Carrier induced ferromagnetism in II-IV-V$_2$ Mn-doped chalcopyrites

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Problem: Low Mn solubility in III-Vs

- Low solubility; Mn$^{2+}$ poorly suited to group III site in III-Vs
- Mn introduces holes and spins in III-Vs
- Look for III-V compatible materials with higher Mn solubility

5% Mn 3.5x10$^{20}$ holes cm$^{-3}$

Smaller lattice constants, higher $T_c$
II-IV-V$_2$ chalcopyrites (e.g. CdGeP2)

**II-IV-V$_2$ Structure:** III-V Zinc-Blende structure “on average”

**Motivation:** Mn$^{2+}$ readily substitutes on group II site
Why are chalcopyrites ferromagnetic?

**Medvedkin proposed**: Hole-creating defects result in ferromagnetism (Medvedkin JJAP 39 L949 (2000))

**Theory**:

Antiferromagnetism (AFM) dominates in bulk, like II-VIs. Dopable (Zhao & Freeman PRB 65 094415 (2002))

Carriers promote ferromagnetism (FM); anti-site defects are energetically prefered under certain growth conditions (Mahadevan & Zunger PRL 88 047205 (2002))
Experimental situation

High $T_c$s have been observed, but the location, distribution of Mn, and nature of magnetism is uncertain

$\text{Cd}_{1-x}\text{Mn}_x\text{GeP}_2$: $T_c > RT$ $x=$ variable Medvedkin JJAP 39 949 (2000)

$\text{Zn}_{1-x}\text{Mn}_x\text{GeP}_2$: $T_c \sim 300K$ $x=0.2$ Medvedkin JCG 236 609 (2002)

$\text{Zn}_{1-x}\text{Mn}_x\text{GeSiN}_2$: $T_c > 200K$ $x\sim 0.05$ Pearton JAP 92 2047 (2002)

$\text{Zn}_{1-x}\text{Mn}_x\text{SnAs}_2$: $T_c = 329K$ $x=0.01$ Choi JJAP 39 949 (2000)

**Question:** Which chalcopyrites have high $T_c$?
Exchange interaction calculations

Guide to $T_c$: Exchange interaction between Mn pairs calculated via energy difference in FM and AFM configurations.

Three Mn pairs calculated:

1. II-II e.g. Mn on nearest-neighbor Zn sites
2. II-IV e.g. Mn on nearest-neighbor Zn/Ge sites
3. IV-IV e.g. Mn on nearest-neighbor Ge sites

Density functional calculations (PW91 GGA, PAW)
64 atom supercells. d electrons in valence.
Antiferromagnetic interactions between II-II pairs

Antiferromagnetism dominates
Also confirmed for 25% Mn [001] superlattices
Ferromagnetic interaction between defects

Predominant ferromagnetic interaction between “anti-site” defects. Largest in Zn-compounds.
Hole doping promotes ferromagnetic interaction between II-II pairs

Strong AFM preferences overcome by hole doping
J vs lattice constant

No simple relation between lattice constant and ferromagnetism

![Graph showing the relationship between lattice constant and energy difference between ferromagnetic and antiferromagnetic states for Zn and CdGeP₂ compounds.](image-url)
No simple relation between lattice constant and ferromagnetism.
Conclusions

Doping or defects promote ferromagnetism

J (hence $T_c$) higher in Zn compounds than prototypical CdGeP$_2$

No simple relation between $T_c$ (or J) and lattice constant, as per simple models.

Many possibilities for influencing $T_c$ (elements, doping, growth), lattice matching to common substrates

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