

Electronic structure and ferromagnetism of Mn-substituted CuAlS₂, CuGaS₂, CuInS₂, CuGaSe₂, and CuGaTe₂

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The electronic and magnetic properties of Mn doping at either cation sites in the class of I–III–VI₂ chalcopyrites are studied by first-principles calculation. It is found that Mn doping at the III site provides holes and stabilizes the ferromagnetic interaction between neutral Mn defects; the neutral Mn_{Cu}⁰ also stabilizes the ferromagnetism, although it provides electrons to the conduction band, instead of holes. The ferromagnetic stability is generally weaker when the cation or the anion becomes heavier in these chalcopyrites, i.e., along the sequences CuAlS₂→CuGaS₂→CuInS₂ and CuGaS₂→CuGaSe₂→CuGaTe₂. Interestingly, CuAlO₂ in the chalcopyrite structure is predicted to have lower FM energy than CuAlS₂ despite its lighter anion and shorter bonds. In general, III site substitution gives stabler ferromagnetism than Cu substitution. Thus, the preferred growth conditions are Cu-rich and III-poor, which maximize Mn_{III} replacement. In *n*-type samples, when Mn_{III} is negatively charged, the antiferromagnetic coupling is preferred. In *p*-type samples, the ground state of positively charged Mn_{Cu}⁺ is also antiferromagnetism. The main feature of the calculated electronic properties of Mn defect at either Cu or III site is explained using a simple picture of dangling bond hybrid and crystal-field resonance.

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I. INTRODUCTION

Ferromagnetism in Mn-substituted semiconductors is thought to arise from the interaction of a hole with the local moment of the *d* electrons of Mn.^{1,2} In II–VI's such as CdTe or ZnSe, the substitution of Mn²⁺ on the *divalent* cation site introduces no holes, so ferromagnetism (FM) is not observed.³ If the system is additionally doped by extrinsic *p*-type dopant (e.g. As-on-VI site), weak FM is observed.⁴ In III–V's such as GaAs, the substitution of Mn²⁺ on the *trivalent* cation site does automatically introduce a hole, so FM is observed, even without additional *p*-type doping. In the ternary pnictide system A^{II}M^{IV}X₂^V such as CdGeP₂ or the ternary chalcopyrite system A^IM^{III}X₂^{VI} such as CuAg-10.1 6.985 0 0 6.985 247.55 0 285131 .420Tc [(sv9996 T-1.2165 T-1.23 Tmthe)-3IVM

the t_2 levels split into $t_a = d_{xz}; d_{yz}$ and $t_b = d_{xy}$. We find that the electron actually resides in a level that mixes e_b with t_b character, rendering to it some delocalized t_2 -like character. Thus, Mn on Cu site also introduces ferromagnetism. The ferromagnetic stability for Mn on the Cu site is generally lower than for Mn on the III site, with minor exceptions. The order of ferromagnetic stability for Mn-on-Cu (for Mn atoms being fourth neighbors) is reduced in the series $\text{CuGaSe}_2 \rightarrow \text{CuGaS}_2 \rightarrow \text{CuGaTe}_2 \rightarrow \text{CuAlS}_2 \rightarrow \text{CuInS}_2$.

(iii) Ferromagnetism depends on the orientation of the Mn atoms within the chalcopyrite lattice. The highest stabilization exists for Mn atoms oriented along the $\langle 110 \rangle$ direction,

e.g., one Mn at (for Mn atoms) $86.6(10.457T032rsrec5-167dec.96xi\ 0\ Tf\ rsrecws24o26n3271duces)271-i4 /F2ei95.439-8ngat$

pure host chalcopyrites. We calculated the ideal bond length, Al–S (2.27 Å), Ga–S (2.30 Å), Ga–Se (2.43 Å), Ga–Te (2.63 Å), and In–S (2.50 Å), in very good agreement (less than 2% difference) with the measured bond length listed in Ref. 20. Substitution of Mn on the column III site creates a *shorter* bond with S in CuAlS₂, a *longer* bond in CuInS₂, but in CuGaS₂, CuGaSe₂, or CuGaTe₂, the bonds are unchanged by Mn substitution, suggesting a similar tetrahedral radius for Ga and Mn in those compounds.

Figure 1(a) shows the Mn 3*d* projected local density of states (LDOS). Going from deeper to shallower levels, we see the sequence $e_+^{\text{CFR}} \rightarrow t_+^{\text{CFR}} \rightarrow t_-^{\text{DBH}} \rightarrow t_+^{\text{DBH}} \rightarrow e_-^{\text{CFR}} \rightarrow e_+^{\text{CFR}}$. The labeling “dangling bond hybride” (DBH) and “crystal-field resonance” (CFR) will be explained in the following and Figs. 2(a) and 2(b) show, respectively, the spin-up and spin-down wave function square at Γ of these states. We see the following:

(i) The e^{CFR} states are *e*-like, i.e., have lobes that point in-between the nearest neighbors. Those state are highly lo-

calized on Mn, and can be thought of as nonbonding. The lowest state e_+^{CFR} lies deep inside the host valence band and

The overall electron configurations of Mn_{Al}^0 can thus be designated as $[e_+^2 t_+^3]_{\text{CFR}}(t_-^3 t_+^2)_{\text{DBH}}[e_-^0 t_-^0]_{\text{CFR}}$. The total moment is thus $\mu = 2 + 3 - 3 + 2 = 4$. Since the CFR states are Mn-localized and carry five spin-up electrons, whereas the DBH is more extended, and carries a hole, such a ground state is often designated as “ $d^5 +$ hole.” It is interesting to compare the degree of localization of up-spin vs down spin states. Figure 2 shows that t_-^{DBH} is more delocalized than t_+^{DBH} .

Since Mn_{Al}^0 contains a hole at the t_+^{DBH} state, raising the Fermi energy E_F via n -type doping will lead to the capture of an electron from the Fermi sea into this orbital, transforming Mn_{Al}^0 to Mn_{Al}^- . The change in *total* energy for this acceptor reaction is the acceptor transition energy $E(0/-)$, and is calculated as explained in Sec. II and Eq. (2). Figure 3(a) shows the calculated acceptor level for Mn_{III} in a few chalcopyrites. We see that all the acceptor levels of Mn_{III} are ranging between 180 and 350 meV. The acceptor level becomes progressively shallower along the series $\text{CuGaS}_2 \rightarrow \text{CuAlS}_2 \rightarrow \text{CuGaSe}_2 \rightarrow \text{CuGaTe}_2 \rightarrow \text{CuInS}_2$.

The electronic structure of Mn_{Al} obtained through numerical calculations [Figs. 1(a) and 2] can be explained qualita-

Å), and Cu-Te (2.55 Å)

the electron resides in a level that is $(\frac{2}{3}d_{x^2-y^2})$ and $(\frac{1}{3}d_{xy})$. Consequently, the electron at E_F does have some t_2 -like character. Figure 3 shows that the donor level of Mn_{Cu} is very deep (more than 710 meV) for all these chalcopyrites.

The electronic structure of Mn_{Cu} obtained through numerical calculations can be explained qualitatively by a simple model [Fig. 4(b)]. Here, we first note that whereas the dangling bond t_2 orbital of the Al vacancy in CuAlS_2 lies *above* the VBM, that due to a Cu vacancy lies about 1.90 eV *below* the host VBM.²¹ Thus, in Fig 4(b), we placed the $t(p)$ level below the $t(d)$ level of Mn. This order of unperturbed levels produces the level scheme seen in our calculation. The $t_+(p)$ level of the host hybridize with the $t_+(d)$ level of the impurity to give the deep t_+^{DBH} bonding level, and the t_+^{CFR} antibonding level. Note that for Mn_{Al} the order is reverted, since $t_+(d)$ is below $t_+(p)$. Similarly, the $t_-(p)$ level of the host hybridize with the $t_-(d)$ level of the impurity to yield the bonding t_-^{DBH} and antibonding t_-^{CFR} . Like in Mn_{Al} , here too the e_-^{CFR} and e_+^{CFR} levels are mostly unperturbed. Thus, the fact that the *host* dangling bond V_{Cu} is deeper than the host dangling bond V_{Al} leads to the different level ordering for Mn-on-Al [Fig. 4(a)] and Mn-on-Cu [Fig. 4(b)].

IV. FERROMAGNETIC AND ANTIFERROMAGNETIC ENERGIES FOR TWO Mn IN CHALCOPYRITES

So far we have considered a single Mn atom per supercell, for studying the electronic structure. To study the magnetic ground state, we have placed *two* Mn atoms in a 64 atom chalcopyrite supercell, and computed the total energies for the ferromagnetic E_{FM} and antiferromagnetic E_{AFM} spin arrangement. We studied several possible configurations for a Mn pair in these chalcopyrites. The calculated $\Delta E_{\text{FM}} = E_{\text{FM}} - E_{\text{AFM}}$ of different Mn pair configurations for CuAlS_2 , CuGaS_2 , CuInS_2 , CuGaSe_2 , and CuGaTe_2 are listed in Table II. The total energy of the most stable configuration for Mn doped at III site or at the Cu site is taken in Table II as reference energy. The pseudopotential results using ultrasoft potentials are in excellent agreement with the previous all-electron full-potential linearized augmented plane wave (FLAPW) calculations.^{22,8} The latter calculation gives ΔE_{FM} of -77 and -64 meV for Ga440 in CuGaS_2 and CuGaSe_2 , respectively, whereas current pseudopotential calculation gives -81 and -61 meV, respectively. This indicates that the pseudopotential calculation is appropriate to give a reasonable description of the magnetic properties of Mn doped chalcopyrites. Table II shows the following:

(i) *Chemical trends of FM*: The ferromagnetic state is favored ($\Delta E_{\text{FM}} < 0$) for all the *neutral* charge states when Mn substitutes either the Cu or the column III site.²³ In general, III-substitution gives stabler FM than Cu-substitution. Thus, the preferred growth conditions for FM are Cu-rich and III-poor. The sample should not be strongly *n*-type (i.e., avoid excessive S deficiency) because then the acceptor will be $\text{fi34 0cr76.use thb70n ua,2 TD (2TJ -21.69 -1.15 ,25y)]\text{To2247(II).1(t}$

(iii) In the case of Mn_{Cu} we have the DBH electrons deep in the valence band below t_+^{CFR} , whereas in Mn_{Al} they were near the VBM, above t_+^{CFR} . The t^{DBH} states, shown around $E_{\text{VBM}} - 1.8$ eV, are occupied by three spin-up and three spin-down electrons. Inspection of the LDOS in the S next to Mn show that those DBH states have small spin splitting, are mostly anion-like, and are mostly contributed from off- Γ point wave functions (and thus are not seen in the Γ point wave function plot of Fig. 5). The order of levels for Mn_{Cu} , going from deep to shallower levels is thus, $t_+^{\text{DBH}} \rightarrow t_-^{\text{DBH}} \rightarrow e_+^{\text{CFR}} \rightarrow t_+^{\text{CFR}} \rightarrow e_-^{\text{CFR}}$, quite different from the order in Mn_{Al} . The formal configuration is thus $(t_+^3 t_-^3)_{\text{DBH}} [e_+^2 t_+^3 e_-^1]_{\text{CFR}}$ with a moment of $3 - 3 + 2 + 3 - 1 = 4 \mu_B$ and an electron in e_- . However, because the tetragonal crystal-field splitting of the e and t_2 levels is large in Mn_{Cu} , there is a secondary coupling between the split components $e_b(d_{x^2-y^2})$ and $t_b(d_{xy})$, which is allowed by the reduced symmetry due to the Mn defect. Thus,

(ii) *For column III site substitution, considering the Mn*

distance: the Mn–Mn distance for Cu022 is reduced to 2.83 Å from their ideal distance (3.77 Å), and one bonded S atom is pushed away from each Mn by more than 0.40 Å. In contrast, for the AFM phase of Cu022 in CuAlS₂, the Mn–Mn distance is 3.57 Å, not far from its ideal value.

(v) *Charge dependence of FM*: When the charge state of Mn_{Al}^q changes from $q=0$ (holes in the DBH) to $q=-1$ (no holes), the FM disappears, and the ground state is AFM. The same is true for Mn_{Cu}^q when it changes from $q=0$ (electron carriers in conduction band) to $q=+1$ (no electron carriers). This means that when the material is doped excessively *n*-type, the hole will disappear and FM will vanish. In chal-