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 $\delta = E_{FM} - E_{AFM}$ 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 →GaP→GaAs→CuGaS$_2$→CuGaSe$_2$→GaSb≈CuGaTe$_2$. The stronger FM stabilization in III–V's is attributed to the stronger covalent coupling between the Mn 3d

be explained by a simple model,[4,16,25] depicted in Fig. 2. We describe the electronic structure of Mn_{Ga} as a result of coupling between the d orbitals of the Mn ion with the orbitals formed by a Ga vacancy in $CuGaSe_2$ or GaAs. The d

neighbor being $(1,1,0)a-(0,0,0)a$ pair] have the highest FM stability. This crystallographic orientation has the strongest coupling between t^{DBH} on adjacent Mn–As bonds since it is the only direction where *bond chains* occur, i.e., like Ga–As–Ga–As- $\cdots$ in III–V's, or Cu–Se–Ga–Se- $\cdots$ in chalcopyrites.

We next compare our calculated stability energies δ with results in literature. For example, using GGA exchange correlation and relaxed lattice constant we obtained -188 and -63 meV/Mn for Mn pairs of first neighbors and third neighbors in GaN:Mn, respectively, while Sanyal, Bengone, and Mirbt give -156 and -58 meV/Mn, respectively, employing local density approximation (LDA) and experimental lattice constant.[24] As for the GaAs:Mn, Ref. 24 presented $\delta=-130$ meV/Mn for nearest neighbor pair of Mn, which is in good agreement with ours (-124 meV/Mn). However, for the second nearest neighbor Mn pair, our δ value (-30 meV/Mn) is much smaller than that in Ref. 24 (-70 meV/Mn), while Ref. 27 also gives -30 meV/Mn using LDA. In addition, Sanyal and co-workers, concluded that the ferromagnetic interaction in GaN:Mn is short ranged[24] without considering the Mn pair separated by $(1,1,0)a$. In fact, the interaction for Mn pair of fourth neighbor is very strong (c.f. Table I).

The order of FM stability (absolute value of δ), e.g., for the first nearest neighbor and fourth nearest neighbor among III–V's is GaN>GaP>GaAs>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 $3d$ 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 μ_B within $R=1.2$ Å), are much higher than that in the Se sphere (0.003 μ_B within $R=1.2$ 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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[22] Although e and t_2 levels in chalcopyrites split due to the tetragonal structure, we still use the tetrahedral nomenclature for discussing similarity with Mn in III–V. As shown in Fig. 1, the spin-up t_2 level of CuGaSe$_2$:Mn split by 1.7 eV into $t_a=d_{xz}$; d_{yz}, and $t_b=d_{xy}$ at Γ point, whereas the splitting of e and spin-down t_2 levels are not remarkable.
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