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FeS₂, pyrite is a promising material for photovoltaic application due to a large quantum absorption coefficient, a suitable optical band gap of 0.95eV and its abundance[1]. Understanding the nature of its band gap within first-principles calculations is of great importance for a reliable surface- and defect-analysis. However, local exchange-correlation (xc) functionals of density-functional theory (DFT), e.g. functionals based upon a local-density (LDA) or generalized-gradient-approximation (GGA), suffer from a severe underestimation of the band gap in semiconductors and insulators. A considerable improvement of the band gap is usually achieved by more sophisticated methods such as hybrid-functionals like the HSE06-functional[2] or the GW-approximation[3] of many-body perturbation-theory. However, applying these methods to FeS₂ pyrite does not lead to better agreement with the experimentally observed band gap, even a worsening is found[4]. The cause of this peculiar behavior is not quite clear. Therefore, we conducted a systematic study using HSE06 and GW on a couple of pyrite-type compounds and structurally-related marcasite-type compounds.

Methods

- All-electron, full-potential DFT
- LAPW basis
- xc-functionals: LDA, PBE, PBE0, HSE06[3], EXX-OP, ...
- http://www.judft.de

SPEX®:
- GW-approximation (G₆W₀)
- Hartree-Fock approximation
- dielectric function, optical absorption

[2]: J. Heyd et al., Journal of Chemical Physics (2001)
[4]: R. Sun et al., PRB (2011) and S. G. Choi et al., PRB (2012)

Electronic Structure (PBE)

- covalent bonds of the S-dimers and the (almost) octahedral symmetry determine the electronic structure of pyrite and marcasite

- interesting change of orbital character from VBM to CBM around Γ for both FeS₂, pyrite and marcasite
- strongly localized Fe 3d (red) bands at VBM (near X)
- delocalized S 3p (black) band at CBM of pyrite (Γ), but Fe 3d character at CBM of marcasite (Δ)
- strong influence of Wyckoff parameter u on band gap:
  - size of band gap mainly determined by u
  - the heavier the cation the smaller the band gap for the same u

- many unoccupied states are necessary for converging transition energies between states of different l-character
- for a proper description of energetically high-lying bands, it is unavoidable to use many local orbitals (LOs) and a large plane-wave cut-off kmax
- transition energies of states of same l-character converge much faster [similar to case ZnO:
  see B. C. Shih et al., PRL (2010) and C. Friedrich et al., PRB (2011)]
- dependence on the start value for a “one-shot” GW calculation analyzed via G₆W₀@PBE+U:
  - linear behavior of Eₓₓ with respect to U for smaller values of U
  - smaller gradient for G₆W₀@PBE+U than for pure PBE+U, i.e. slight dependence on the start point
  - constrained RPA: U_{RPA}
- larger values of U cause a dehybridization of p- and d-states leading to a reduction of the gap size

Band Gaps

FeS₂: 0.64, 2.34, 0.63, 0.95
RuS₂: 0.14, 1.08, 0.87, 1.4
OsS₂: 0.76, 1.73, 0.99, 2.0
ZnS₂: 2.11, 3.21, 3.17, 2.5
NiP₂: 1.00, 1.43, 1.42, -

Marcasite-compounds (X → Γ):

FeS₂: 0.95, 2.82, 1.25, 0.4
FeSe₂: 0.52, 2.15, 0.84, 0.5-1.0
FeTe₂: 0.44, 1.68, 0.80, 0.2-0.5
CrCl₂: 0.27, 3.05, 0.33, -

Conclusions

- pyrite- and marcasite-type compounds are very challenging systems due to a complex interplay between (strongly) localized Fe 3d- and delocalized p-states at Γ
- PBE gives surprisingly good results compared to experiment for some of the compounds
- HSE06 predicts the largest transition energies for all compounds, in particular for the compounds with Fe (correlation effects of Fe could be a problem)
- G₆W₀ convergence depends strongly on character of the bands; transitions between bands of different l-character are difficult to converge

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