Transition metal dopants in the wide band gap semiconductor ZnS: a first-principles study

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Introduction & Motivation

Defect center has become a competitive field nowadays since they offer promising basis for future technologies such as hardwares for *quantum computation, atomic scale sensing, quantum simulation, and spintronic devices*. Transition metal (TM) dopants in semiconducting materials provides interesting tunable features and additional functionalities as they can exhibit *long coherence time at room temperature, long range spin-spin interaction* due to strong spin-orbit coupling, etc.

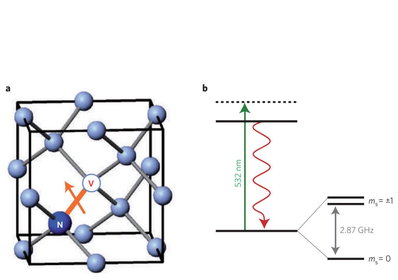

Figure 1: Crystal structure of the NV-center in diamond, a widely studied single defect material, shown with its energy level [1]

Our overarching goal is to systematically study **various TM dopants** in **different host materials** to determine the best performing combination. Towards this goal, here we report our study on the **substitutional X** and nearest neighbor (NN) **X-vacancy** centers in **ZnS** where **X = Cu, Co, Ni, Fe.**

Methodology

We performed first principles plane-wave based **spin-polarized** Density Functional Theory (DFT) calculations using the Perdew-Burke-Ernzerhof (**PBE**) exchange and correlation functionals as implemented in the **Quantum ESPRESSO** code [2]. We used a scalar relativistic Projector Augmented Wave (**PAW**) pseudopotential with non-linear core correction.

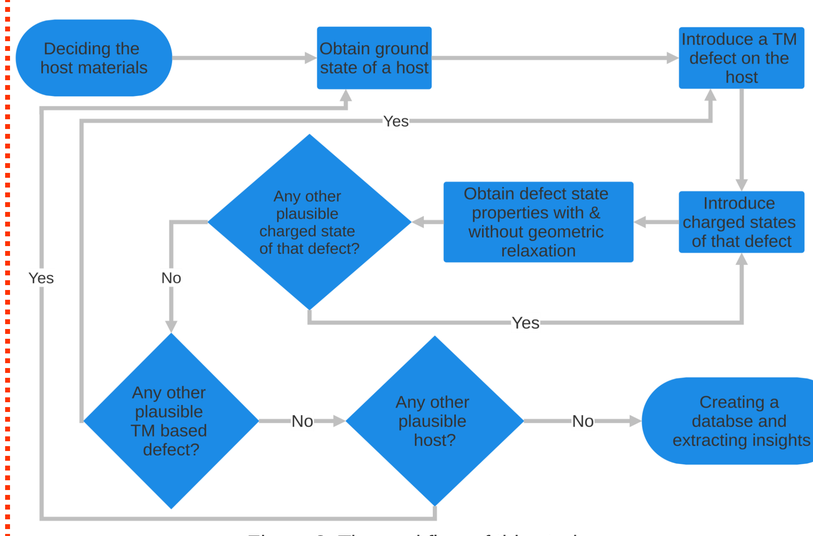

Figure 2: The workflow of this study.

DFT calculations has been performed both on **relaxed** and on **unrelaxed** geometry.

Following our calculation, we have extracted:

- Structural properties
- Electronic properties
- Magnetic properties
- Defect formation energies [4]

DFT calculations has been performed both on **relaxed** and on **unrelaxed** geometry.

Calculation done on 64 atoms supercell containing 32 **Zn** and 32 **S**. So, single TM dopant Zn-substitution corresponds to 3.125% of doping concentration which is low enough to capture the physics exhibited by experimental dilute limit doping.

The parameters that were converged before proceeding any calculations: **(1)** Kinetic energy cutoff (105 Ry), **(2)** Charge density cutoff (420 Ry), **(3)** K-point grid density (unshifted, $4 \times 4 \times 4$), **(4)** Lattice parameters (5.442 Å), **(5)** Smearing type and broadening (Gaussian, 0.01 Ry).

Structural properties of ZnS and its defect centers

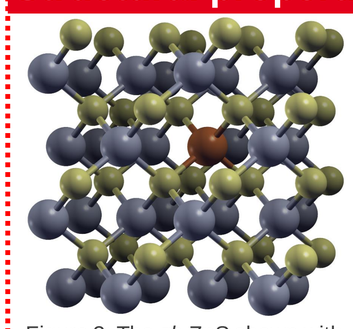

Figure 3: The *zb* ZnS shown with a substitutional TM defect.

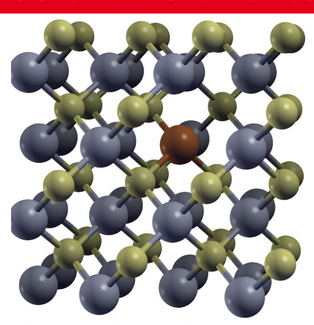

Figure 4: The *zb* ZnS shown with a NN TM-vacancy defect.

TM impurity changes the bond length near the isolated defect. The magnitude of the change depends strongly on charge state.

NN TM-vacancy changes the bond length too but it reduces some symmetry due to the asymmetric nature of the TM-vacancy defect.

The lattice parameter is found for pristine *zinc-blende (zb)* structure of ZnS to be 5.442 Å which is within 0.59% with respect to reported experimental value 5.410 Å [5].

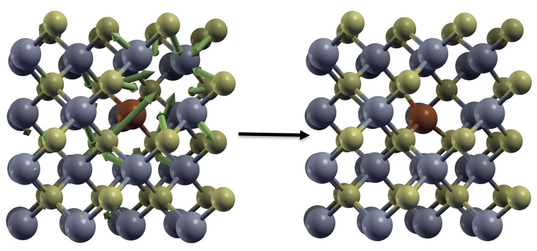

Figure 5: On the left side, an unrelaxed structure is shown where the green arrows denote the internal forces on the atoms. On the right side, the structure is relaxed using the BFGS algorithm where the forces becomes negligible.

Defect formation energy

For a point defect D, with charge state q, the defect formation energy as a function of Fermi level is given by [4]:

$$E_f^D(q, E_F) = E_{\text{total}}^D - E_{\text{total}}^{\text{Pristine}} + E_{\text{corr}}^q - \sum n_i \mu_i + q(E_F + E_{\text{VBM}}^{\text{Pristine}} + \Delta V_{q/b})$$

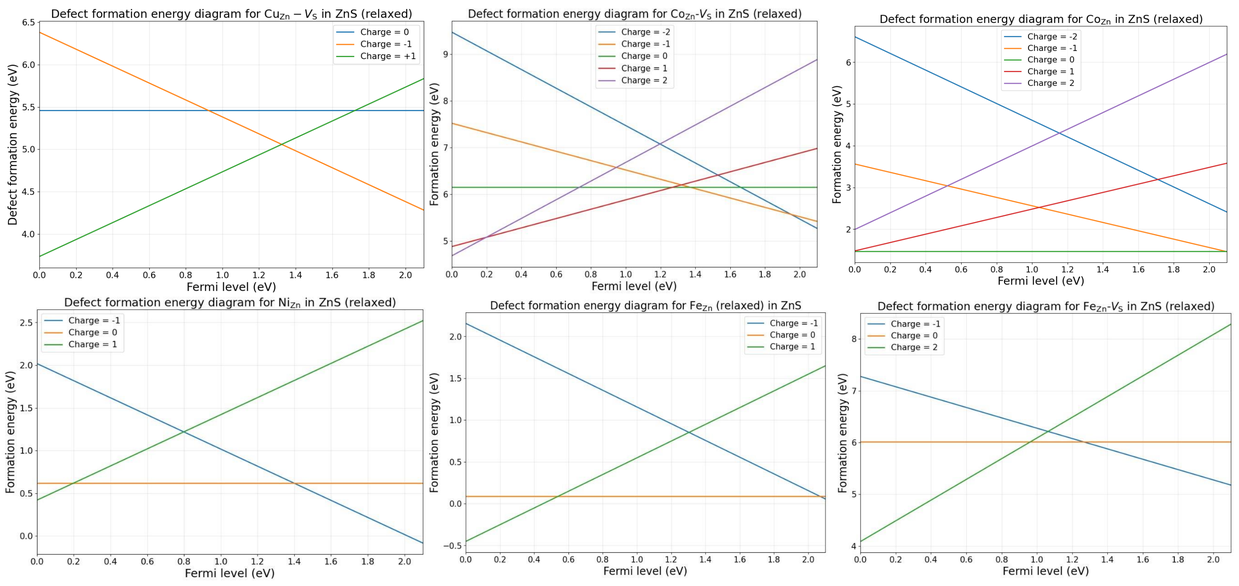

Figure 6: Some selected defect formation energy diagrams

Analyzing these diagrams, we can see that different charge states can exist and by varying the Fermi level (for example, by means of applying gate voltage), we can get our desired charge state. These diagrams are for Zn-rich environment.

But which charge states do we desire? The answer lies in their electronic and magnetic properties.

Electronic and magnetic properties

ZnS has a electronic band gap of 3.54 eV. While previous calculations using hybrid functional can give a very accurate value with less than 0.01 eV accuracy, we found the gap to be 2.15 eV using PBE functional. This underestimation is well expected in PBE level of theory. However, the defect formation energies will remain valid.

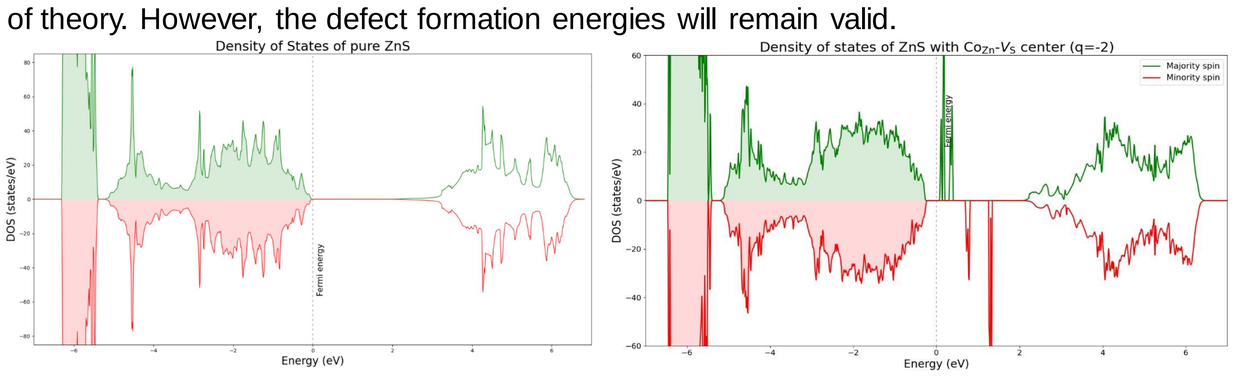

Figure 6: Pure ZnS has symmetric density of states (DOS), i.e., it is non-magnetic. However, an isolated Co-vacancy in ZnS with q=-2 breaks this symmetry (exchange splitting) and thus it become magnetic. Our calculation reveals a magnetic moment of 1 μB in the supercell which is localized around the defect.

Dopants	Charge state	Unpaired electrons	Total relaxed magnetization	Magnetic moment of defects
Co-vacancy	q=-2	1	1.00 μB	1.2200 μB
	q=-1	2	2.00 μB	1.6301 μB
	q=0	3	3.00 μB	2.0921 μB
	q=+1	4	2.00 μB	1.6971 μB
	q=+2	5	3.00 μB	2.1672 μB

Table 1: Magnetic moment calculate using spin-polarized DFT for Co-vacancy defect center in ZnS.

We found a wide range of magnetism can occur and they can be mostly interpreted by the number of unpaired electron in the valence shell. In Table 1, the magnetic moment information for Co-vacancy system is provided as a representative.

Our subsequent analysis revealed that the localized peak in the defect DOS curve is due to the localized 3d-orbital of the TM dopant. The level structure can give us further information such as symmetry breaking of 3d-orbital into t2g and eg states.

Applications

The most obvious applications of these TM doped ZnS material is in **dilute magnetic semiconductors** since many of them can render the non-magnetic semiconductor to a magnetic one. Magnetic semiconductor is essential for **spintronic devices.**

TM defect centers in ZnS, or other materials with zero nuclear spin, can be used as a better alternative to the **nitrogen vacancy (NV) center in diamond**. TM defects shows several **order-of-magnitude higher spin-orbit coupling** than NV center in diamond. Zero nuclear spin is desired since non-zero nuclear spin can give rise to the undesired broadening in the optical spectrum due to the spin-spin interaction between the electrons and the nucleons. .

References

[1] Koenraad, P. M. & Flatte, M. E. *Nature Mater.,* **10**, 91 (2011).

[2] Giannozzi, P. *et al.*, J. Chem. Phys., **152**, 154105 (2020).

[3] Freysoldt, C. *et al.*, *Phys. Status Solidi B*, **248**, 1067-1076 (2011).

[4] Thompson, S. M. *et al.*, *ACS Nano*, **17**, 5963– 5973 (2023).

[5] Sharma, M. *et al., Phys. Rev. B*, **100**, 045151 (2019).

To see the relaxation animations, and a comprehensive list of visualizations, scan the QR code, or visit:
tinyurl.com/TM-in-ZnS

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CONCLUSION & FUTURE WORK

We showed that TM impurities as well as NN TM-vacancy in ZnS can give rise to interesting phenomena such as exchnage splitting. We also showed that there can exist multiple charged states of these defect each providing its own functionalities that has potential applications in near future quantum technologies.

This ongoing project will be extended to:

- Other host materials than **ZnS** that has zero nuclear spin such as **MgO**.
- Other defects such as **TM-TM double dopants** and **TM-next NN vacancies**.
- Include Hubbard corrections (DFT+U), GW calculations.
- Extract optical and thermal properties.
- Utilize the dataset to train machine learning models.