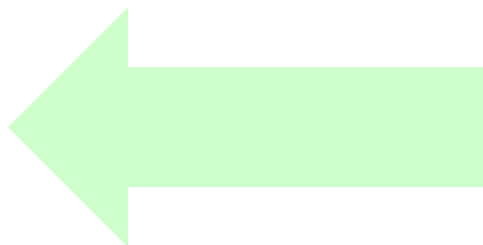
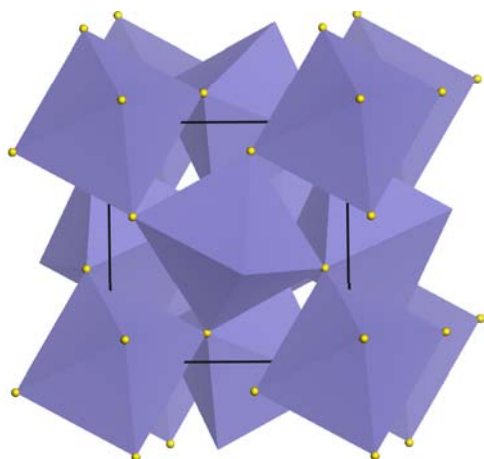


Applications of density functional theory for Pyrite



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University of California, Irvine


Density Functional Theory & Approximations

$$E[\rho] = \int dr v(r)\rho(r) + F[\rho]$$

$$F[\rho] = T[\rho] + \frac{1}{2} \int dr dr' \frac{\rho(r)\rho(r')}{|r-r'|} + E_{exc}[\rho]$$

$$N = \int dr \rho(r)$$

$$\frac{\delta T[\rho]}{\delta \rho(r)} + v_{eff}(r) = \mu$$


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

$$v_{eff}(r) = v(r) - \int dr \frac{\rho(r)}{|r-r'|} + \frac{\delta E_{exc}}{\delta \rho(r)}$$

$$\rho(r) = \sum_{i=1}^N |\Psi_i(r)|^2$$

LDA

$$E_{exc}^{LDA}(\rho(r));$$

$$V_{exc}^{LDA}(\rho(r))$$

GGA

$$E_{exc}^{GGA}(\rho(r), \nabla \rho(r));$$

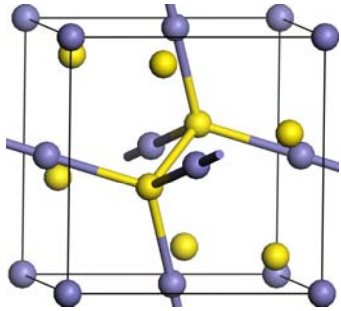
$$V_{exc}^{GGA}(\rho(r), \nabla \rho(r), \nabla \nabla \rho(r))$$

**LDA+U, sx+LDA
SIC, GW, TDDFT**

...



What can we do for studies of Pyrite



Structural properties

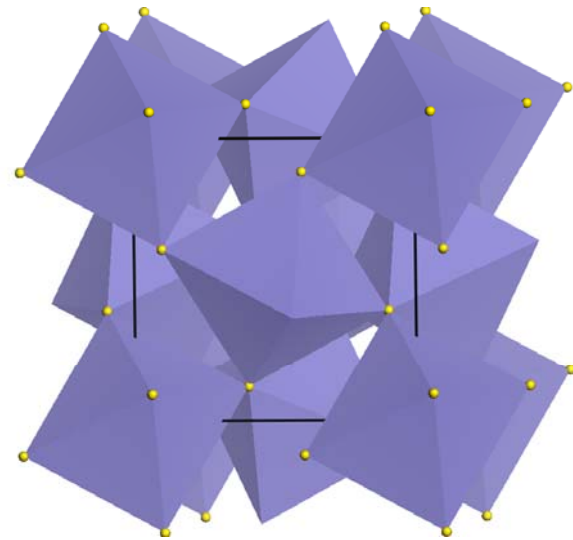
Elastic constants, formation energies for vacancies, dopants, and other deficiencies, stability of nanostructures, surfaces and interfaces ...

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 ...

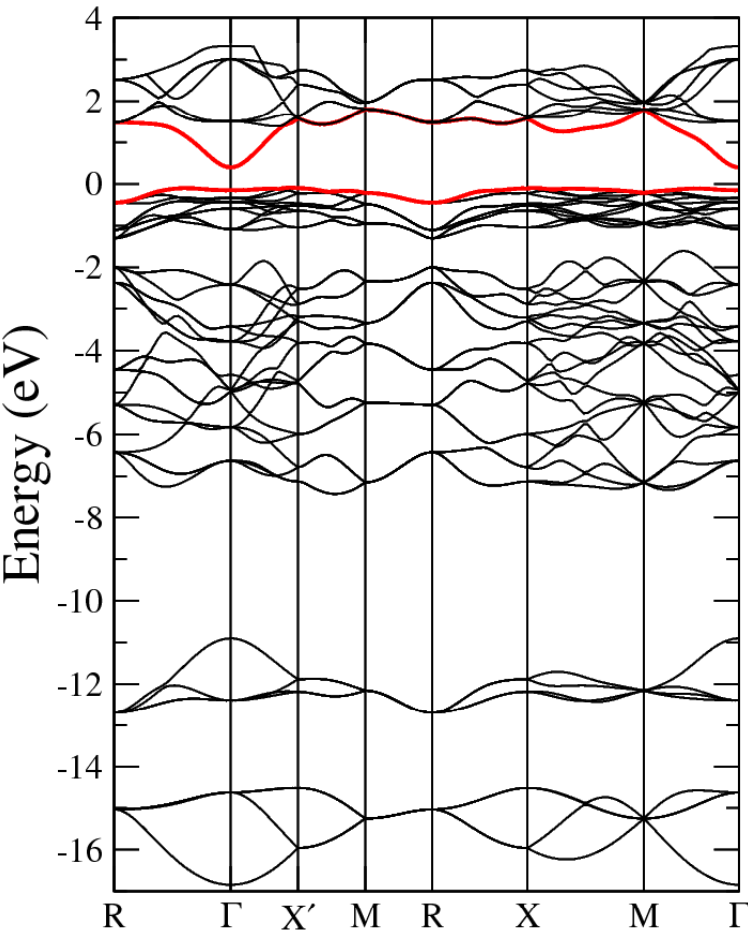


Perfect structures

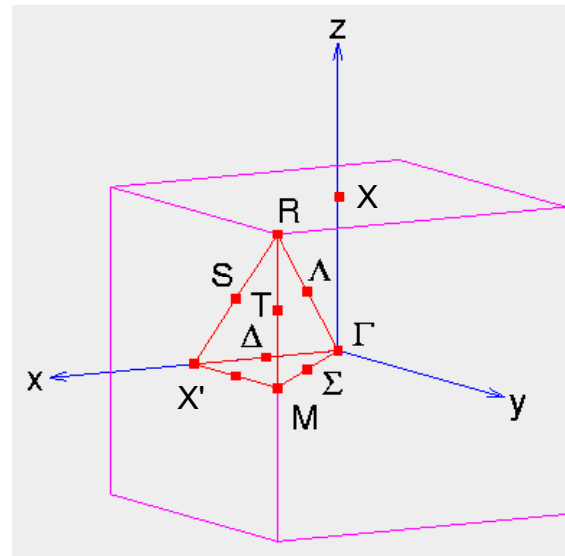


grains

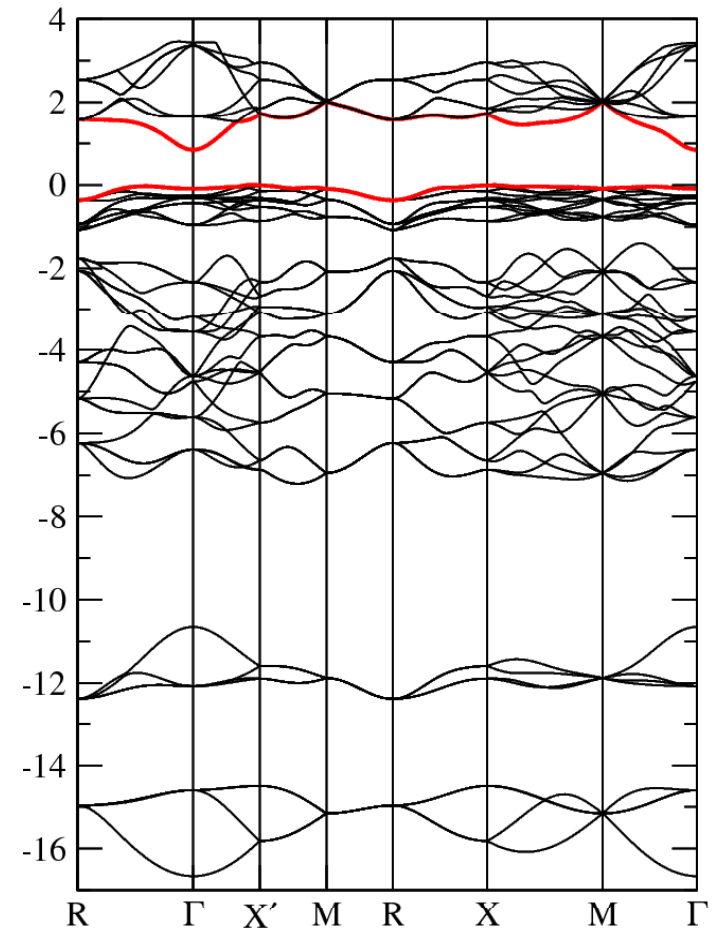
Calculated Band Structures of the bulk FeS₂: $E \sim \hbar k$



$$\Phi_j(\mathbf{r}) = e^{i(\mathbf{k} + \mathbf{G}_j) \cdot \mathbf{r}}$$



The 3D Brillouin zone



	GGA (exp. a)	GGA (opt. a)	GGA+U	Exp.
a (Å)	5.417	5.403	5.422	5.417
E _g (eV)	0.65	0.50	0.81	0.95

The calculated density of states (DOS)

-- how many states at certain energy

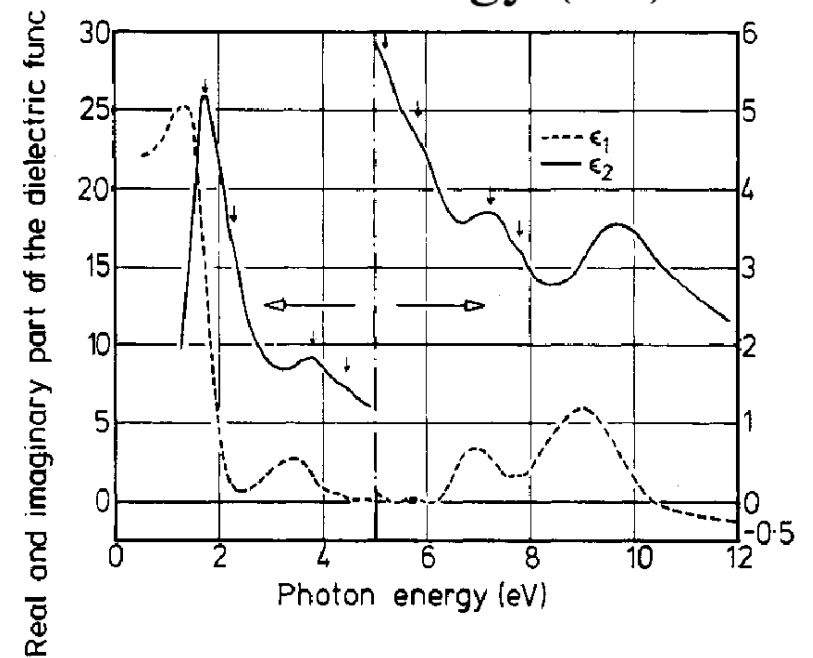
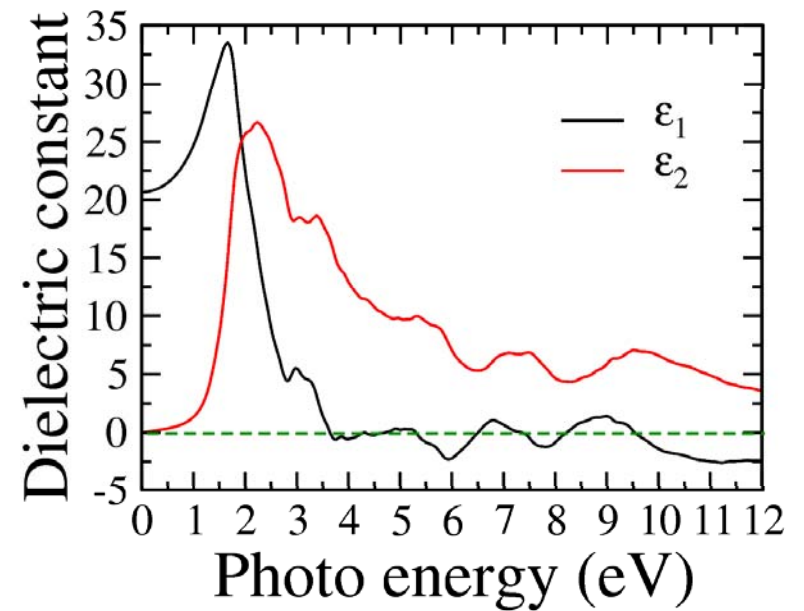
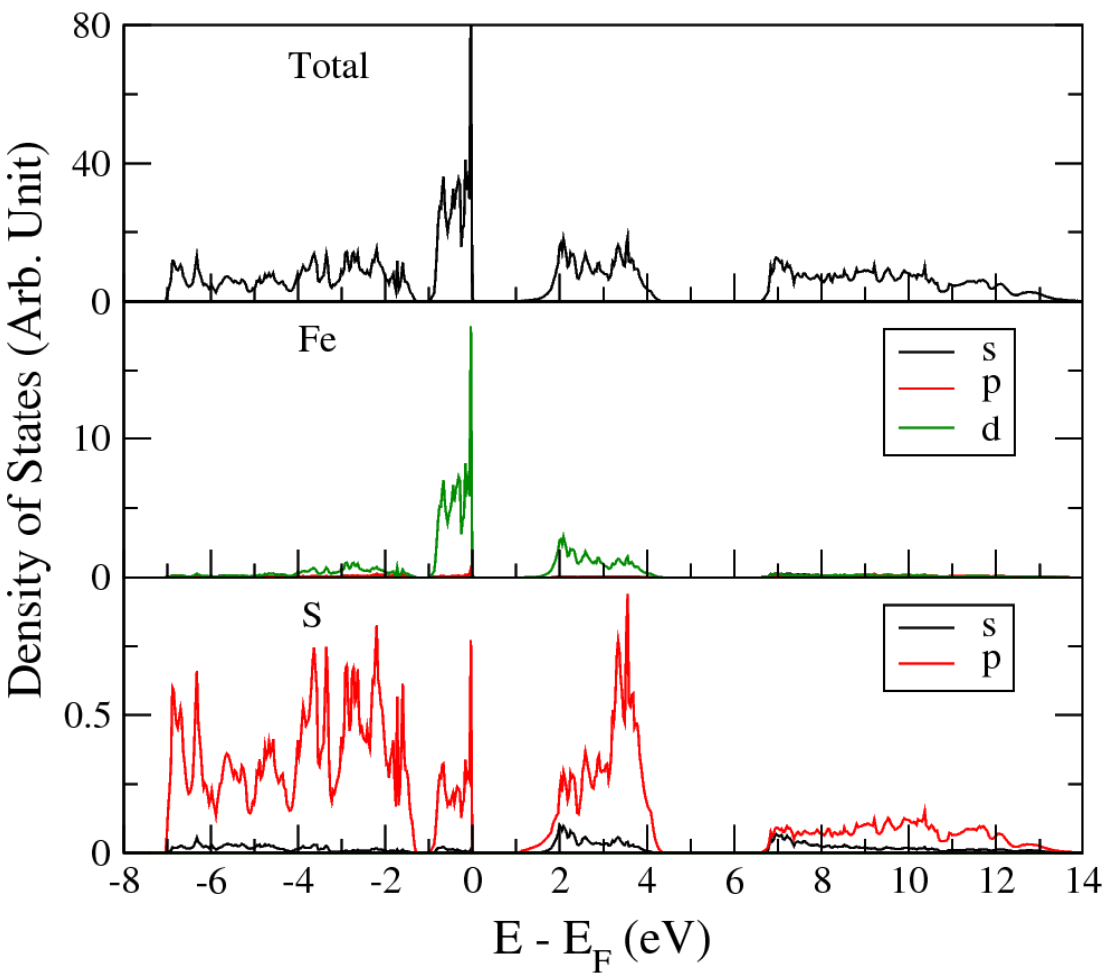
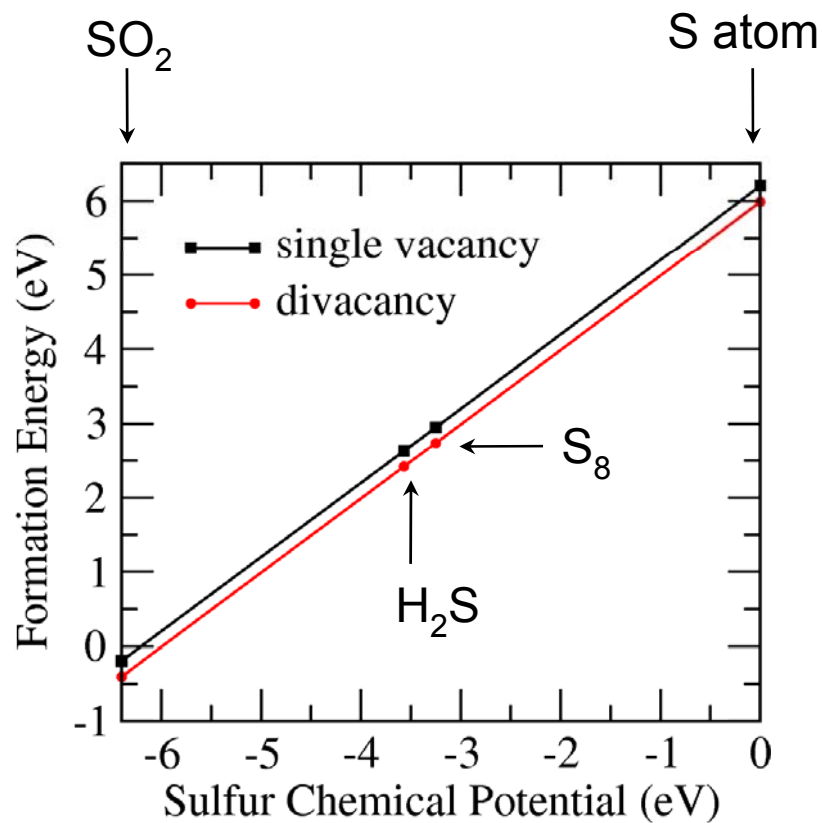
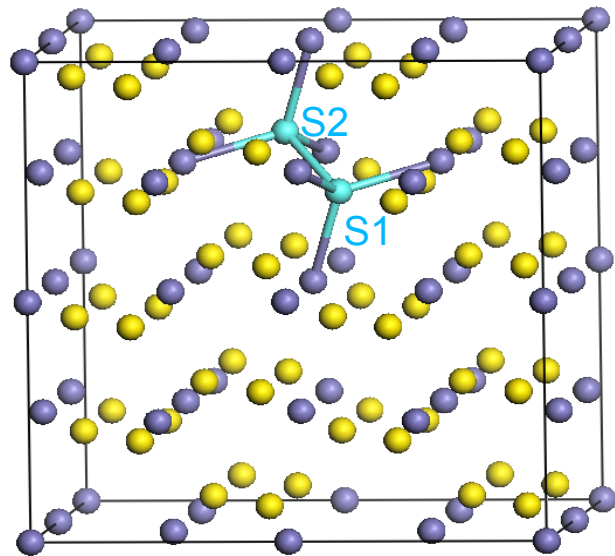
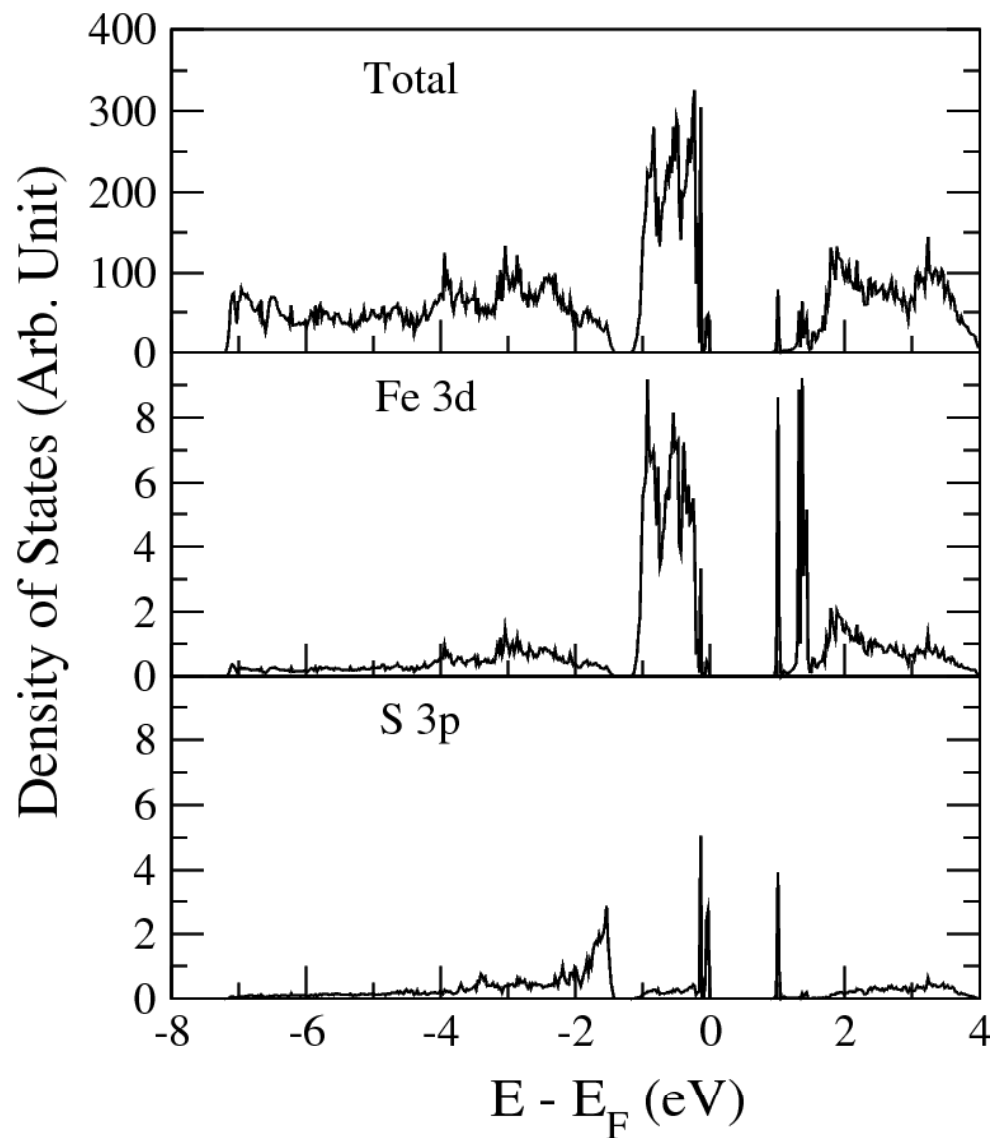


Figure 4. Dielectric function of FeS₂ at 300 K. A Schlegel and P Wachter, *J. Phys. C: Solid State Phys.* 9 3363 (1976).

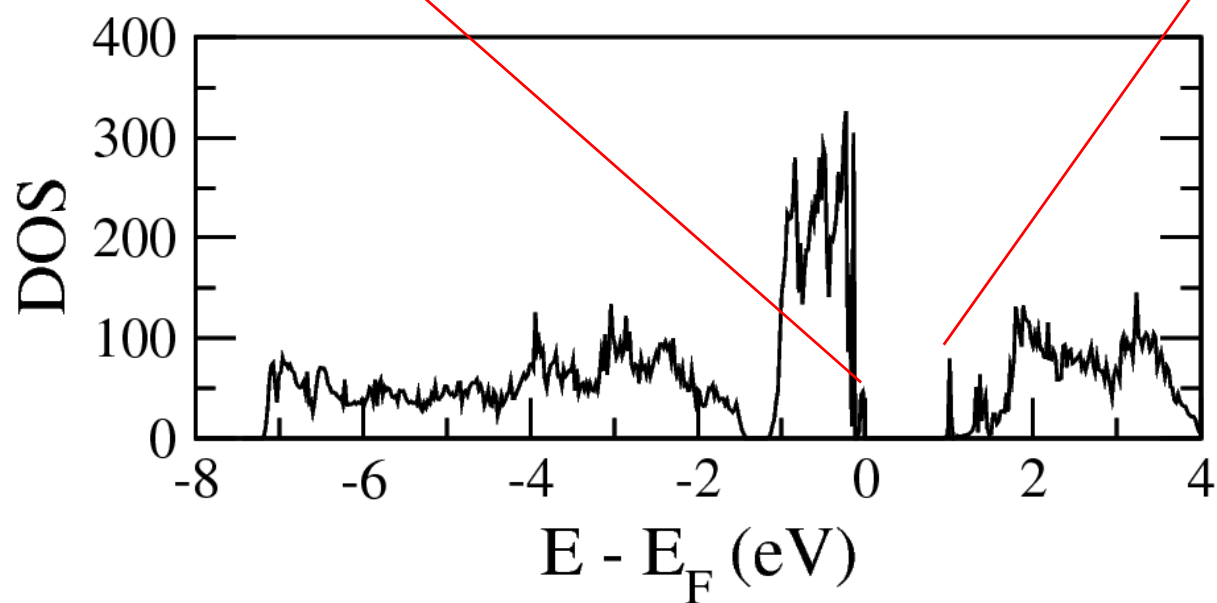
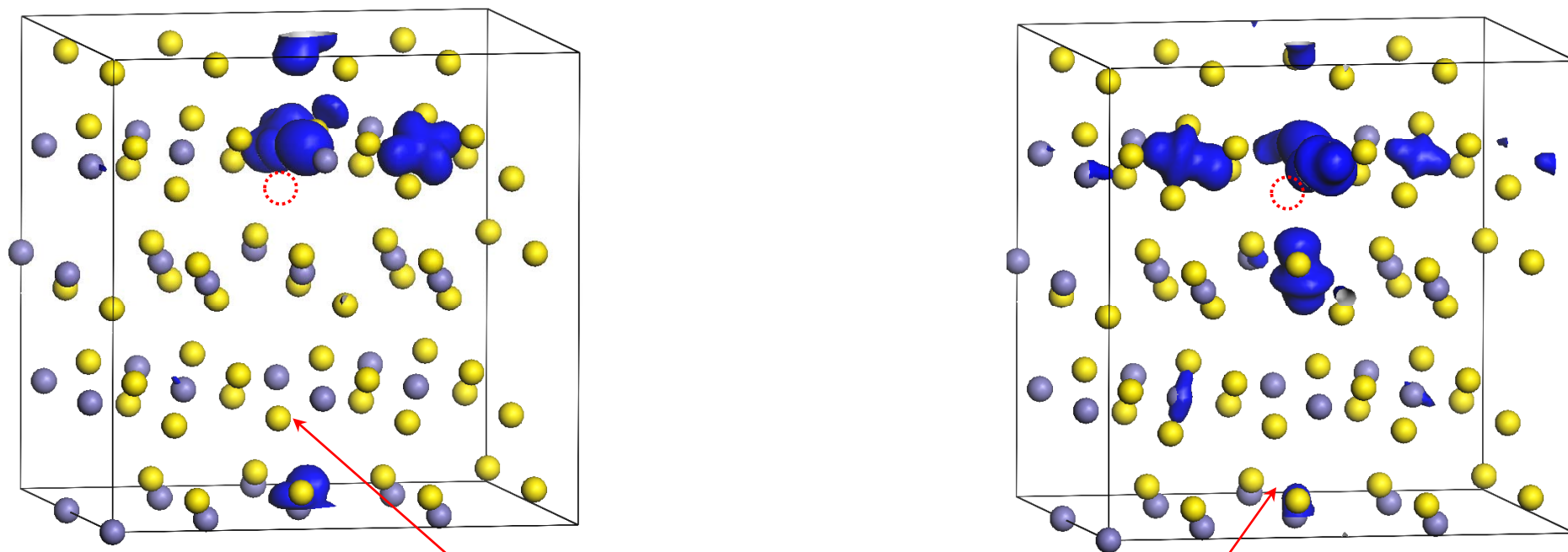
Formation of single and pair S-vacancies in Pyrite



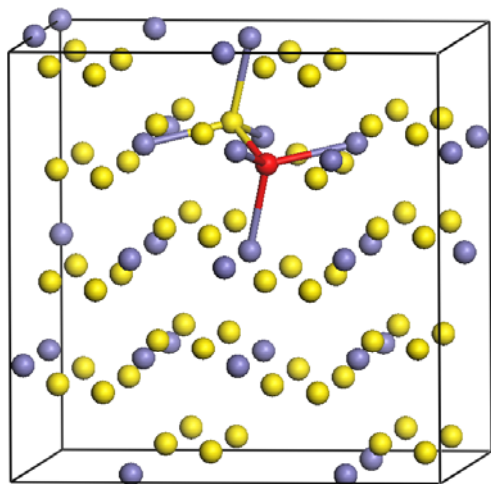
DOS for single sulfur vacancy



Single state wave function/charge density

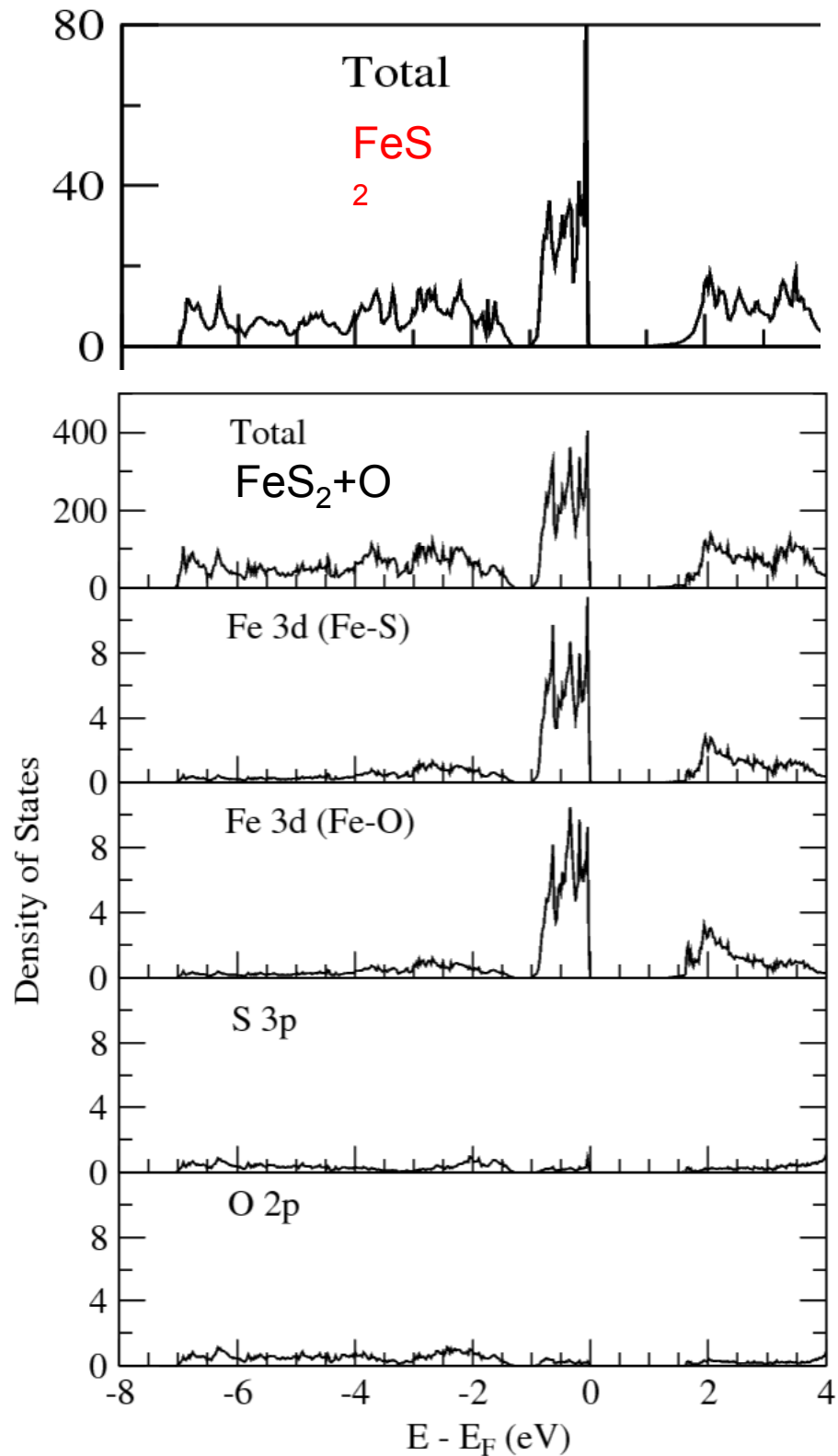
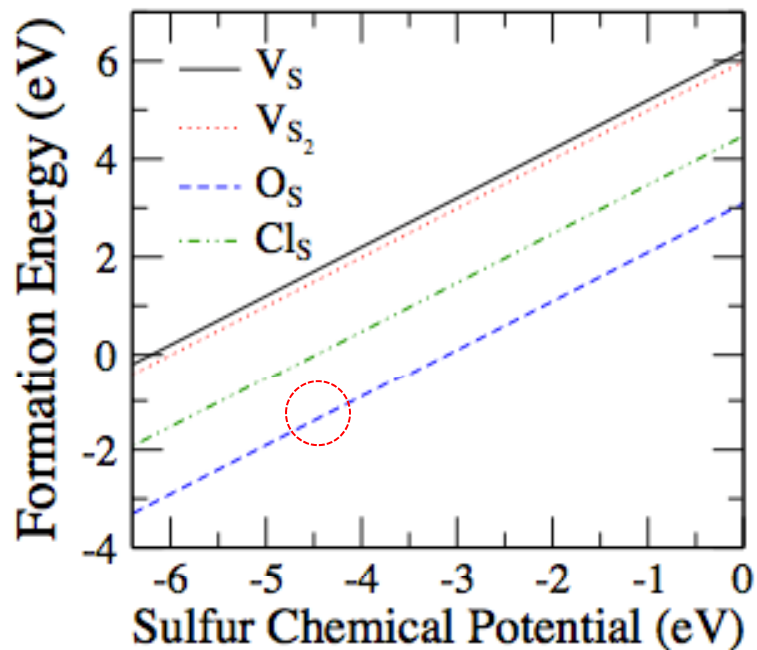


O-substitution for S

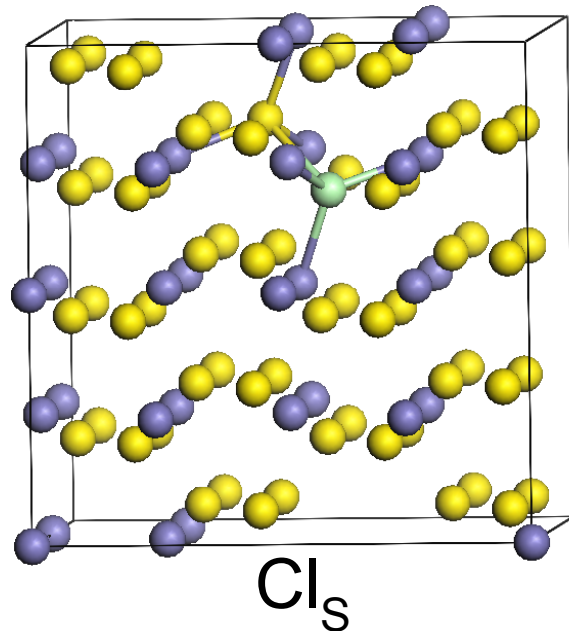
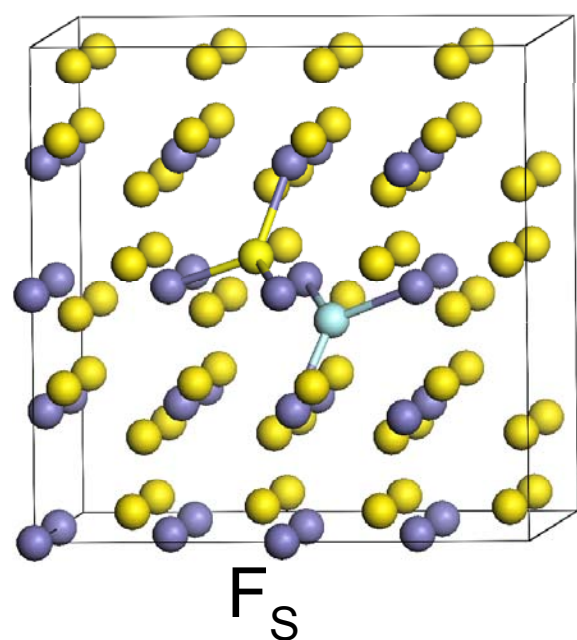
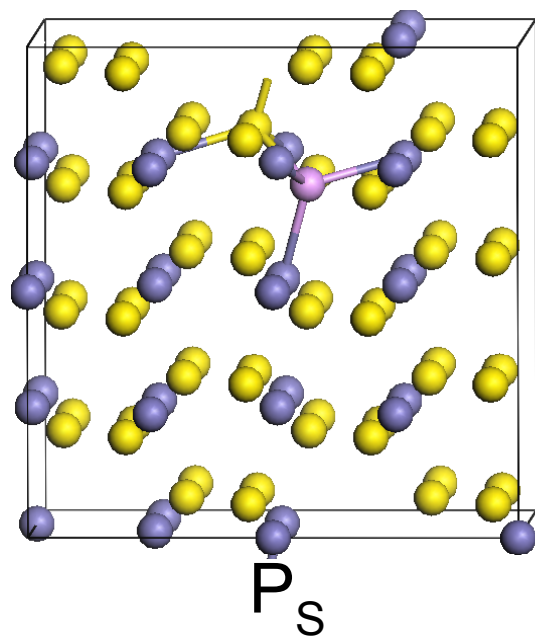
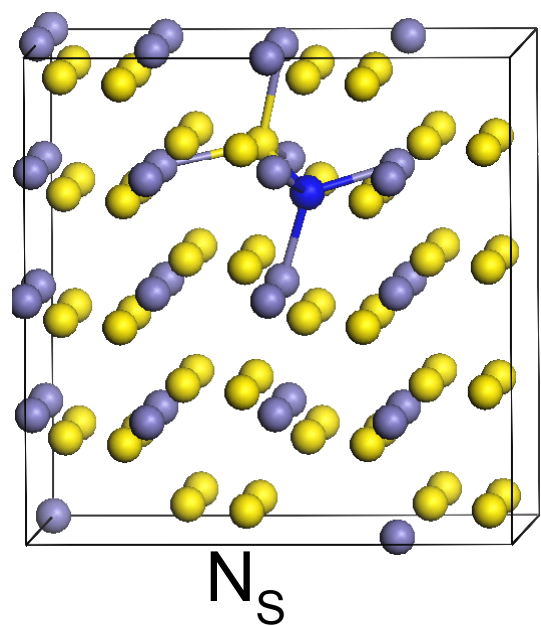


$$d_{\text{S-Fe}} = 2.29 \text{ \AA}$$
$$d_{\text{S-O}} = 1.73 \text{ \AA}$$
$$d_{\text{O-Fe}} = 2.32 \text{ \AA}$$

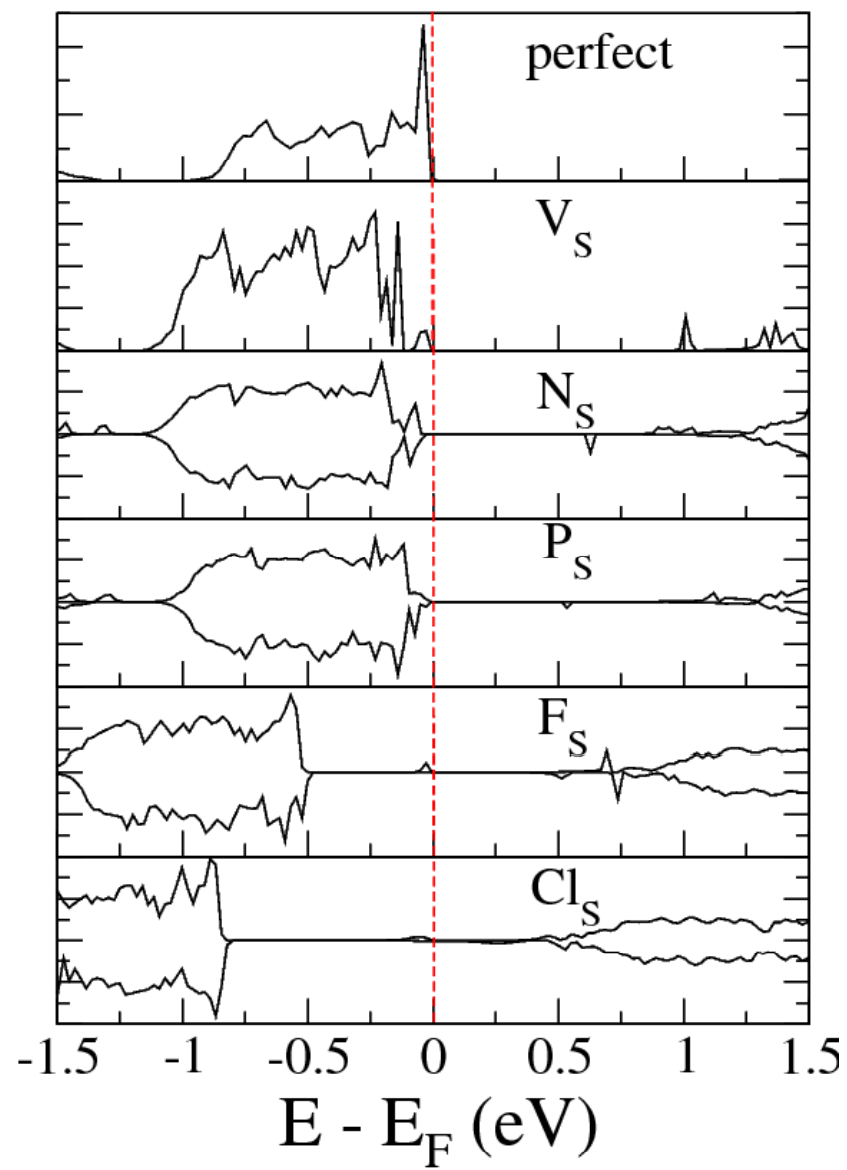
$$d_{\text{S-Fe}} = 2.27 \text{ \AA (in bulk)}$$
$$d_{\text{S-S}} = 2.16 \text{ \AA (in bulk)}$$



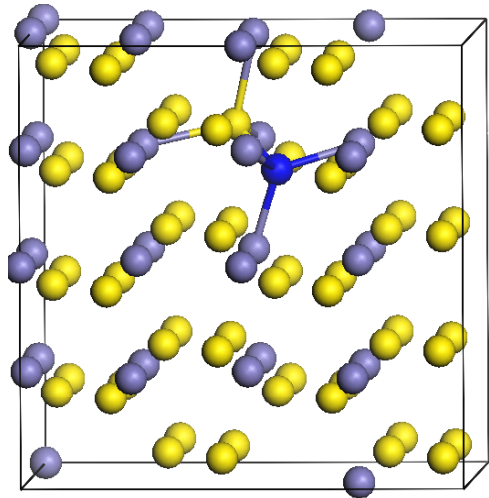
The effect of other dopants on the band gap and carrier density



Density of States



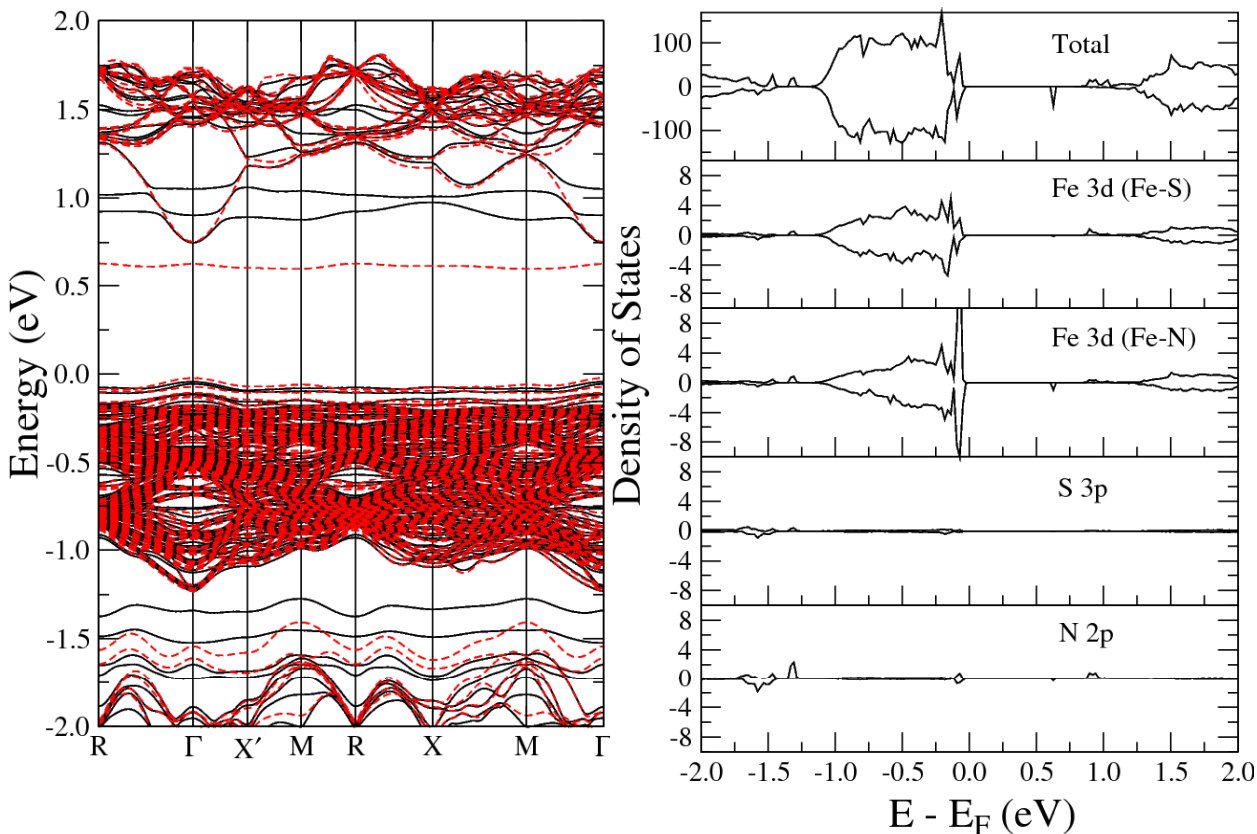
Can we add in holes? N-doping



$$\begin{aligned}d_{\text{S-Fe}} &= 2.33 \text{ \AA} \\d_{\text{S-N}} &= 1.74 \text{ \AA} \\d_{\text{N-Fe}} &= 2.10, 2.48 \text{ \AA}\end{aligned}$$

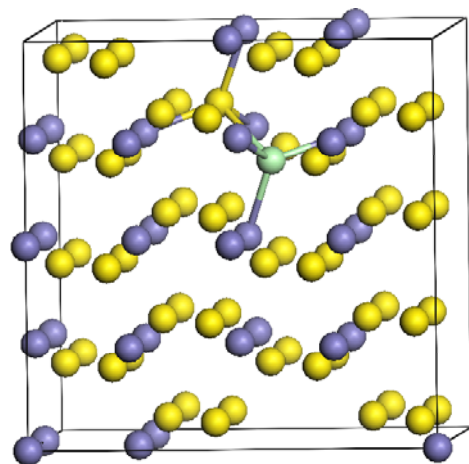
$$\begin{aligned}d_{\text{S-Fe}} &= 2.27 \text{ \AA (in bulk)} \\d_{\text{S-S}} &= 2.16 \text{ \AA (in bulk)}\end{aligned}$$

The N-level is too high above the valence band. Therefore, it cannot provide holes for transport.



Some Fe states are split at the top of valence bands, and there is a $1.0 \mu_B$ local magnetic moment.

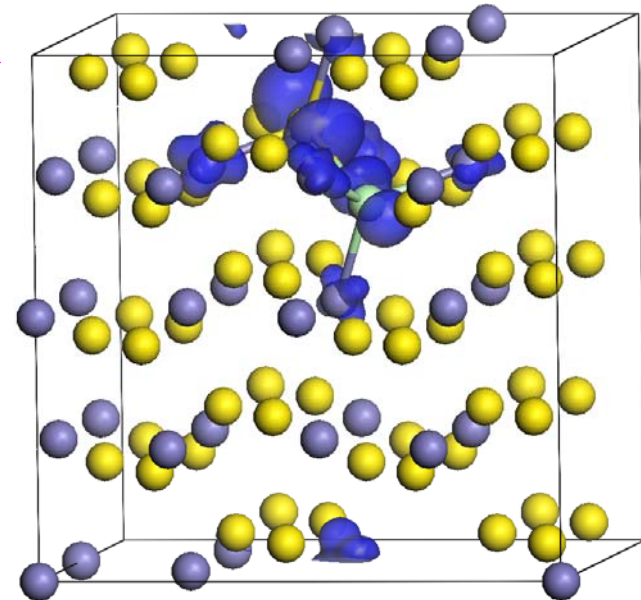
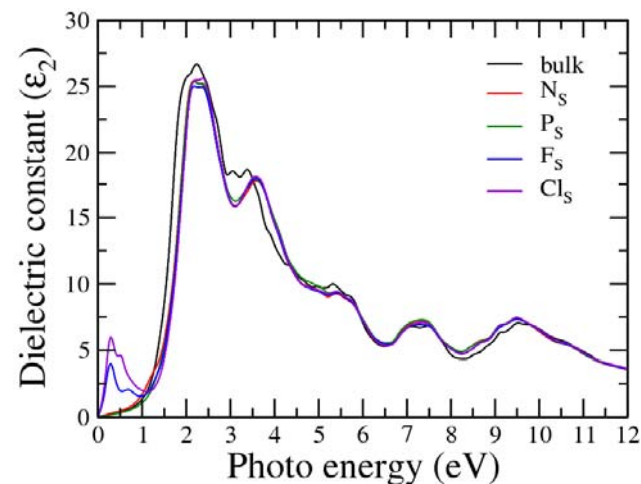
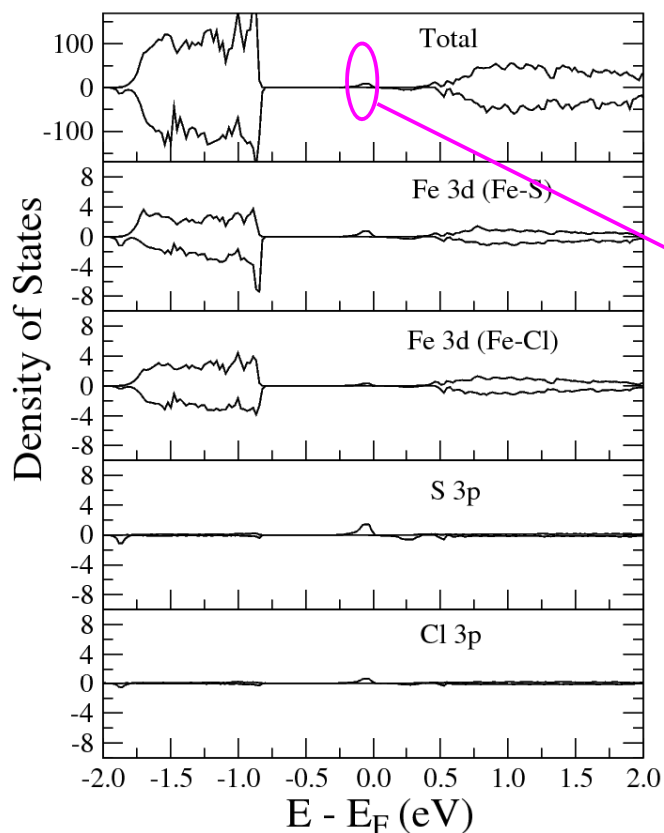
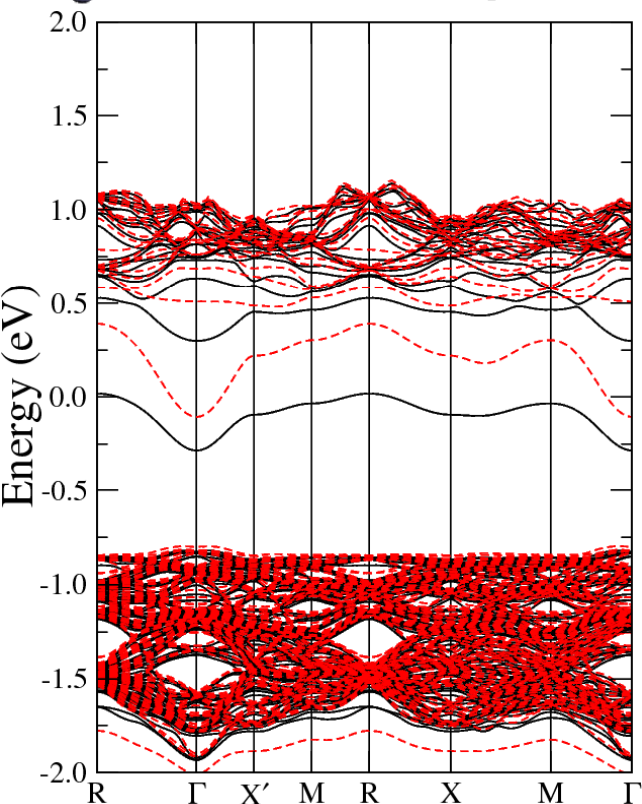
Can we add electrons? Cl-doping



$d_{S-Fe} = 2.21 \text{ \AA}$
 $d_{S-Cl} = 2.56 \text{ \AA}$
 $d_{Cl-Fe} = 2.28 \text{ \AA}$

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

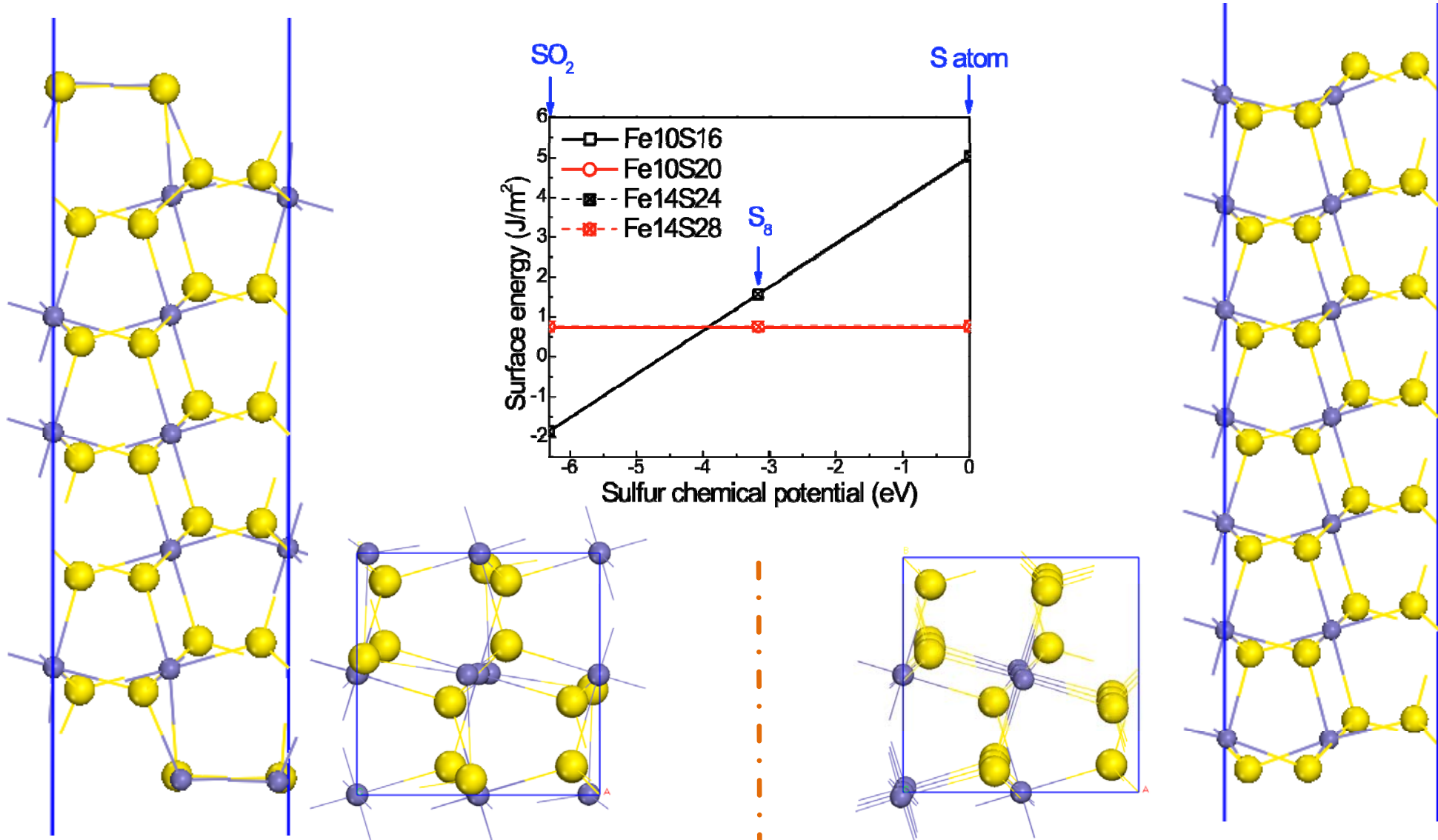
Cl appears to be a good dopant, that provides a $0.996 \mu_B$ local magnetic moment; produces $3 \times 10^{18}/\text{cm}^3$ delocalized electrons for transport; and shifts the absorption edge down to 0.3 eV.



FeS₂ surface simulated with a 7 layer-slab model

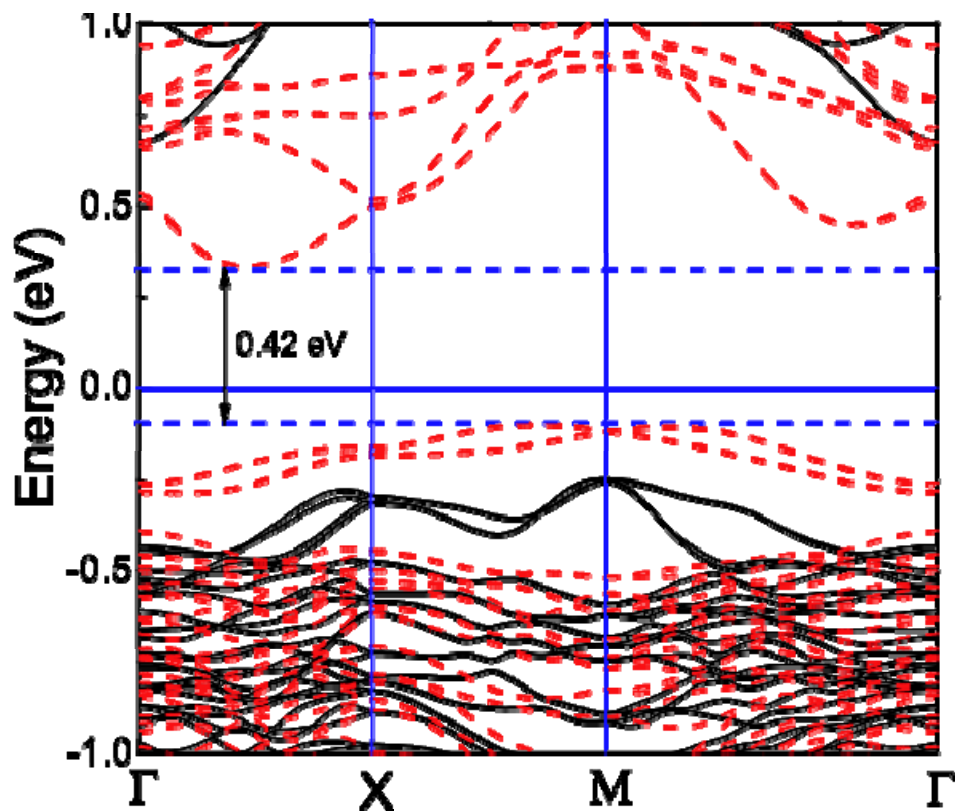
Non-stoichiometric model

Stoichiometric model

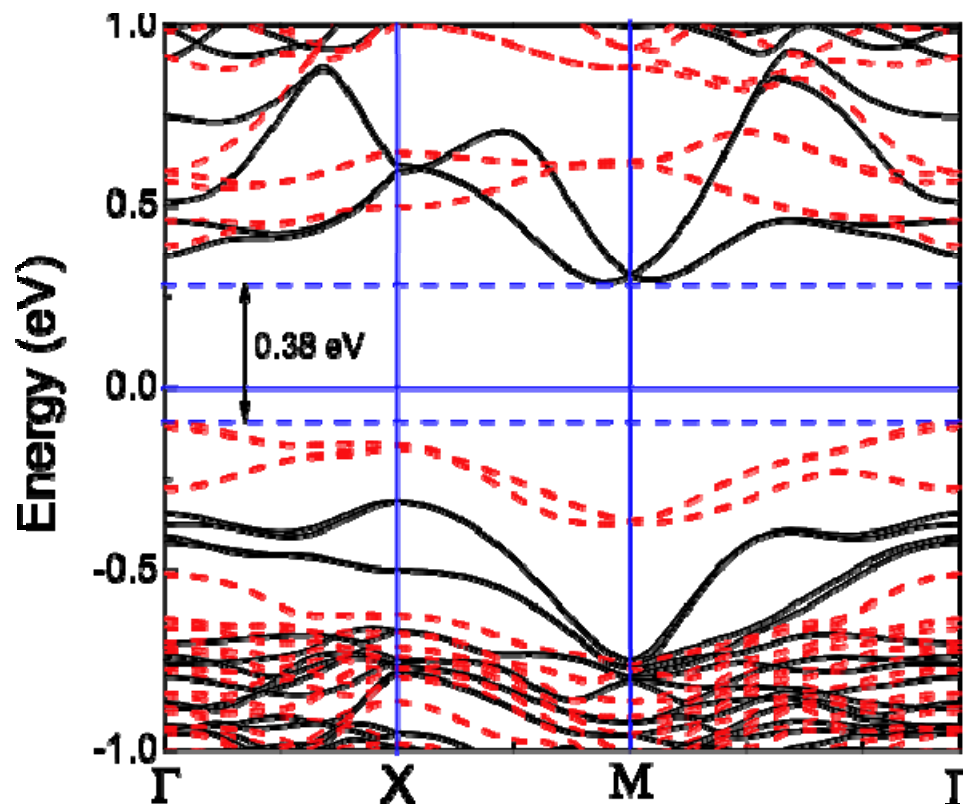


Surface Band Structures

Non-stoichiometric model

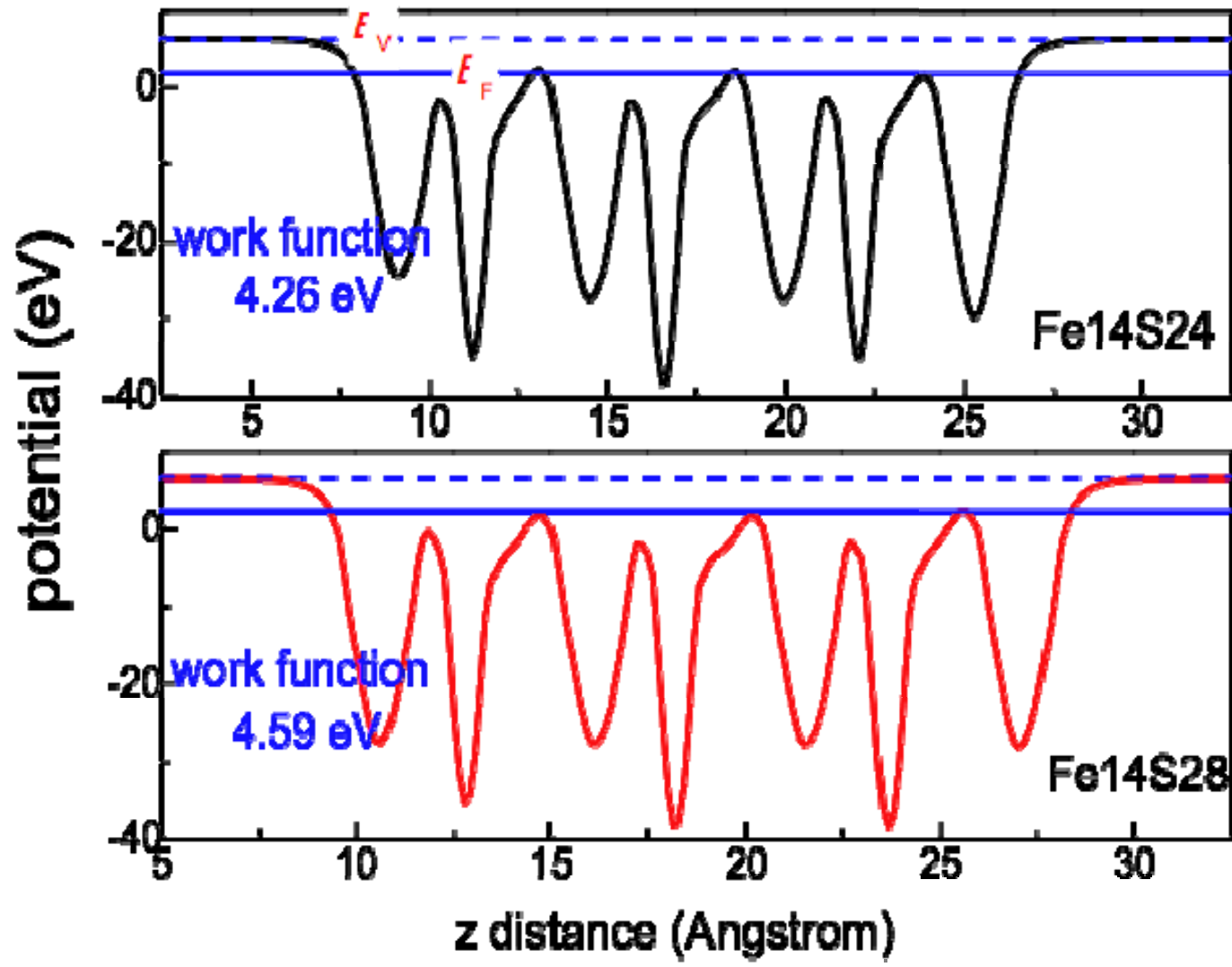


Stoichiometric model



13 solid -- majority spins
dashed -- minority spins

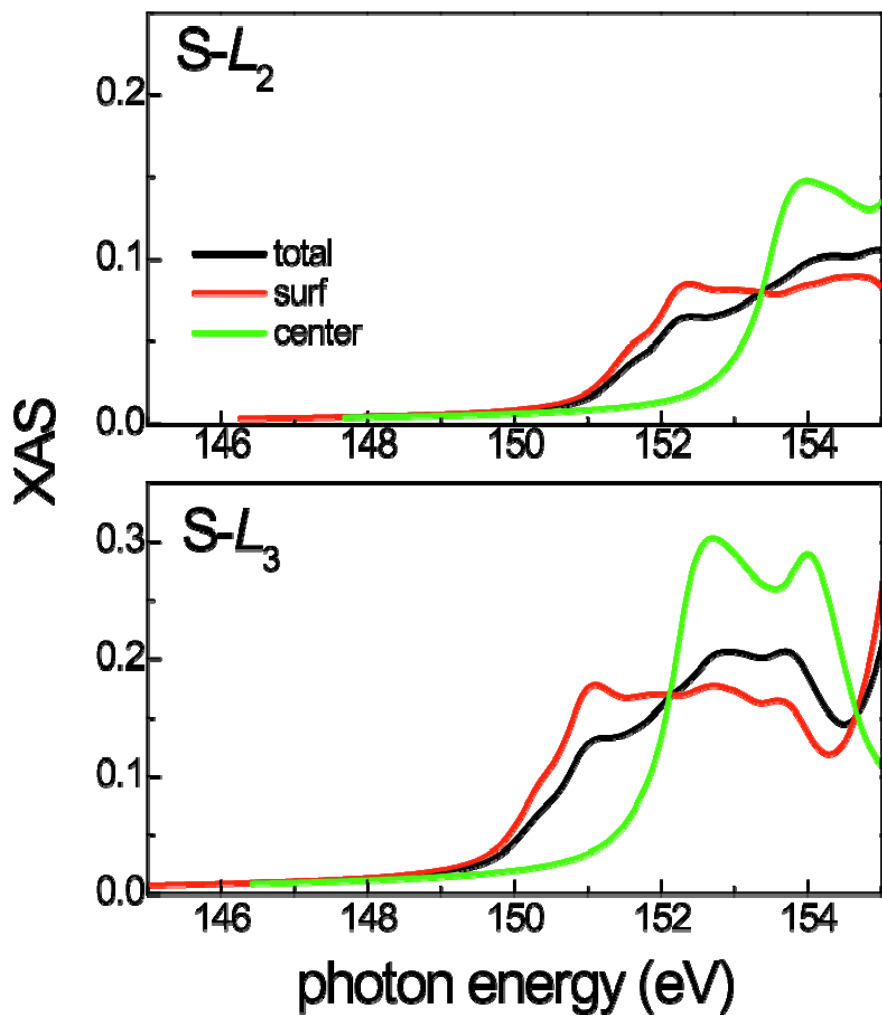
Determination of Work Function



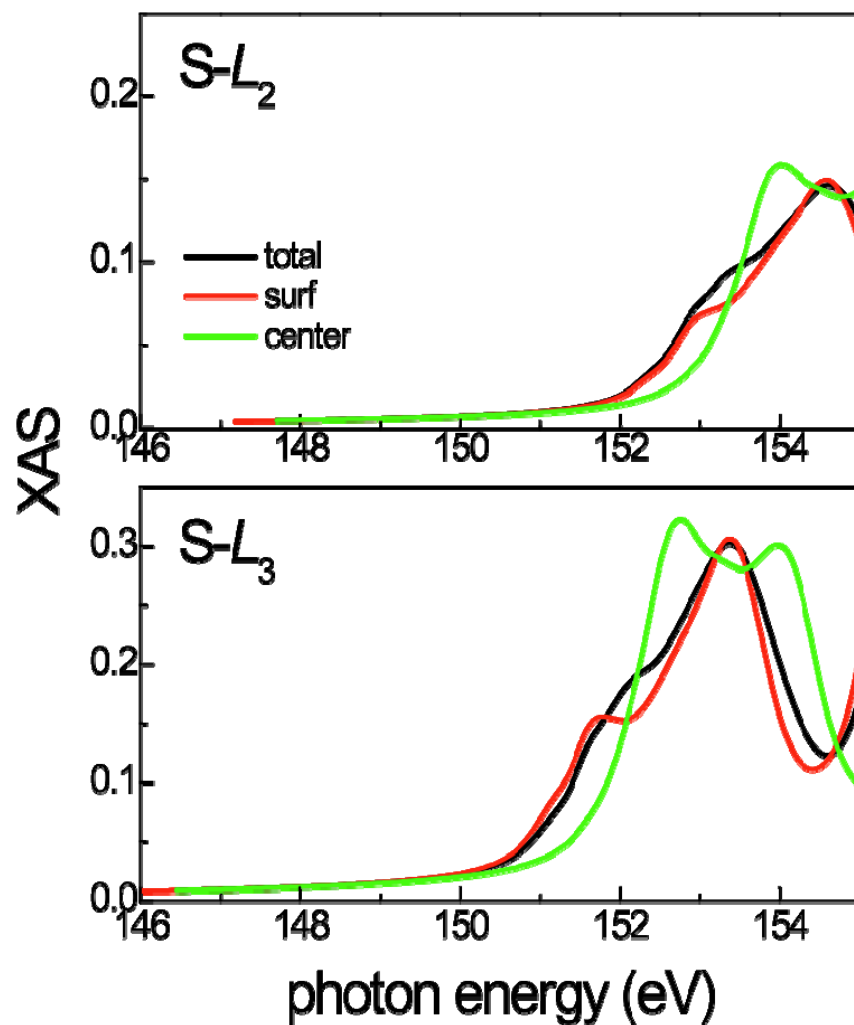
Expt: 5.0 eV

Surface core-level shifts and x-ray absorption spectroscopy (XAS)

Non-stoichiometric model

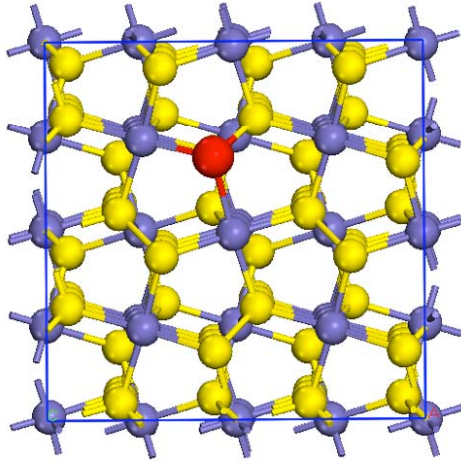


Stoichiometric model

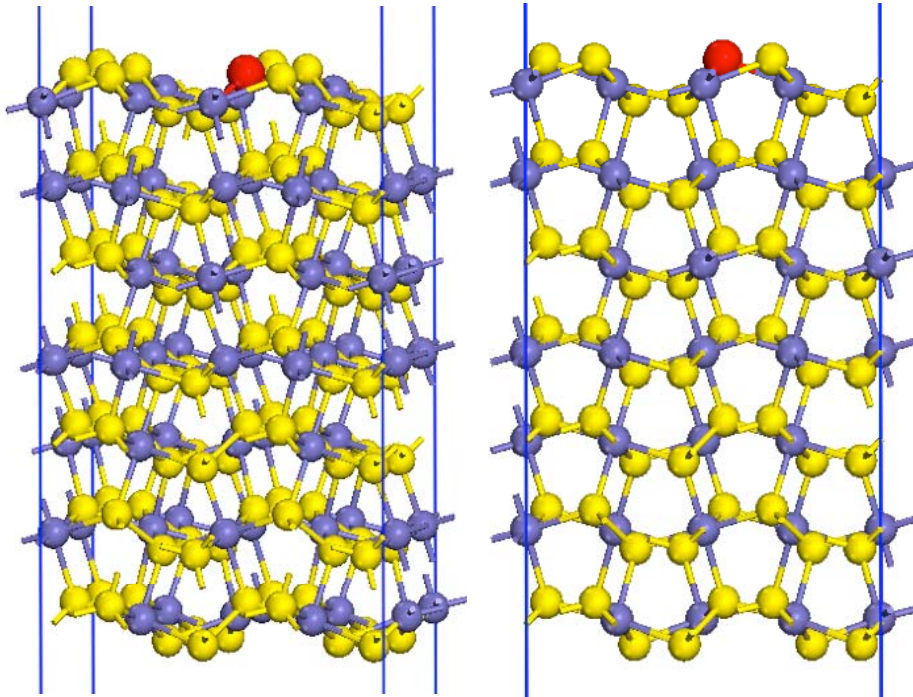
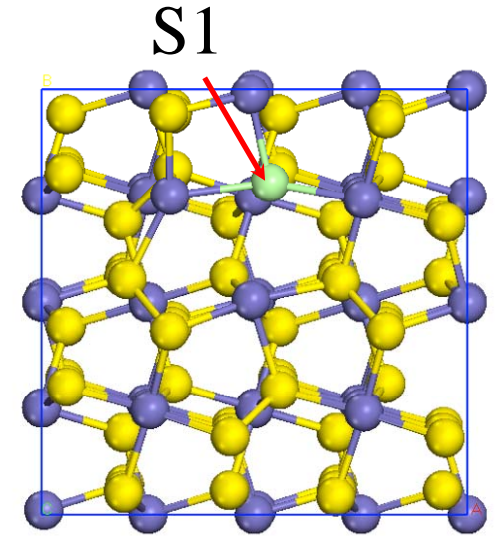


Fe₅₆S₁₁₁ : one vacancy on surface

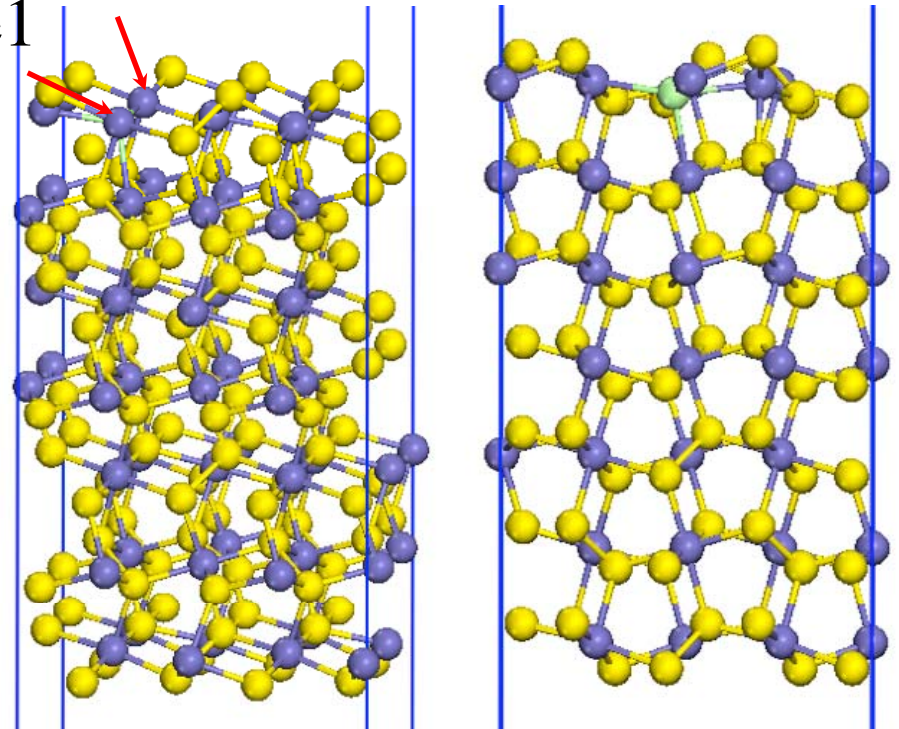
initial
conf.



final
conf.



Fe1
Fe2

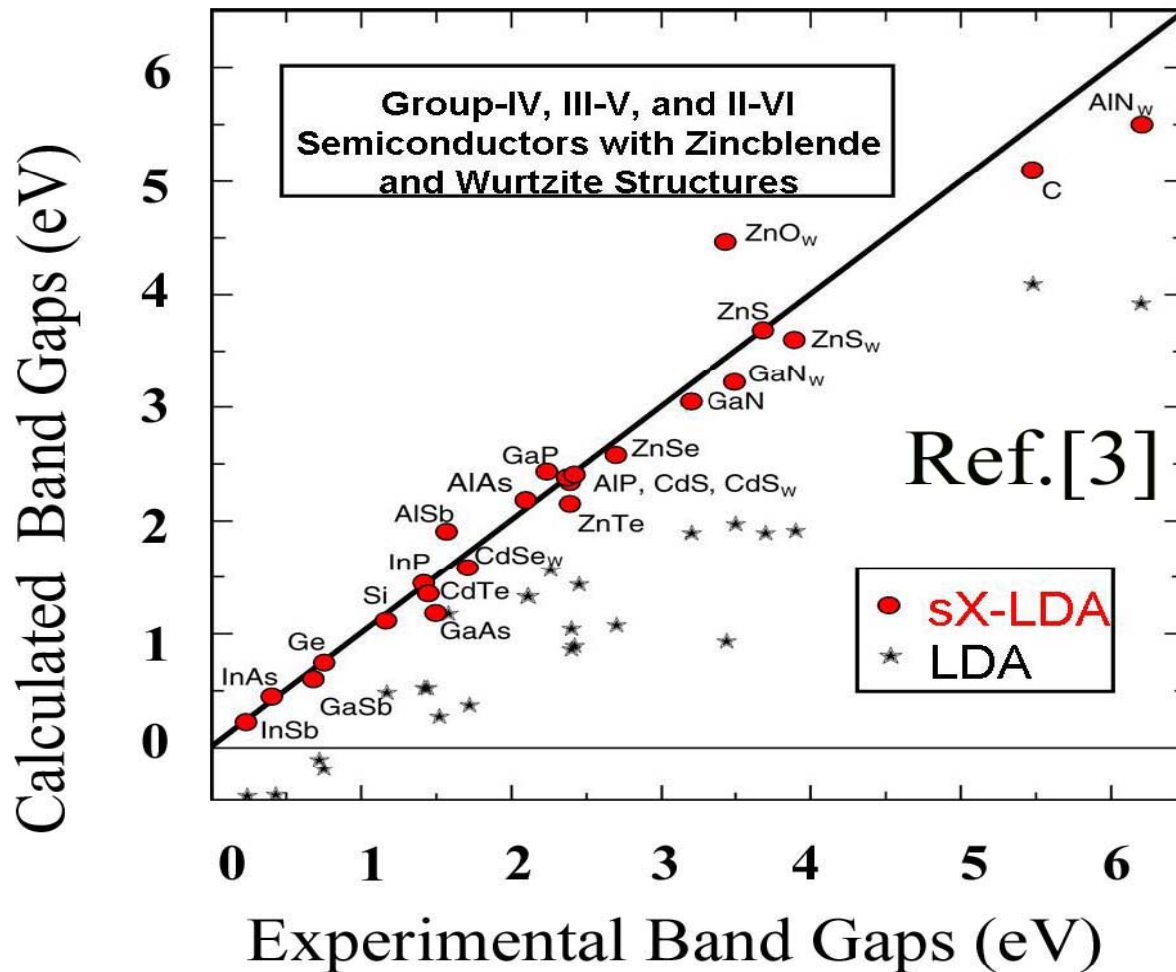


Conclusions

1). Density functional calculations can provide various useful information for studies of Pyrite bulk, surfaces, and nanostructures.

2). It is essential that our calculations are conducted through collaborations with other efforts.

Gap problem?



Screened-exchange-LDA or other corrections (LDA+U) may improve band gaps over LDA/GGA!

[1] B.M. Bylander, L. Kleinman; PRB 41,7868 (1990)

[2] R. Asahi, W. Mannstadt, A.J. Freeman; PRB 59, 7486 (1999)

[3] C.B. Geller *et al*, Appl. Phys. Lett. 79, 368 (2001)

Numerical solution of KS-equation

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

$$\Psi_i(\mathbf{r}) = \sum_j c_i^j \Phi_j(\mathbf{r}) \quad \leftarrow \Phi_j(\mathbf{r}) = e^{i(\mathbf{k} + \mathbf{G}_j) \cdot \mathbf{r}}$$

$$\delta(\langle \Psi | H | \Psi \rangle - \lambda \langle \Psi | \Psi \rangle) = 0$$

$$\begin{pmatrix} H_{1,1} & H_{1,2} & \cdots & H_{1,N-1} & H_{1,N} \\ H_{2,1} & H_{2,2} & \cdots & H_{2,N-1} & H_{2,N} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ H_{N-1,1} & H_{N-1,2} & \cdots & H_{N-1,N-1} & H_{N-1,N} \\ H_{N,1} & H_{N,2} & \cdots & H_{N,N-1} & H_{N,N} \end{pmatrix} = \varepsilon \begin{pmatrix} S_{1,1} & S_{1,2} & \cdots & S_{1,N-1} & S_{1,N} \\ S_{2,1} & S_{2,2} & \cdots & S_{2,N-1} & S_{2,N} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ S_{N-1,1} & S_{N-1,2} & \cdots & S_{N-1,N-1} & S_{N-1,N} \\ S_{N,1} & S_{N,2} & \cdots & S_{N,N-1} & S_{N,N} \end{pmatrix}$$

$$H_{ij} \equiv \langle \Phi_i | H | \Phi_j \rangle; S_{ij} \equiv \langle \Phi_i | \Phi_j \rangle$$

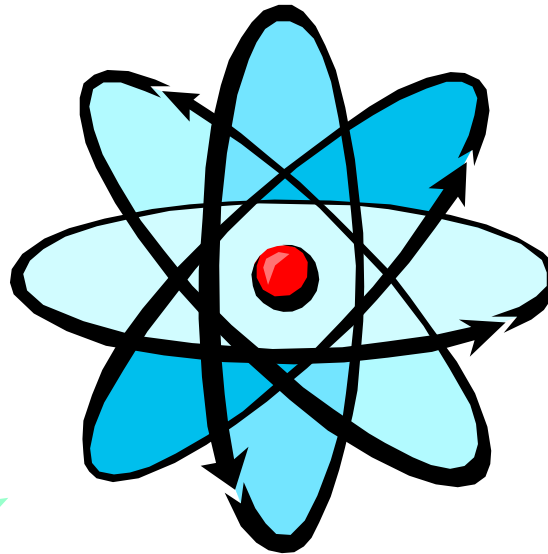
Materials properties depending on electronic structures

Mechanical properties

Magnetic properties

Optical properties

Transport Properties



Chemical Properties

\sum_i & ∇_i

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