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Comparison of predicted ferromagnetic tendencies of Mn substituting the Ga site in III–V’s and in I–III–VI$_2$ chalcopyrite semiconductors

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We report density-functional calculations of the ferromagnetic (FM) stabilization energy $\delta = E_{\text{FM}} - E_{\text{AFM}}$ for differently oriented Mn pairs in III–V’s (GaN, GaP, GaAs) and chalcopyrite (CuGaS$_2$, CuGaSe$_2$, CuGaTe$_2$) semiconductors. Ferromagnetism is found to be the universal ground state ($\delta < 0$) in all cases. The order of FM stability in III–V’s is GaN $>$ GaP $>$ GaAs, whereas in chalcopyrites it is CuGaS$_2$ $>$ CuGaSe$_2$ $>$ CuGaTe$_2$. Considering both groups, the order is GaN $\rightarrow$ GaP $\rightarrow$ GaAs $\rightarrow$ CuGaS$_2$ $\rightarrow$ CuGaSe$_2$ $\rightarrow$ GaSb $\approx$ CuGaTe$_2$. The stronger FM stabilization in III–V’s is attributed to the stronger covalent coupling between the Mn 3$d$ spins and the anion $p$ orbitals. In contrast to expectations based on Ruderman–Kittel–(Kasuya)–Yosida, (i) all Mn–Mn pair separations show FM, with no FM to antiferromagnetic oscillations and, (ii) FM is orientationally dependent, with (110) Mn–Mn pairs being the most FM. © 2004 American Institute of Physics.

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Substitution of the trivalent Ga site in III–V semiconductors by divalent Mn creates a hole which mediates ferromagnetic interactions between the $d^3$ spins of the Mn ions. The $n$-type doping (e.g., via Mn interstitials or As antisites) compensates the holes, thereby weakening or even removing the ferromagnetism. The search for Ga-containing host semiconductors which are not $n$ type has largely focused so far on GaN, GaP, and GaAs, leading, however, to rather low fermi-level transition temperatures (in GaAs), or to the unwanted precipitation of competing phase (in GaN). Here we inquire whether another class of Ga-containing semiconductors could be interesting for Mn-induced ferromagnetism, namely I–III–VI$_2$ chalcopyrite. Previous calculations have shown promise. Here we will contrast the calculated ferromagnetic stabilization energy $\delta = E_{\text{FM}} - E_{\text{AFM}}$ for Mn ions in chalcopyrite and in III–V’s by comparing, via density functional theory, the total energies $E$ of supercells in ferromagnetic (FM) and antiferromagnetic (AFM) spin arrangements. We find that for low concentration of Mn (i) both classes of materials show $\delta < 0$, i.e., FM is the ground state. (ii) The most negative stabilization energy occurs when the Mn ions are located along the (110) chain connecting in III–V’s the atoms Ga–As–Ga–As–…, and in I–III–VI$_2$ the atoms Cu–Se–Ga–Se–… (iii) In III–V’s, the strength of ferromagnetism (e.g., for the first-neighbor Mn atoms) decreases along the series GaN $\rightarrow$ GaP $\rightarrow$ GaAs $\rightarrow$ GaSb, whereas in chalcopyrite it decreases along the series CuGaS$_2$ $\rightarrow$ CuGaSe$_2$ $\rightarrow$ CuGaTe$_2$. Finally, (iv) comparing all compounds, the FM stability decreases along GaN $\rightarrow$ GaP $\rightarrow$ GaAs $\rightarrow$ CuGaS$_2$ $\rightarrow$ CuGaSe$_2$ $\rightarrow$ GaSb $\approx$ CuGaTe$_2$. We have previously shown that ferromagnetism in this compounds results from direct Mn 3$d$ coupling with the anion $p$ orbital, not from the Ruderman–Kittel–(Kasuya)–Yosida (RKKY) coupling. The sequence of FM stability above reflects the magnitude of this coupling.

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be explained by a simple model,\textsuperscript{4,16,25} depicted in Fig. 2. We describe the electronic structure of Mn\textsubscript{Ga} as a result of coupling between the d orbitals of the Mn ion with the orbitals formed by a Ga vacancy in CuGaSe\textsubscript{2} or GaAs. The d orbitals of a Mn\textsuperscript{2+} ion, are split into \( e(d) + t_2(d) \) by the point-ion field and into up spin (\( + \)) and down spin (\( - \)) via the exchange interaction. The vacancy orbitals \( t_2(p) \) are actually dangling bonds of the anions surrounding the vacant Ga site. Calculation of \( V_{\text{Ga}} \) in CuGaSe\textsubscript{2} show that at \( \Gamma \), the \( t_2(p) \) vacancy level is at \( E_{\text{VBM}} + 40 \text{ meV} \), i.e., slightly above the valence band minimum (VBM). If this energy of the cation vacancy lies between the energies of up-spin and the down-spin Mn \( 3d \) orbitals (Fig. 2), one obtains a level scheme as shown at the center panel of Fig. 2. The spin-up Mn orbital \( t_+(d) \) hybridizes with the spin-up dangling bond \( t_+(p) \), to form the bonding \( t_+^{\text{CFR}}(dp) \) and the anti-bonding \( t_+^{\text{DBH}}(dp) \) levels. The bonding orbital contains mostly \( t_+(d) \) character, whereas the anti-bonding orbital contains more \( t_+(p) \) character. Analogously, the spin-down Mn orbital \( t_-(d) \) hybridizes with the spin-down host dangling bond \( t_-(p) \) to form the bonding \( t_-^{\text{CFR}}(dp) \) and the anti-bonding \( t_-^{\text{DBH}}(dp) \). The coupling matrix element \( V_{dp} \) increases with covalency and with the reduction in bond length. Note that \( t_-^{\text{DBH}} \) is below \( t_+^{\text{DBH}} \) ("negative DBH exchange splitting") since \( t_+^{\text{DBH}} \) is repelled downward [by \( t_-(d) \)] more than \( t_-^{\text{DBH}} \) is repelled upward [by \( t_+(d) \)]. In contrast, \( t_-^{\text{CRF}} \) is below \( t_+^{\text{CFR}} \) ("positive CFR exchange splitting"). Thus, the direction of spin polarization on the Mn site (decided by CFR) is opposite to the direction of spin polarization on the nearest anion sites (decided by DBH). This is the fingerprint of antiferromagnetic coupling between Mn 3d and the anion \( p \) orbitals. Since the host dangling bonds do not have an \( e \)-like representation in the relevant energy range, the Mn \( e_-(d) \) and \( e_+(d) \) levels are mostly unperturbed, and appear as \( e_-^{\text{CFR}} \) and \( e_+^{\text{CFR}} \). Note that the \( e_+^{\text{CFR}} \) level is now lower than the \( e_-^{\text{CFR}} \) level (opposite to what a point-ion crystal-field theory would suggest) due to bonding with the DBH. Thus, the simple model of Fig. 2 reproduces the essential feature (e.g., level ordering) of the full first-principles calculations, and shows that the hole at the Fermi level resides in a spin-up dangling bond hybrid, \( t_+^{\text{DBH}} \).

Table I shows the ferromagnetic stabilization energy \( \delta \) for pairs of Mn ions in III–V’s and in I–III–VI\textsubscript{2} chalcopyrites. We see that in all cases, substitution of the column III site leads to ferromagnetism (\( \delta < 0 \)). This is because of the occurrence of a \( t_-^{\text{DBH}} \) hole in both systems. The strength of the stabilization energy depends on the crystallographic orientation and interatomic separation of the two Mn atoms. In sharp contrast with the expectation from the RK(K)Y model,\textsuperscript{26} all Mn–Mn separations up to fourth nearest neighbor show only ferromagnetic behavior with no FM/AFM oscillations. The orientation dependence [not expected by RK(K)Y] is such that (110)-oriented Mn–Mn pairs, [e.g., the first neighbor being \( (\pm 1,0,0) \alpha a \) and the fourth

### Table I. Comparison of ferromagnetic stabilization energy \( \delta = E_{\text{FM}} - E_{\text{AFM}} \) (meV/Mn) for two Mn\textsubscript{Ga} pairs in a 64-atom supercell in III–V and I–III–VI\textsubscript{2} semiconductors. One Mn is located at \((0,0,0)\alpha a\), while the other is located as listed in the table (\( \eta \approx 0.2\alpha a \)).

<table>
<thead>
<tr>
<th>System</th>
<th>( \eta = \frac{1}{2} )</th>
<th>((1,0,0)\alpha a )</th>
<th>((1,1,0)\alpha a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN (ZB)</td>
<td>(-\frac{11}{28} )</td>
<td>(-\frac{11}{28} )</td>
<td>(-\frac{11}{28} )</td>
</tr>
<tr>
<td>GaP</td>
<td>(-\frac{139}{28} )</td>
<td>(-\frac{139}{28} )</td>
<td>(-\frac{139}{28} )</td>
</tr>
<tr>
<td>GaAs</td>
<td>(-\frac{124}{28} )</td>
<td>(-\frac{124}{28} )</td>
<td>(-\frac{124}{28} )</td>
</tr>
<tr>
<td>GaSb</td>
<td>(-\frac{56}{28} )</td>
<td>(-\frac{56}{28} )</td>
<td>(-\frac{56}{28} )</td>
</tr>
<tr>
<td>CuGaS\textsubscript{2}</td>
<td>(-\frac{81}{28} )</td>
<td>(-\frac{81}{28} )</td>
<td>(-\frac{81}{28} )</td>
</tr>
<tr>
<td>CuGaSe\textsubscript{2}</td>
<td>(-\frac{71}{28} )</td>
<td>(-\frac{71}{28} )</td>
<td>(-\frac{71}{28} )</td>
</tr>
<tr>
<td>CuGaTe\textsubscript{2}</td>
<td>(-\frac{52}{28} )</td>
<td>(-\frac{52}{28} )</td>
<td>(-\frac{52}{28} )</td>
</tr>
</tbody>
</table>

FIG. 1. Projected \( e \) and \( t \) DOS levels for Mn\textsubscript{Ga} in GaAs and CuGaSe\textsubscript{2} in a sphere radius of 1.20 Å. Spin up DOS is shown in solid lines, whereas spin-down in dashed line. The Fermi level is set to zero.

FIG. 2. The energy level diagram of Mn in GaAs and CuGaSe\textsubscript{2}. The level splitting due to the tetragonal structure in CuGaSe\textsubscript{2} is not shown in this figure.
The order of FM stability (absolute value of $\delta$, e.g., for the first nearest neighbor and fourth nearest neighbor among III–V’s is GaN $> \text{GaP}, \text{GaAs}, \text{GaSb}$, whereas in the chalcopyrites it is CuGaS$_2$, CuGaSe$_2$, CuGaTe$_2$. Comparing all compounds, we find that GaN:Mn, GaP:Mn, and GaAs:Mn have stronger FM stability than all the studied chalcopyrites. Ferromagnetism in GaSb:Mn is comparable to that in CuGaTe$_2$:Mn, but weaker than CuGaS$_2$:Mn and CuGaSe$_2$:Mn. Since the anion (column VI) in chalcopyrites is more ionic than the anion (column V) in III–V’s, the covalent bonding $V_{pd}$ between Mn 3$d$ and anion $p$, and thus the AFM coupling, is weaker in chalcopyrites, resulting in a weaker FM stabilization. This is evidenced by the fact that the magnetic moments in the As sphere in GaAs:Mn ($0.035 \mu_B$ within $R=1.2 \text{Å}$), are much higher than that in the Se sphere ($0.003 \mu_B$ within $R=1.2 \text{Å}$) of CuGaSe$_2$:Mn, which indicates the stronger AFM coupling in III–V’s. The strength of covalent coupling $V_{pd}$ is partially reflected in the band gaps. Individually, within the III–V or the chalcopyrite series, the FM stability scales consistently with the energy gap. However, this is no longer the case considering both III–V’s and chalcopyrites. For example, CuGaS$_2$ has an energy gap of 2.43 eV, being larger than that of GaP (2.26 eV) or GaAs (1.43 eV), yet the FM stability of CuGaS$_2$:Mn is weaker than in GaP:Mn or GaAs:Mn. Indeed, III–V’s have stabler ferromagnetism than chalcopyrites for comparable energy gaps.

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