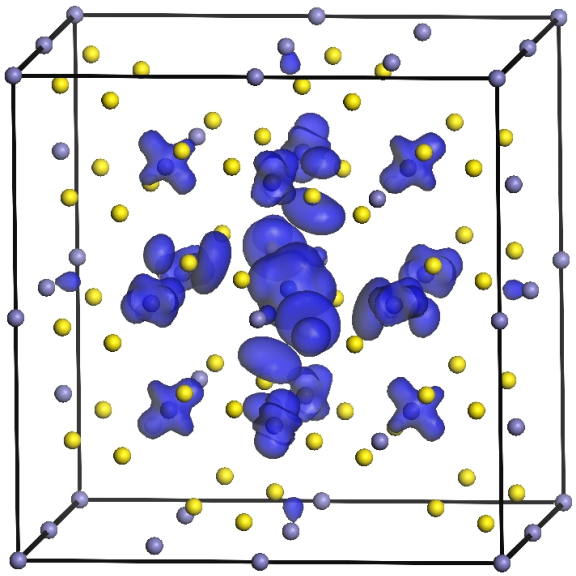
Cation doping: Co



$d_{S\text{-}Fe}$ = 2.27 Å (in bulk)

Fe at the center of octahedron





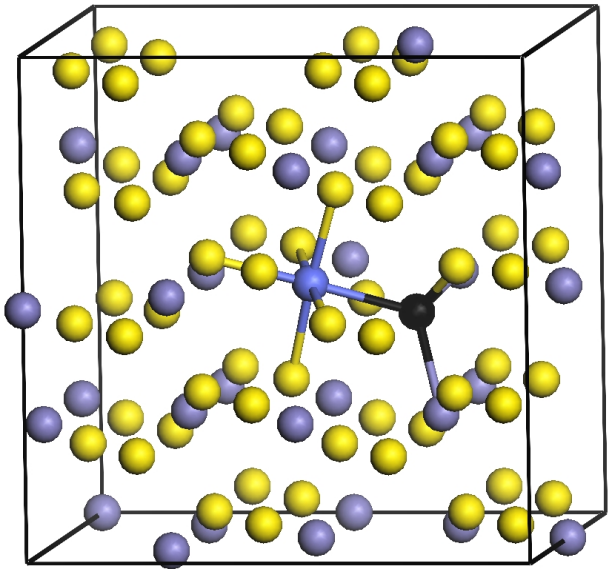
spin density

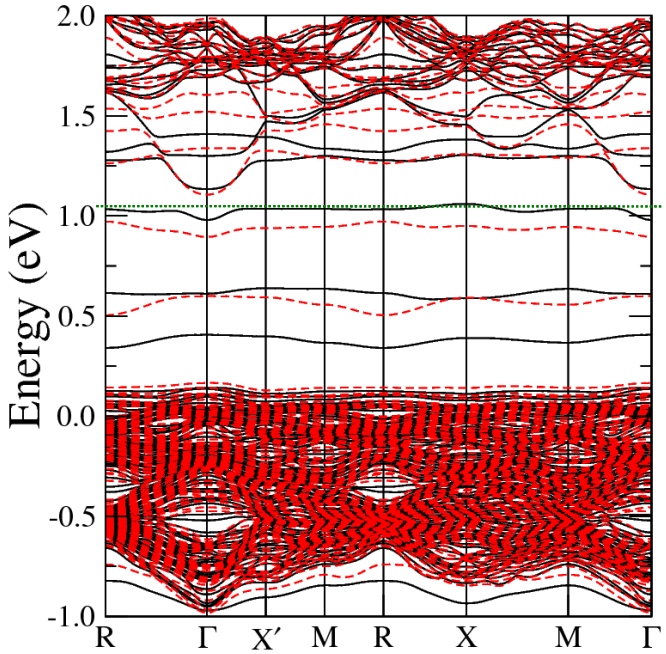
The Co dopant donates free electron carries no matter how much its concentration is!
The local structure and projected DOS show clear anisotropy.

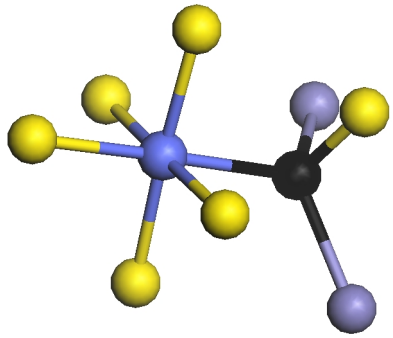
A spin moment of 0.94 μ_B is induced, of which 87% (0.82 μ_B) locates on Co atom, while the rest resides on Fe atoms within a wide range nearby Co atom.

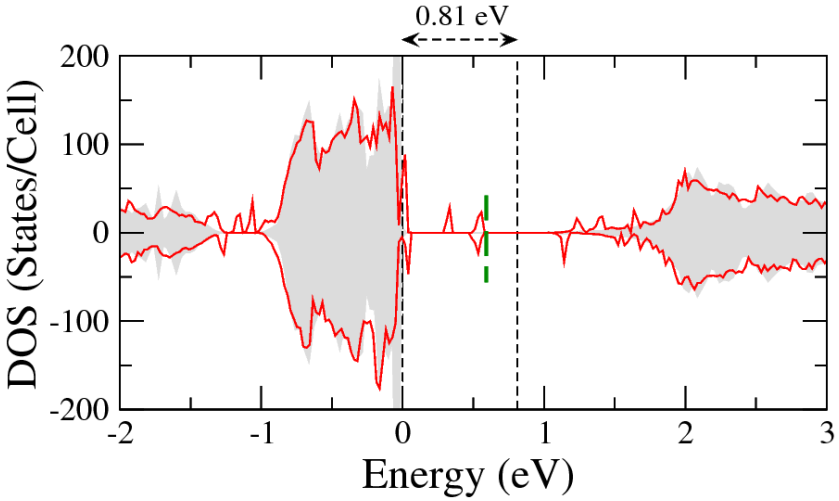
III. Results and discussions

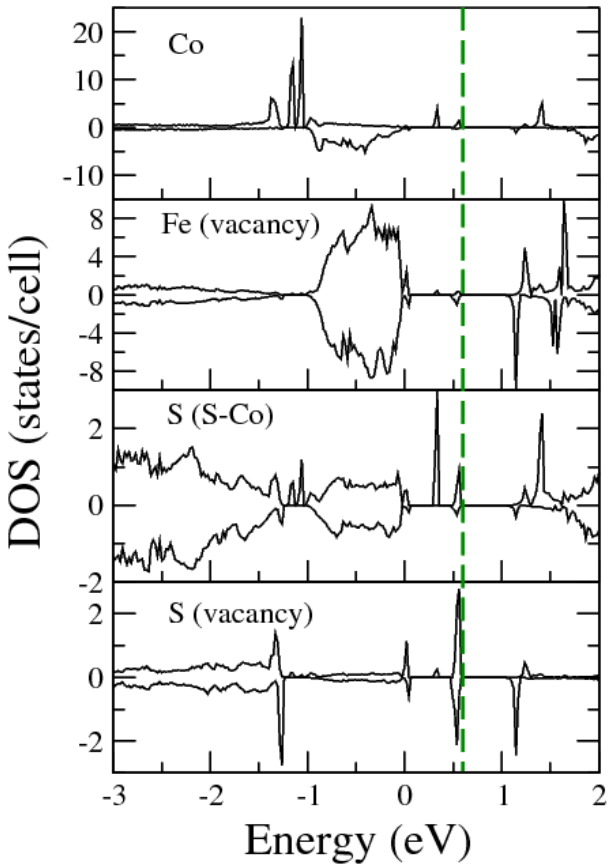
Sulfur vacancies near Co_{Fe}







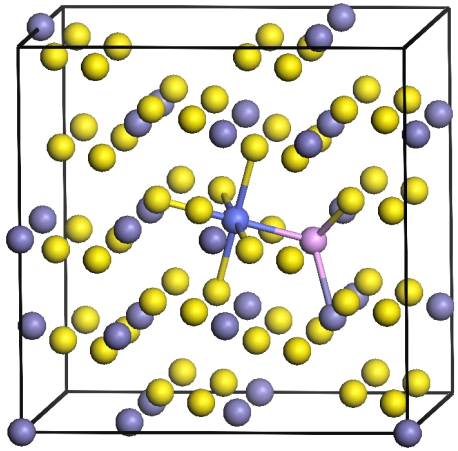


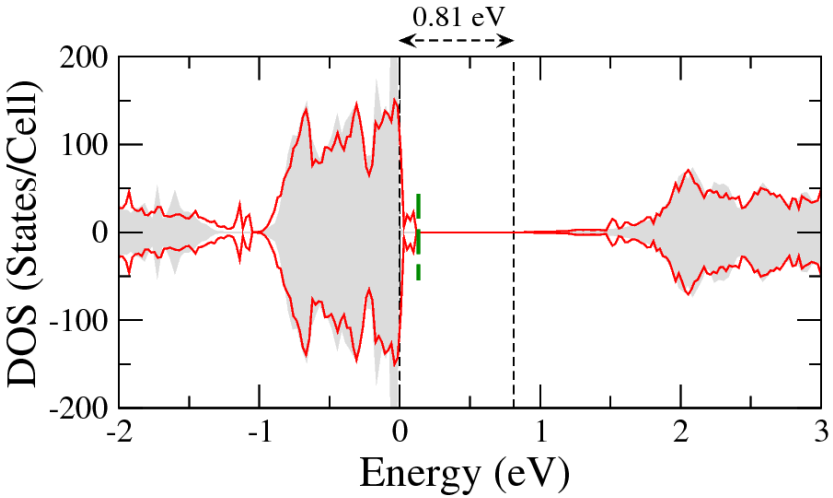


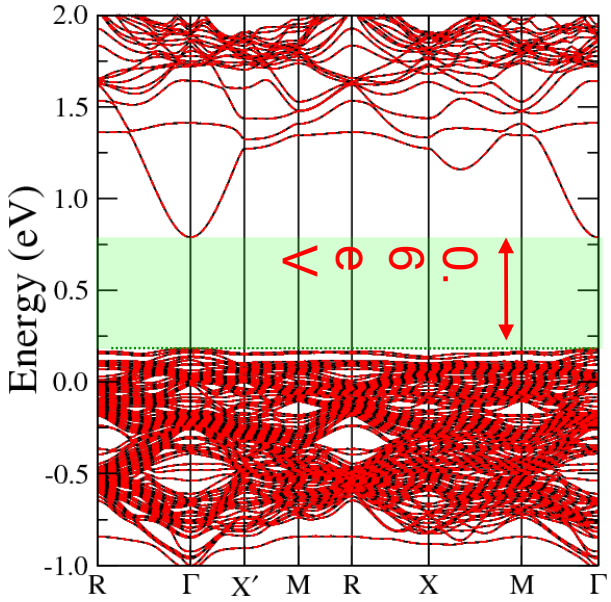
Coexisting of Co_{Fe} and V_S induces more complex gap states, compared with either Co_{Fe} or V_S

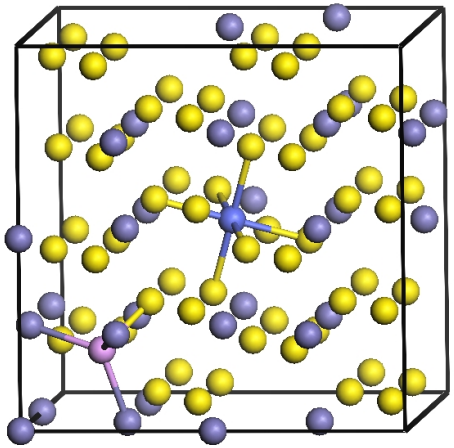
III. Results and discussions

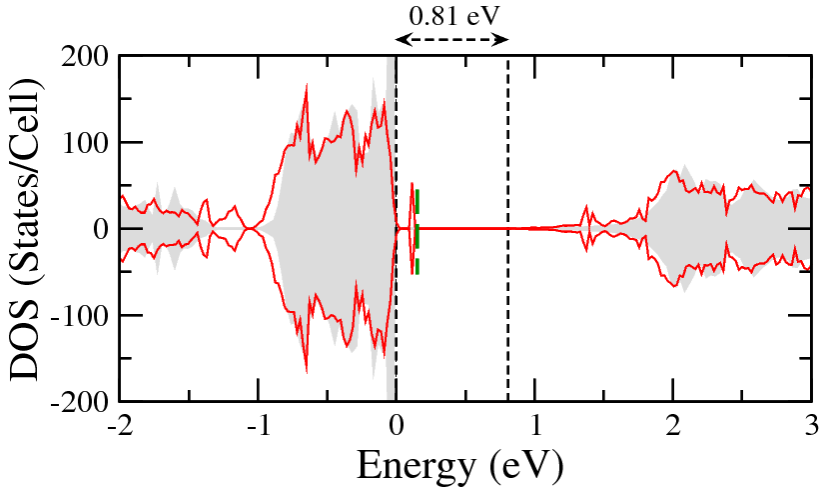
Codoping with Co_{Fe} and P_S

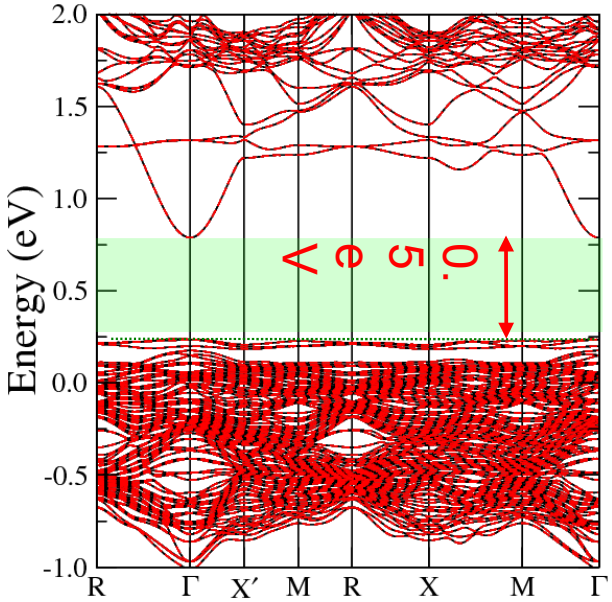












The Co_{Fe} and P_S together will eliminate the deep gap states from P impurity.

IV. Conclusions and perspective

Conculsions:

(1). Sulfur vacancy (V_S) could form easily in oxygen rich environment; oxygen may incorporate into FeS_2, which improves the electronic properties of FeS_2.

(2) Anion doping with N, P, F or Cl may be an effective way to suppress the formation of V_S. Cl impurity introduces $3x10^{18}/cm^3$ free electron carriers, which may enhance electric transport in FeS_2 and thus make the conversion of solar energy to electric energy more effectively.

(3) Co impurity could donate free electron carriers, independent of its concentration. This free electrons are responsible for the removal of deep gap states when P impurity coexists in the system.

Perspective:

Codoping: 2 Co_{Fe} + P_S, 2 Co_{Fe} + N_S

Thank you !