

# Tailoring ferromagnetic chalcopyrites

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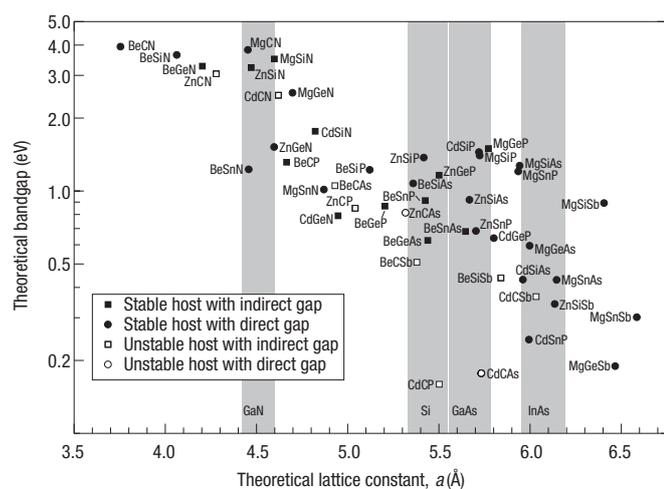
If magnetic semiconductors are ever to find wide application in real spintronic devices, their magnetic and electronic properties will require tailoring in much the same way that bandgaps are engineered in conventional semiconductors. Unfortunately, no systematic understanding yet exists of how, or even whether, properties such as Curie temperatures and bandgaps are related in magnetic semiconductors. Here we explore theoretically these and other relationships within 64 members of a single materials class, the Mn-doped II-IV-V<sub>2</sub> chalcopyrites (where II, IV and V represent elements from groups II, IV and V, respectively); three of these compounds are already known experimentally to be ferromagnetic semiconductors. Our first-principles results reveal a variation of magnetic properties across different materials that cannot be explained by either of the two dominant models of ferromagnetism in semiconductors. On the basis of our results for structural, electronic and magnetic properties, we identify a small number of new stable chalcopyrites with excellent prospects for ferromagnetism.

One of the tantalizing promises of dilute magnetic semiconductors is to combine, in a single material, the advantages of non-volatility and bandgap engineering<sup>1–3</sup>. In normal (non-magnetic) semiconductors, precise tailoring of band structure is possible owing to our detailed understanding—both empirical and theoretical—of the mechanisms underlying band formation. Unlike the situation for normal semiconductors, however, there does not yet exist any comprehensive understanding of how the magnetic properties of magnetic semiconductors are related to their structural and electronic properties.

For example, there is no firm understanding of the relationship between the properties of the host semiconductor and the Curie temperatures attainable by doping with magnetic impurities such as Mn. Experimentally, a number of materials issues—including Mn content, compensation, and phase purity—are not yet sufficiently under control to permit a systematic description across different semiconductors. Theoretically, there is an emerging consensus that although the ferromagnetism originates from the interaction between itinerant electrons (or holes) and localized electrons, there is no single model that can systematically relate the physical and electronic properties of the host semiconductor to its resulting magnetic properties when doped<sup>4</sup>. Models based on the weak- and strong-coupling limits of this interaction (the Zener<sup>5,6</sup> and double-exchange<sup>7,8</sup> models, respectively) do make specific predictions, but it is increasingly evident that real materials are not sufficiently well described by either limit for these predictions to be reliable across different hosts.

Here we address this problem by exploring theoretically these relationships within a single materials class: the II-IV-V<sub>2</sub> chalcopyrites consisting of the 64 possible combinations of II=(Be,Mg,Zn,Cd), IV=(C,Si,Ge,Sn) and V=(N,P,As,Sb). Three of these—CdGeP<sub>2</sub>, ZnGeP<sub>2</sub> and ZnSnAs<sub>2</sub>—have been shown to become ferromagnetic upon Mn doping, with remarkably high Curie temperatures<sup>9–12</sup>. It is an open question whether other chalcopyrites can be made ferromagnetic; nor is it known which properties of the host chalcopyrite are important for ferromagnetism and, in particular, for high Curie temperatures. These are the central issues that we address here.

For each chalcopyrite, we use density-functional theory (DFT) in the generalized-gradient approximation<sup>13–15</sup> to compute several properties of the undoped hosts: equilibrium crystal structure, that is, lattice parameters *a* and *c* and the single internal coordinate; phase stability, as determined by the enthalpy of formation; and electronic bandgap, which may be direct or indirect. A comprehensive survey of the

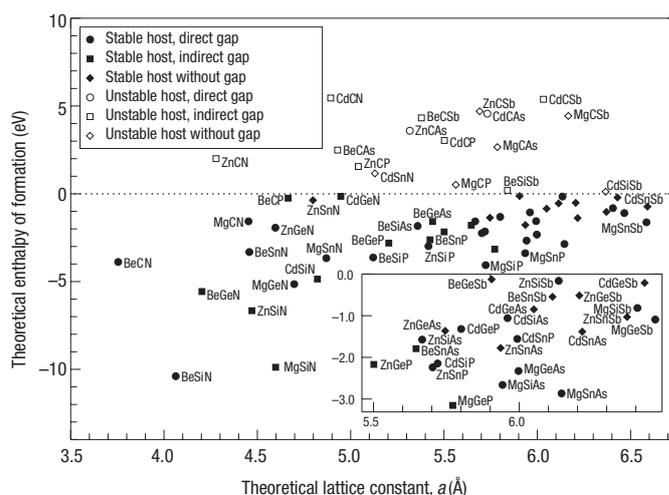


**Figure 1** Theoretical bandgap versus theoretical lattice constant for the II-IV- $V_2$  chalcopyrites considered here. Shaded areas indicate hosts that are expected to be closely ( $\pm 2\%$ ) lattice matched to either GaN, Si, GaAs or InAs. Filled symbols denote stable host compounds (negative enthalpies of formation). Chalcopyrites whose calculated gaps are zero (see text) are not shown.

magnetic properties within such a large class of materials is impractical, so we consider here only a few key quantities that control magnetism. As Mn is isoelectronic with the group-II elements, it is believed that carrier-mediated ferromagnetism in the II-IV- $V_2$  chalcopyrites is favoured when Mn occupies the group-IV site, where it is likely to be electrically active<sup>16</sup>. For this reason, we first explore the competition between substitutional Mn doping on the II and IV sites by computing the Mn impurity formation energy on each site. Second, we address whether occupation of the group-IV sites is indeed likely to lead to a ferromagnetic phase; in particular, for each host we compute the Heisenberg spin coupling for an experimentally reasonable Mn concentration. The magnitude (and sign) of this coupling should serve as a useful ‘roadmap’ for the experimental exploration of new ferromagnetic chalcopyrites.

Of the 64 chalcopyrites considered here, about one-third are known to exist and have been studied experimentally. A few crystallize in both the chalcopyrite and sphalerite structure (for example,  $\text{CdGeP}_2$  and  $\text{ZnSnSb}_2$ ), while two take the wurtzite structure ( $\text{BeSiN}_2$  and  $\text{ZnGeN}_2$ ); for simplicity we treat all 64 in the chalcopyrite structure. For those with measured lattice parameters ( $a$ ,  $c$ ), we can compare our theoretical predictions. As expected from DFT calculations,  $a$  is given very accurately (within  $\sim 1\%$ ), while  $c$  is less so (within  $\sim 15\%$ ). As Fig. 1 shows, nearly half of the 64 chalcopyrites enjoy a close lattice match to an important mainstream semiconductor.

As with all semiconductors, DFT in the generalized-gradient approximation significantly underestimates bandgaps. For chalcopyrites whose measured gaps are in the range 1–2 eV, the DFT values are approximately 1 eV smaller than measured, consistent with previous findings<sup>17</sup>. Hence the theoretical gaps shown in Fig. 1 must be viewed with caution: the true gaps are likely to be about 1 eV larger than predicted. Likewise, hosts that have no gap within DFT may in reality have a gap (which is likely to be 1 eV or smaller). These caveats aside, the trend in Fig. 1 is standard for covalently bonded semiconductors: smaller lattice constants are associated with larger bandgaps. In particular, the nitrides have the smallest lattice constants and largest gaps, while the antimonides have the largest lattice constants and smallest gaps. From the perspective of our survey, the



**Figure 2** Theoretical enthalpy of formation versus theoretical lattice constant for II-IV- $V_2$  chalcopyrites. Negative enthalpy implies a stable host compound. Inset, expanded view identifying data points not labelled in the full plot.

range and distribution of lattice constants and bandgaps is satisfyingly large, guaranteeing our ‘roadmap’ good coverage of this unexplored territory.

Not all of the chalcopyrites considered here are thermodynamically stable, even in the absence of Mn. Figure 2 shows the calculated enthalpies of formation,  $\Delta H_f(\text{II-IV-}V_2) = E(\text{II-IV-}V_2) - E(\text{II}) - E(\text{IV}) - 2E(V)$ , where the latter terms are the total energies of the ground-state elemental phases. Of the 64 chalcopyrites, three-quarters have negative enthalpies, suggesting many potentially stable host materials. (We have not considered phase stability with respect to disproportionation into compound products, and so the terms ‘stable’ and ‘unstable’ should be understood here with this caveat.) The trend in Fig. 2 is similar, and indeed intimately related, to that of Fig. 1: smaller lattice constants are usually associated with higher stability. Hence, as expected, the nitrides tend to be the most stable chalcopyrites and the antimonides the least stable. Note that there are important deviations from this trend: for example, nearly all the carbides are unstable.

The solubility of Mn in a host chalcopyrite is an extremely important issue for two reasons. The first pertains to the well-known tendency, within Mn-doped semiconductor materials, toward phase separation with increasing Mn content<sup>1,2</sup>. This tendency is reflected in the very low equilibrium solubility limit of Mn in, for example, III-V hosts—typically of the order of parts per thousand or less. These limits can be greatly exceeded, by 2–3 orders of magnitude, by relying on kinetic barriers to maintain the metastable phase. It is not feasible to address this issue theoretically for the chalcopyrites. Instead, we propose using the theoretical solubility limit of Mn as a rough proxy for the metastability doping limit. The solubility limit of Mn,  $x_{\text{sol}}$ , is determined by its impurity formation energy,  $\Delta H_f(\text{Mn})$ , simply according to  $x_{\text{sol}} = \exp(-\Delta H_f(\text{Mn})/k_B T)$ , where  $k_B$  is the Boltzmann constant and  $T$  is temperature. In this formulation, a negative formation energy implies that spontaneous incorporation of Mn impurities will be limited only by kinetics<sup>18</sup>.

The second reason concerns ferromagnetism itself. In general, the solubility limits for Mn substituting on the group II and IV sites (denoted respectively as  $\text{Mn}_{\text{II}}$  and  $\text{Mn}_{\text{IV}}$ ) will be different. Mahadevan and Zunger have shown that, in the case of  $\text{CdGeP}_2$ , substitutional





non-magnetic semiconductors. Many issues play a role in this process, including the spin polarization of states at the Fermi level, the band velocities of those states, native defects and other structural inhomogeneities, and spin scattering at the interface<sup>3</sup>. Here we focus on the first of these. For dilute Mn doping (12.5% and 6.25%, and presumably below this as well), all of the 21 stable ferromagnetic chalcopyrites identified above are ‘idealized half-metals’, by which we mean that at zero temperature and for an ordered arrangement of Mn, there are states at the Fermi level only in one spin channel. The effects of both finite temperature and site disorder will generally reduce the spin polarization from this idealized case. At higher Mn concentration (50%), half-metallicity persists for all but two of these 21 hosts (BeSnN<sub>2</sub>, CdSiN<sub>2</sub>). Even when Mn completely occupies the group-IV sublattice, the resulting stoichiometric compounds are half-metallic in all cases except for the nitrides. Thus the prospects for using ferromagnetic chalcopyrites as spin-polarized sources appear quite favourable.

In summary, we have examined theoretically the prospects for ferromagnetism within the class of all possible II-IV-V<sub>2</sub> chalcopyrites having constituents chosen from the first four rows of the periodic table. As expected for semiconductors, we find that the electronic properties of the host materials (bandgap and enthalpy of formation) are closely related to their structural properties (lattice constant, *a*). Contrary to conventional wisdom, we do not find that Mn is generally more soluble when on the group-II site than when on the group-IV site; instead, the relative site solubility depends on both the nature of the host (for example, carbide versus silicide) and the choice of growth condition, whereas the absolute Mn solubility is largely determined by the host lattice constant. Our results for the Heisenberg coupling between Mn dopants show that the Curie temperatures expected in Mn-doped chalcopyrites do not follow the scaling with lattice constant predicted by the Zener model; nor do they show any systematic variation with bandgap, as the double-exchange model would predict. By identifying those chalcopyrites that simultaneously exhibit thermodynamic stability, favourable Mn doping site, and ferromagnetic Mn interactions, we identify two small sets of chalcopyrites that show excellent prospects for stable ferromagnetism under realistic and attainable experimental conditions.

## METHODS

All the numerical results reported here are based on DFT in the generalized-gradient approximation<sup>13</sup>, using ultrasoft pseudopotentials as implemented in VASP<sup>14,15</sup>. For each host chalcopyrite, the plane-wave cut-off was separately determined by the three constituent elements (four if Mn was included). For the undoped hosts, equilibrium lattice parameters and the internal coordinate were optimized using a 4 × 4 × 4 Monkhorst-Pack sampling of the Brillouin zone. Bandgaps were evaluated by identifying band edges based on a 12 × 12 × 12 sampling that included the zone centre and high-symmetry points.

For enthalpies of formation, the total energies of the elemental phases were calculated using the following structures, which are either ground-state phases or energetically very close to those phases: hexagonal close-packed (Be, Mg, Cd, Zn); diamond (C, Si, Ge); white tin (Sn); molecular dimer (N); black phosphorus (P); and α-As (As, Sb).

Mn impurity formation energies were computed using simple cubic (or, for non-ideal *c/a*, tetragonal) supercells of 64 host atoms. To properly represent the dilute impurity limit, all atomic positions were relaxed with fixed ideal supercell lattice parameters, within the constraint that Mn atoms remain on-centre. A single Monkhorst-Pack *k*-point was used. Chemical potentials were defined with respect to their thermodynamic upper limit determined by the elemental phases listed above. For the Mn chemical potential, a non-magnetic face-centred cubic structure was used to approximate the more complicated α-Mn ground-state phase.

Heisenberg spin couplings for 12.5% Mn-doped chalcopyrites were computed using the method described in ref. 23. The lattice parameters and internal coordinate of each supercell were assumed to

depend linearly on the Mn content (Vegard’s law), and were interpolated using lattice parameters and internal coordinate calculated for the fully Mn<sub>IV</sub>-substituted host. Two Mn per 64-atom supercell were then arranged on a uniform lattice and full atomic relaxation was performed. Total energies for two spin configurations were computed—ferromagnetic, and antiferromagnetic with [100] ordering wave vector—whereupon the energy difference gives *J* within the nearest-neighbour Heisenberg model.

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## Competing financial interests

The authors declare that they have no competing financial interests.