The bandgap of pyrite: bandgap oscillations on an ultrafast timescale

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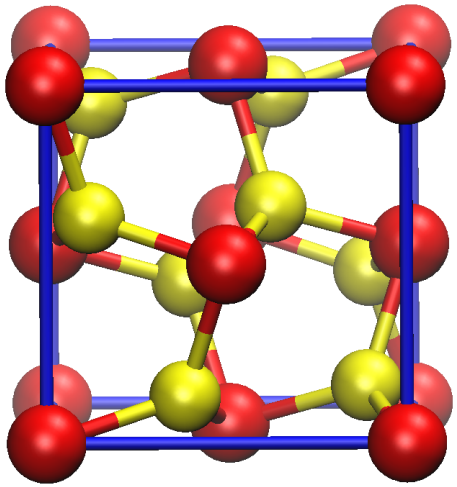
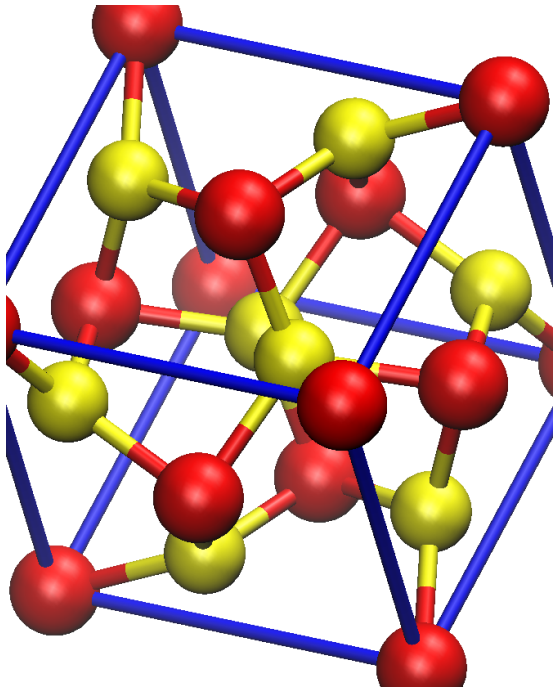
Pyrite (FeS_2)

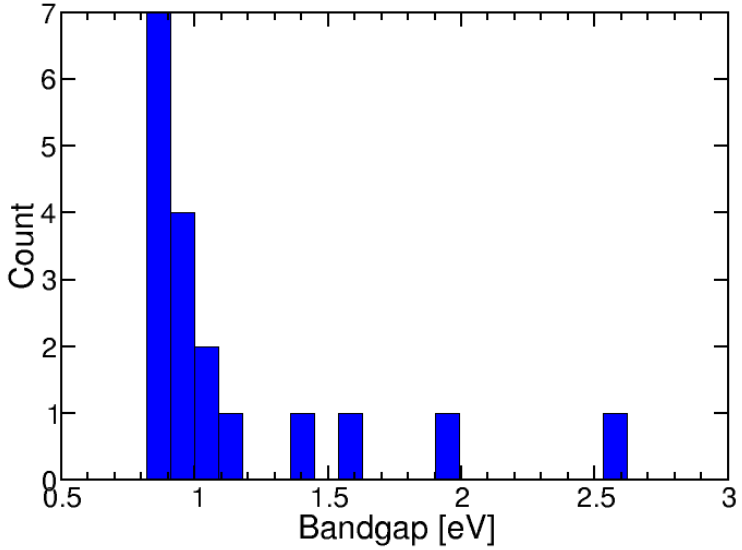




S_2 dimers along <111>

Pyrite as a semiconductor

Histogram of experimentally measured bandgaps



Measurement Techniques

- Photocurrent
- Quantum efficiency
- Reflectance
- Optical absorption
- Transmittance

Ferrer *et al.*, Solid State Comm., **74**, 913 (1990)

Reasons to like pyrite as a solar cell material

Good bandgap (0.95 eV)

- Good at absorbing solar radiation

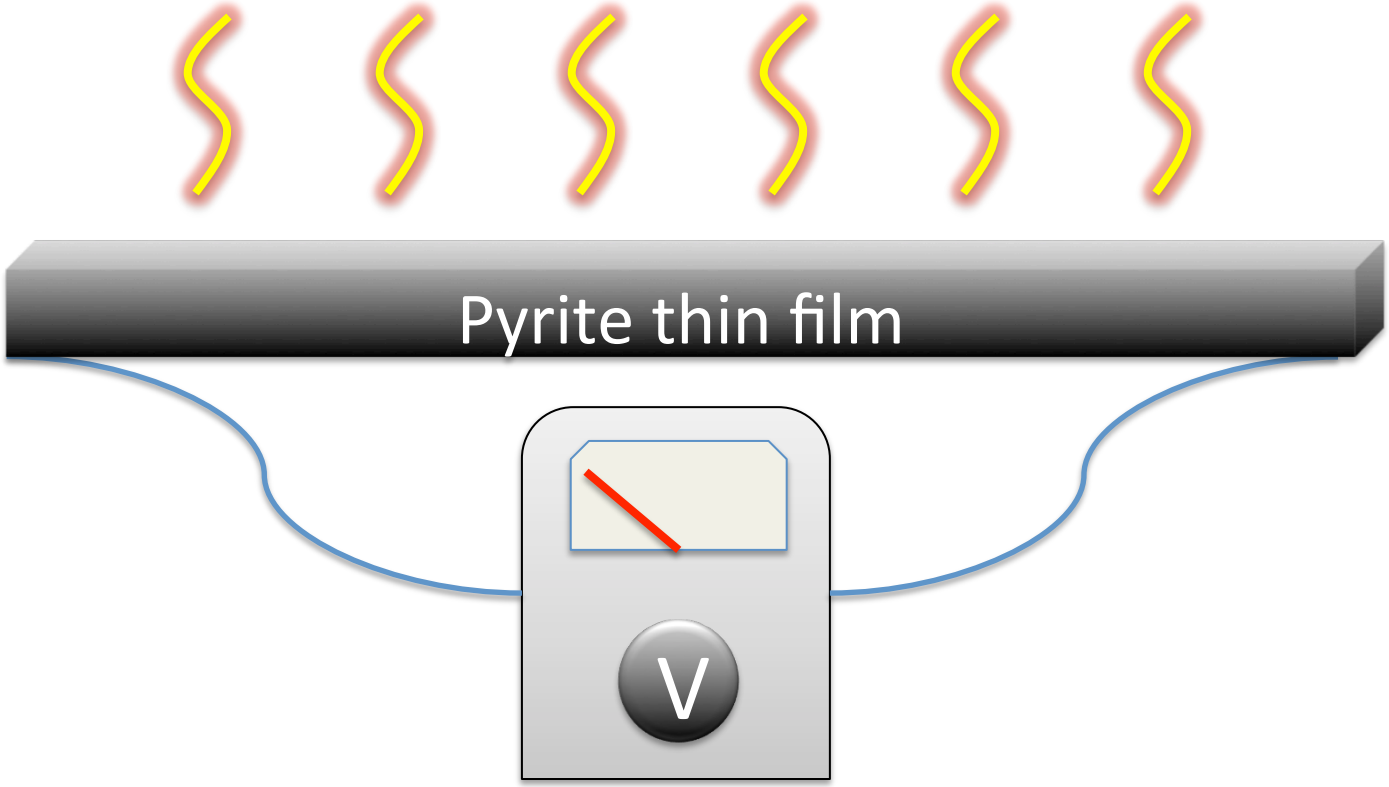
High absorption

- Thin films can absorb virtually all incident radiation

Economics

- Cheap
- Non-toxic
- Abundant

Pyrite fails to perform



V_{OC} = 0.2 eV

Possible explanations

Bulk defects

- Should be minimal

Intrinsic surface states

- Don’t seem to affect bandgap

Surface defects

- Jury is still out

What we're interested in

Low open circuit voltage

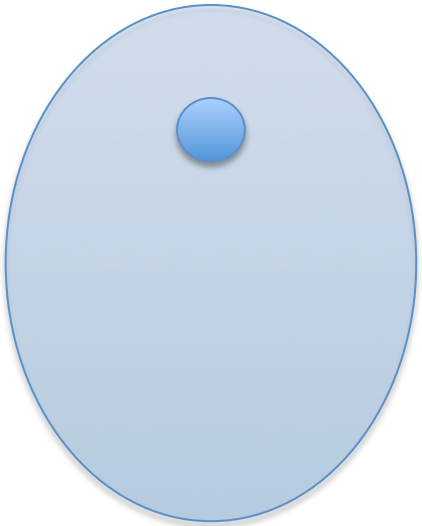
Dynamical properties of the bandstructure

The GW method

Single particle Green's function

Electronic self-energy → $\Sigma = iGW$

Screened Coulomb interaction



Electron plus polarization cloud ➔
weakly interacting quasiparticles

Expansion in screened Coulomb interaction

Methods

DFT

- 600 eV cutoff
- 3x3x3 k-points mesh
- PBE functional
- PAW Pseudopotentials
- Forces converged to within 1 meV/Å

GW

- 200 eV cutoff
- 520 unoccupied bands
- Fully self-consistent (energies and orbitals)
- Converged until all eigenvalues changed by less than 0.01 eV

Bulk bandgap

Accepted bandgap = 0.95 eV

GW calculations

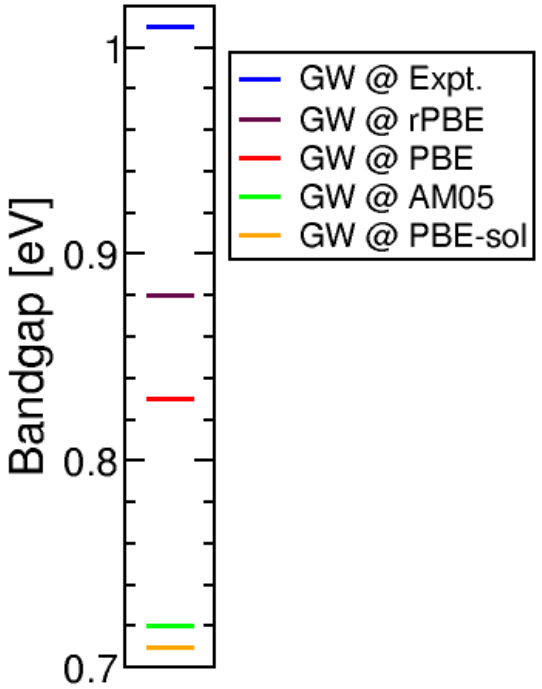
Experimental structure: 1.01 eV

PBE-relaxed structure = 0.83 eV

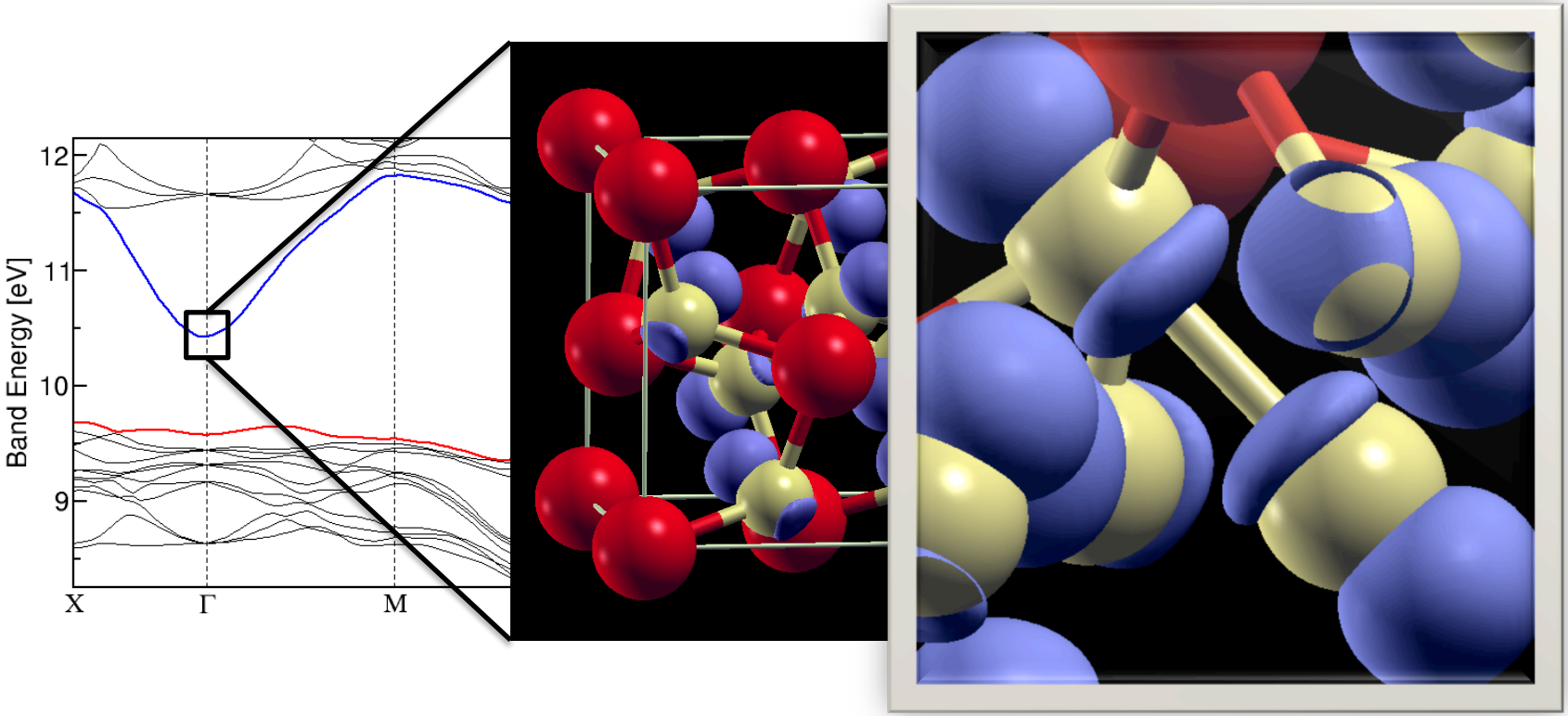
Bulk bandgap

Accepted bandgap = 0.95 eV

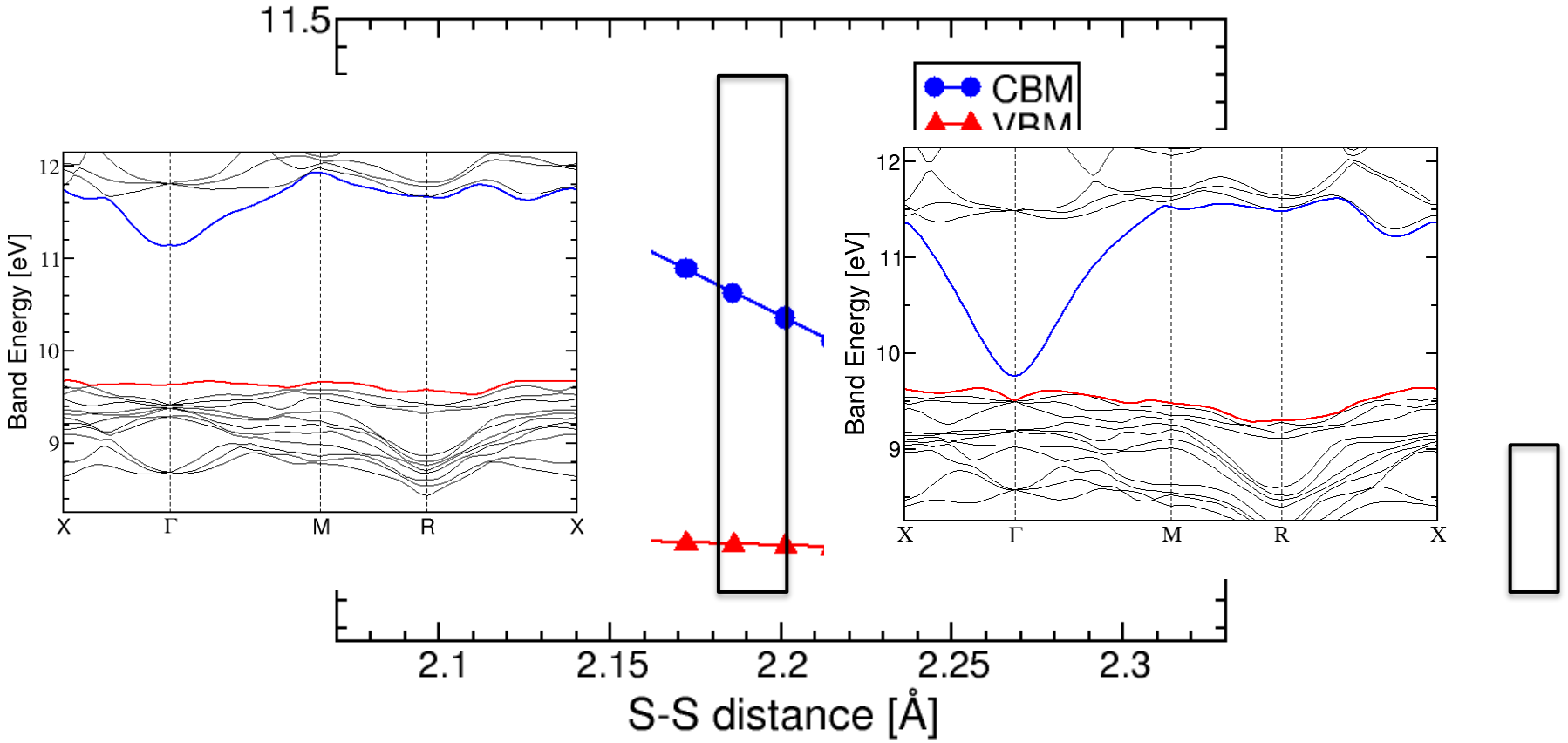
GW bandgap at different geometries



Conduction band minimum



S-S distance dependence of the gap



Why is this important?

- Bandgap is very sensitive to what coordinates are used

- Phonons

$\omega = 347\ cm^{-1}$

T = 100 fs

Bulk bandgap with phonons

Thermal excitation at room temperature

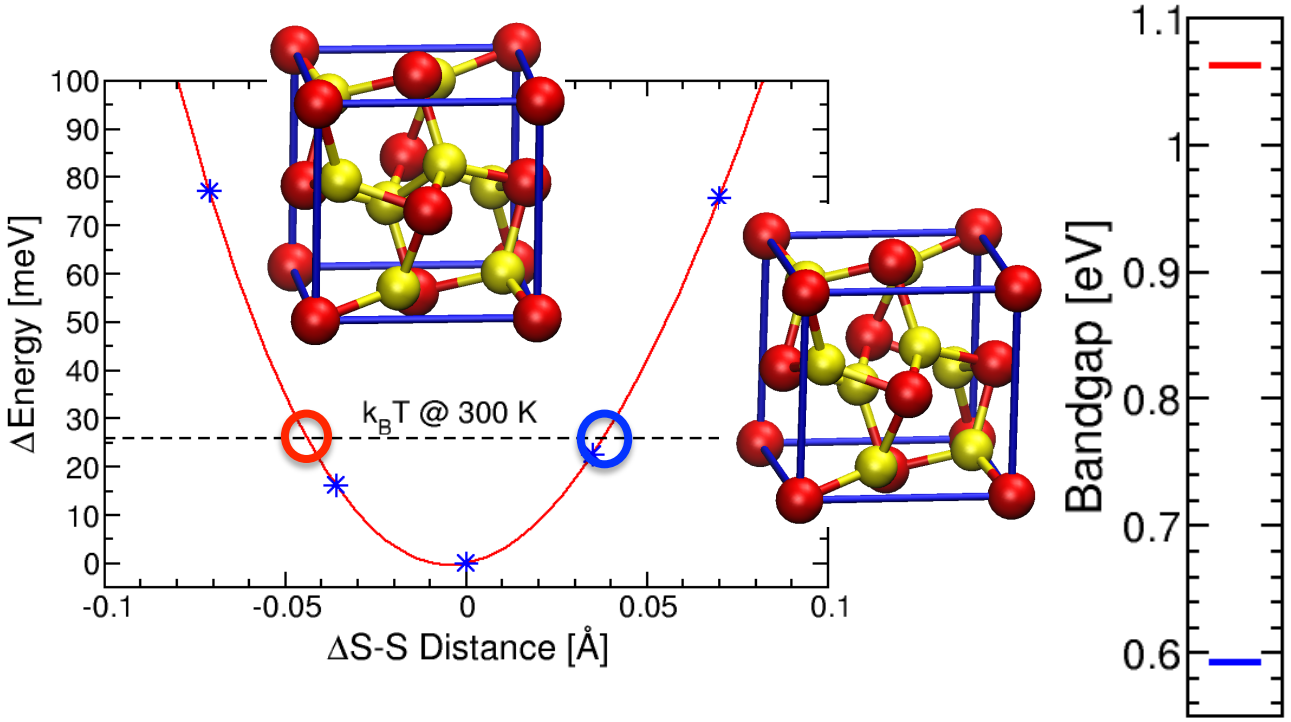
$$E_\omega = \hbar\omega\left(N_\omega + \frac{1}{2}\right)$$

$$N_\omega = \frac{1}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)}$$

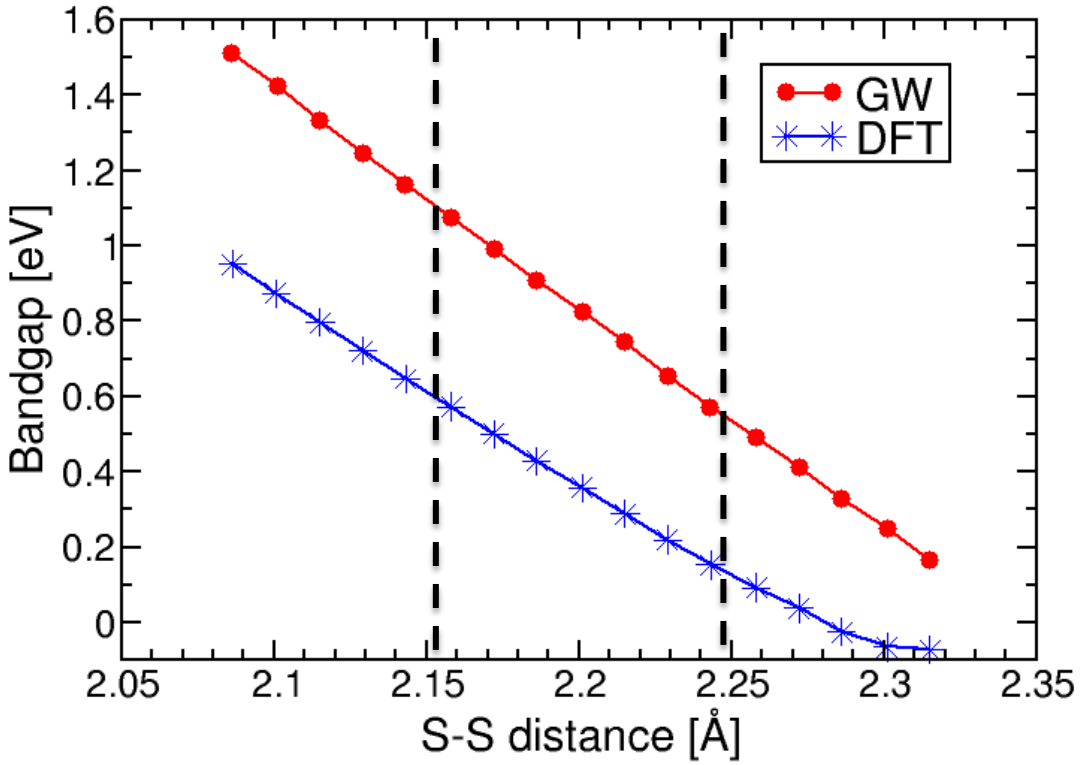
$$\Delta E = 26\,\text{meV} \approx k_B T$$

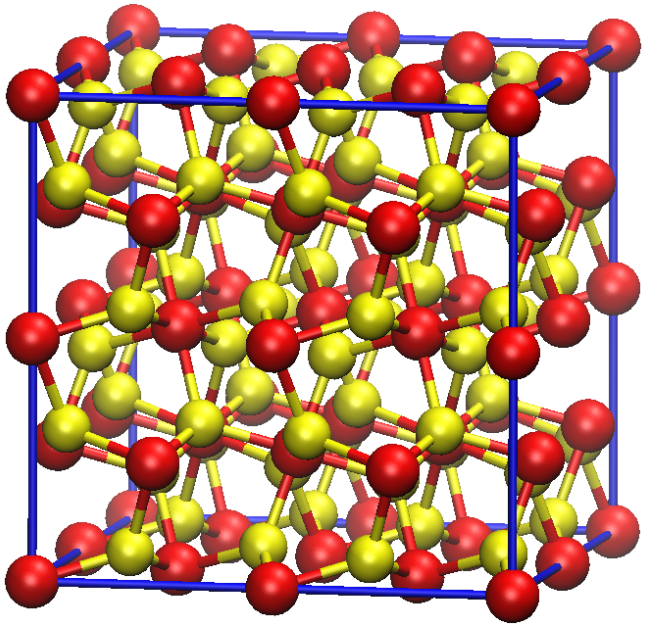
Bulk bandgap with phonons

Thermal excitation at room temperature

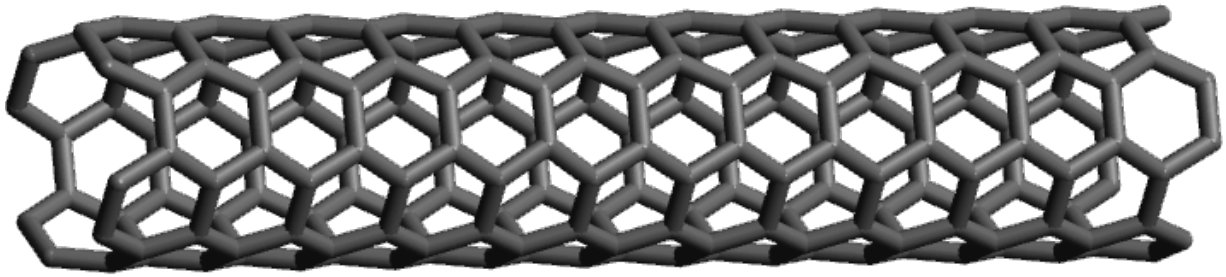


Molecular dynamics





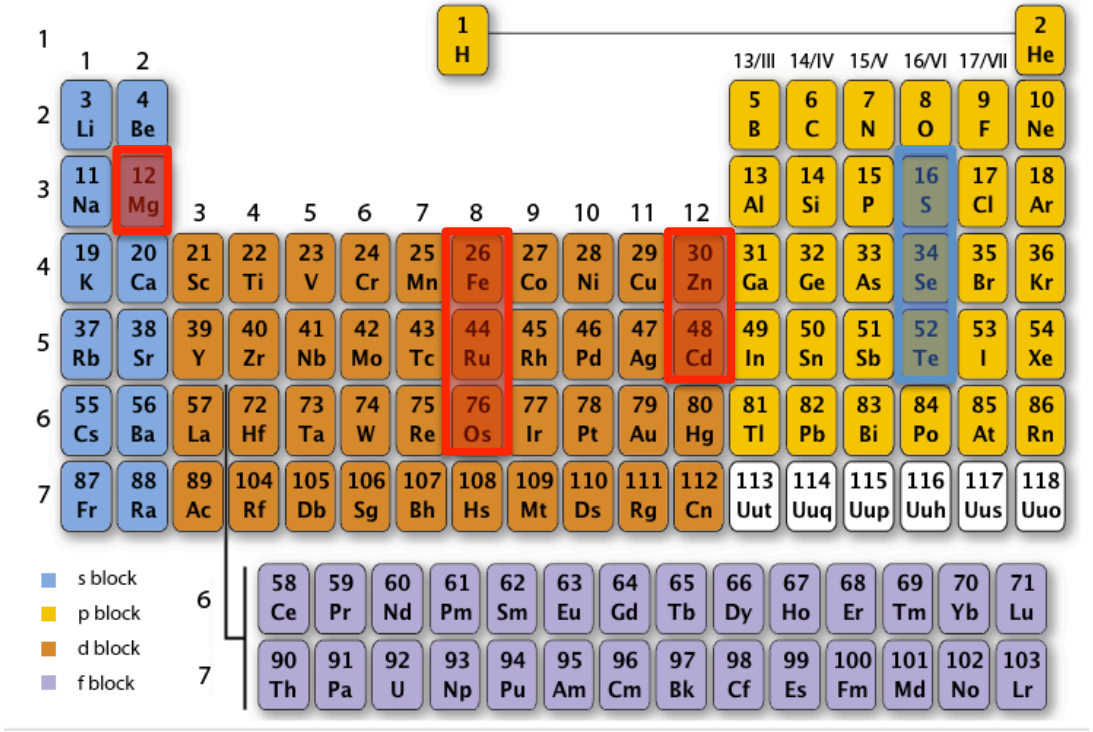
This effect has been seen before



Radial breathing mode

Kim *et al.*, Chem. Phys. **413**, 55 (2013)

We predict this effect in other pyrite-structured systems

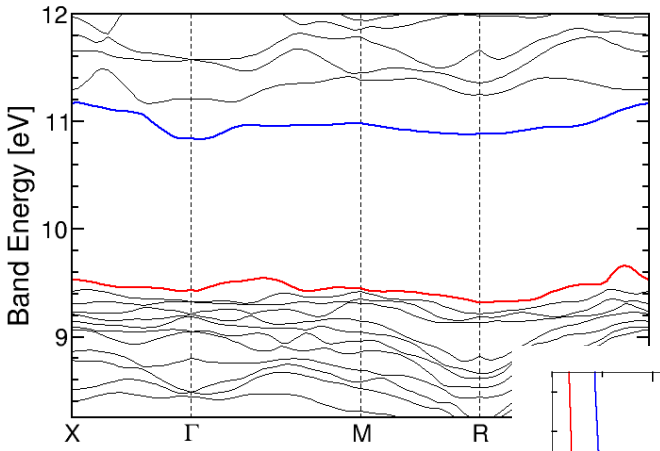


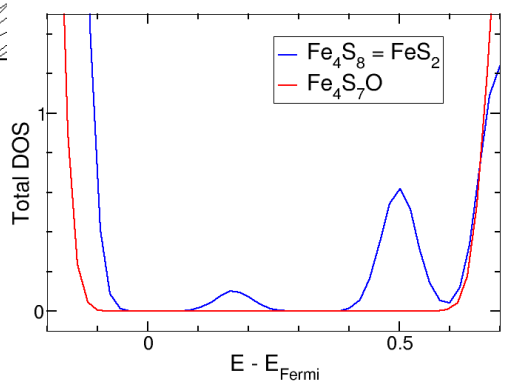
Systems predicted to exhibit oscillating bandgap

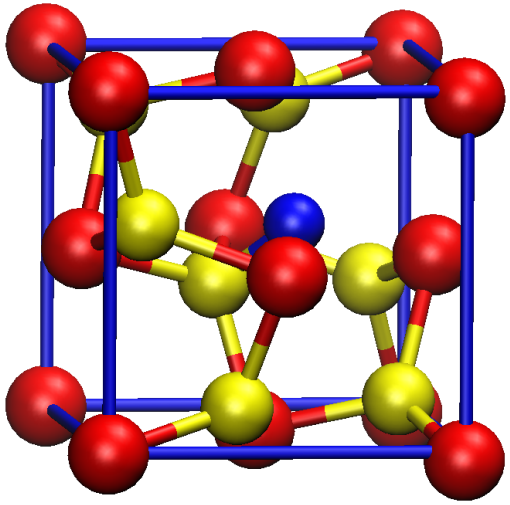
FeS_2	$FeSe_2$	$FeTe_2$
RuS_2	$RuSe_2$	$RuTe_2$
OsS_2	$OsSe_2$	$OsTe_2$
ZnS_2	$ZnSe_2$	$ZnTe_2$
CdS_2	$MgSe_2$	$MgTe_2$

Is there any hope?

Oxygen “defects”







E_g^{GW} = 1.38 eV

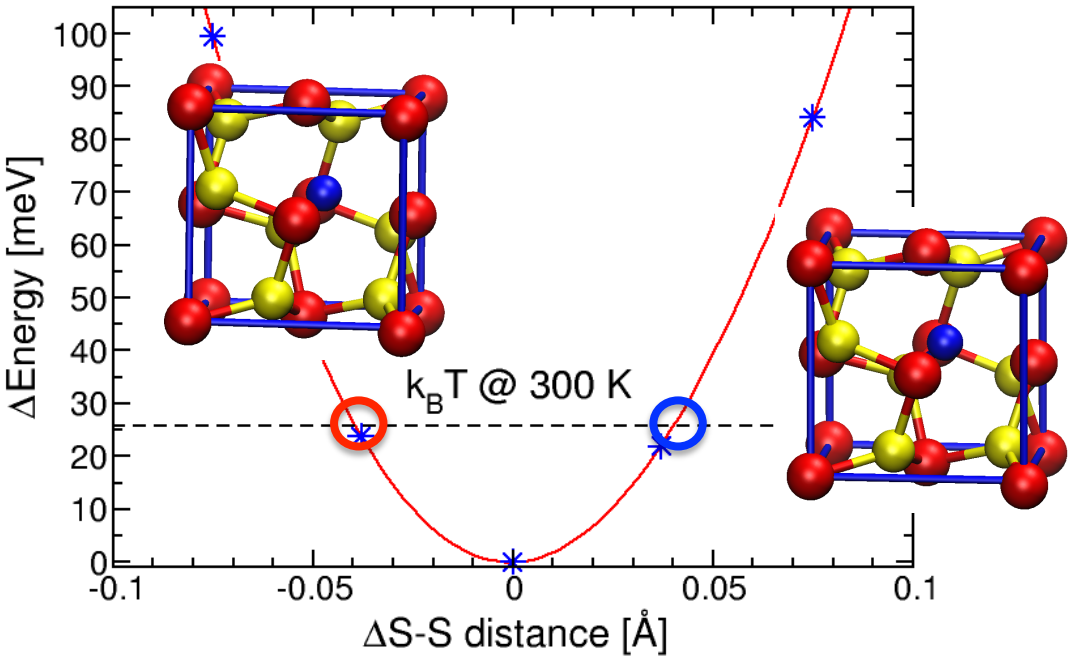
Oxygen defects vs bandgap

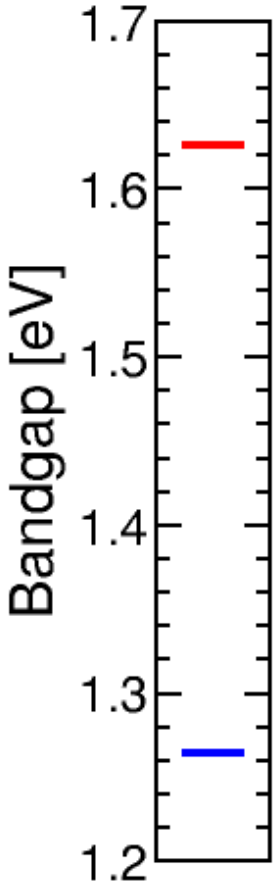
GW calculations

Oxygen/unit cell	Bandgap [eV]
1	1.38
2	1.62
3	1.88
4	2.13

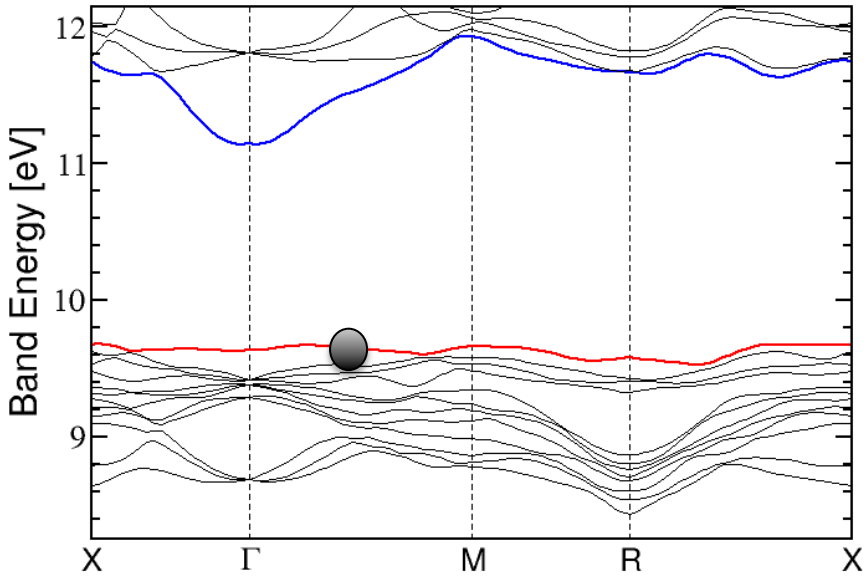
Is there any hope?

Oxygen “defects”





What about conservation of energy?



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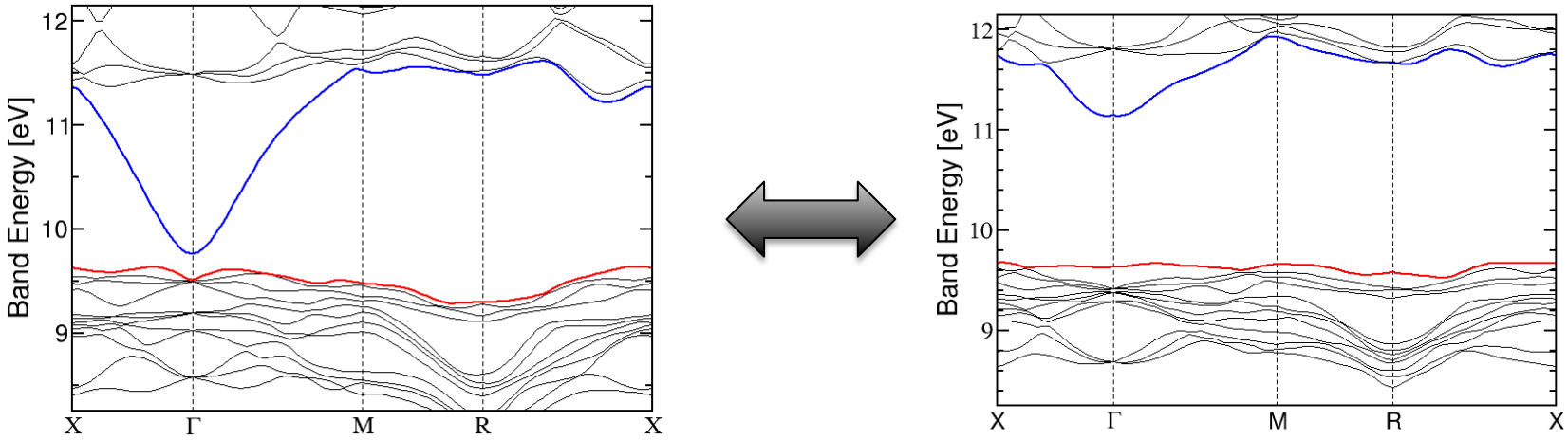

- ~~Thermal population of bands~~
- ~~Energy exchange with phonons~~
- ~~Exchange of electronic kinetic energy~~
- ?

Conclusions

- The bandgap of pyrite depends critically on the sulphur-sulphur distance
- Phonons cause an oscillating bandgap
- Many pyrite-structured systems likely exhibit this oscillation
- Oxygen “defects” cause an opening of the pyrite bandgap and slightly reduce bandgap oscillations

Acknowledgements

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