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National Renewable Energy Laboratory, Golden, Colorado 80401

While *isovalent* doping of GaAs (e.g., by In) leads to a *repulsion* between the solute atoms, two Cr, Mn, or Fe atoms in GaAs are found to have lower energy than the well-separated pair, and hence *attract* each other. The strong bonding interaction between levels with t_2 symmetry on the transition metal (TM) atoms results in these atoms exhibiting a strong tendency to cluster. Using first-principles calculations, we show that this attraction is maximal for Cr, Mn, and Fe while it is minimal for V. The difference is attributed to the symmetry of the highest occupied levels. While the intention is to find possible choices of spintronic materials that show a reduced tendency to cluster, one finds that the conditions that minimize clustering tendencies also minimize the stabilization of the magnetic state. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1921359]

Dilute magnetic semiconductors formed by alloying magnetic $3d$ ions into covalent semiconductors have been studied since the eighties[1–3] and received renewed interest recently[4] when high concentration samples ($\sim$ a few percent) exhibiting ferromagnetism became available, offering new prospects for spintronic applications. An important issue here with the high concentration samples is the tendency of the magnetic atoms M to associate.[5] To set the background for the problem, let us define the "substitution energy" $E_{sub}(n)$ as the energy required to take n atoms of element M from its bulk metallic reservoir (having the chemical potential μ_M) and use it to replace Ga atoms in GaAs, placing the ejected Ga atom in its own reservoir (of energy μ_{Ga}):

$$E_{sub}(n) = E[Ga_{N-n}M_nAs_N] - E[Ga_NAs_N] - n\mu_M + n\mu_{Ga}, \tag{1}$$

where E is the total energy of the system indicated in parentheses, and N denotes the number of atoms. When $E_{sub}(n) > 0$, substitution costs energy with respect to solid *elemental* sources. For isovalent elements such as $M = In$, it was found[6] that $E_{sub}(1) \sim 0.6$ eV/cell for substitution into bulk GaAs, using the extreme values of μ_{In} and μ_{Ga}. For substituting Mn in GaAs one similarly finds $E_{sub}(1) \sim 0.9$ eV/cell.[7] Thus, substitution costs energy relative to elemental metallic sources. The substitution energy $E_{sub}(n)$ is related to the formation enthalpy:

$$\Delta H(n) = E[Ga_{N-n}M_nAs_N] - nE[MAs]$$
$$- (N-n)E[GaAs],$$

according to the relation $E_{sub}(n) = \Delta H(n) + nK$, where, $K = E[MAs] - E[GaAs] + \mu_{Ga} - \mu_M$. The calculated ΔH (1) for dilute Mn in GaAs is 0.37/cell for one Mn in a 64 atom supercell of GaAs. Thus, alloying Mn or isovalent In in GaAs costs energy also with respect to *binary* zinc-blende (GaAs+MnAs) sources, leading to limited solubility and macroscopic phase separation into GaAs+MnAs at temperatures below the "miscibility gap" value.[8] This could be overcome however through surface-enhanced solubility[8,9] present during epitaxial growth where the energy of incorporating M

at the growing surface (or near-surface layers) compete favorably with phase separation at the surface.[8,9]

Having introduced In or Mn into the lattice, one may next inquire whether two such well-separated impurities attract or repel each other. For this reason we define the "$M–M$ pair interaction energy"[6] as the difference in energy of placing two M atoms at different lattice positions relative to the well-separated limit:

$$\Delta^{(2)} = E[Ga_{N-2}M_2As_N] + E[Ga_NAs_N]$$
$$- 2E[Ga_{N-1}MnAs_N]. \tag{2}$$

For isovalent alloying of In in GaAs the calculated[6] repulsion was found to be $\Delta^{(2)} \sim 30$ meV/cell for nearest-neighbors along the (110) direction. However, for two Mn atoms in GaAs an attraction of the order $\Delta^{(2)} \sim -150$ meV has been found in Ref. 10. Thus, Mn exhibits a thermodynamic tendency for atomic association,[10,11] making the formation of "random alloys" difficult, in contrast with the situation for isovalent semiconductor alloys such as GaInAs.[6,8] The reason for the tendency of Mn atoms to associate inside a III–V semiconductor are however unclear. Schilfgaarde and Mryasov[10] concluded that a strong attraction arises from the fact that the intra-atomic exchange J is large in comparison with the hopping interaction strength t between the d orbitals. Alvarez and Dagotto[12] performed a study of the ferromagnetic transition temperature T_c as a function of the ratio J/t, finding that for intermediate and large values of this ratio, large ferromagnetic clusters existed above T_c although long-ranged order was broken. The basic mechanism responsible for clustering was that when several Mn spins are close to one another, small regions can be magnetized efficiently. These regions remain magnetized even above T_c. Timm and co-workers[13] suggested that since the introduction of Mn in GaAs results in the formation of shallow acceptors, these generate an attractive Coulomb interaction that favors clustering.

In this letter we inquire as to the physical origin of this attraction. We find that all TMs which introduce into GaAs partially occupied t_2 levels leading to ferromagnetism (Cr,Mn), or fully occupied (t_2) levels leading to antiferromagnetism (Fe) inherently tend to cluster ($\Delta^{(n)} < 0$). Elements with e levels (V), however, do not introduce strong

[a)]Electronic mail: alex_zunger@nrel.gov
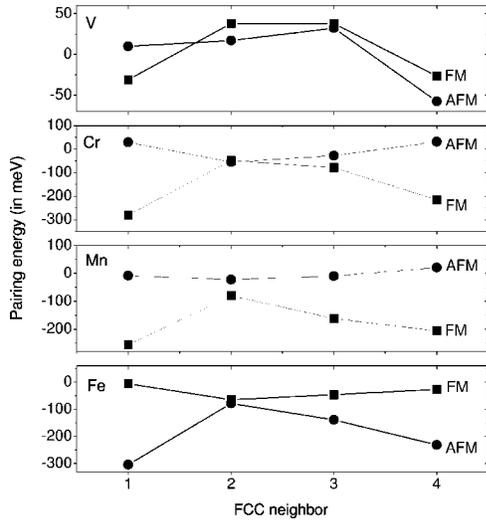
FIG. 1. Pairing energies [Eq. (2)] for two V, Cr, Mn, and Fe atoms in GaAs at 1-4 neighbor Ga-substitutional positions for FM (black squares) and AFM (black circles) arrangement of their spins. This is using computational parameters "set 1."

TABLE I. Clustering energy [Eq. (3)] and the favored magnetic configuration for pairs and for four atom clusters of transition metal atoms. Results are given per 64-atom cell. The "formal" electronic configuration as well as location of acceptor transitions for isolated impurities are also provided. The VASP convergence parameters correspond to "set 1."

TM	$\Delta^{(2)}$ (in meV)	$\Delta^{(4)}$ (in meV)	FM/AFM	Config.	Acceptor
V	−31	−31	FM	e^2	
Cr	−281	−1086	FM	e^2t^1	$E_v+0.74$
Mn	−256	−795	FM	e^2t^2	$E_v+0.11$
Fe	−304	−708	AFM	e^2t^3	

clustering. Clustering does not depend on the type of magnetic interactions,[12] as it is predicted both for FM and AFM cases. It also does not depend on acceptors[13] as it occurs in systems with deep or shallow acceptors. It is strongest along the ⟨110⟩ crystallographic direction.

To evaluate clustering we generalize Eq. (2) to n atoms by calculating

$$\Delta^{(n)} = [E(\mathrm{Ga}_{N-n}\mathrm{M}_n\mathrm{As}_N) - E(\mathrm{Ga}_N\mathrm{As}_N)]$$
$$- n[E(\mathrm{Ga}_{N-1}\mathrm{MAs}_N) - E(\mathrm{Ga}_N\mathrm{As}_N)]. \quad (3)$$

This represents the energy cost for n neutral atoms of type M in a given geometry to form clusters relative to the limit in which the atoms are well-separated. In calculating this we use 64 atom supercells of GaAs constructed with one to four Ga atoms replaced by the transition metal atoms (V/Cr/Mn/Fe). Here the lattice constant of the supercell was fixed at the GGA optimized value of 5.728 Å for pure GaAs.[14] All atomic positions were relaxed by minimizing the total energy as calculated within the plane-wave pseudopotential total-energy momentum space method,[15] using ultrasoft pseudopotentials,[16] and the generalized gradient approximation (GGA)[17] to the exchange correlation as implemented in the VASP code.[18] We used two types of convergence parameters. In the first set (published previously in Ref. 14) we have used the following convergence parameters: A k-point mesh of $4\times4\times4$, an energy cutoff of 227.2 eV for Mn, real space projectors, no Vosko-Wilk-Nusair interpolation scheme and medium precision in the VASP code. This gave $\Delta^{(2)}$ of −256, −80, −162, and −206 meV, respectively, for first, second, third, and fourth neighbors. These results are plotted in Fig. 1. In the second set (highly converged) we have used a k-point mesh of $4\times4\times4$, an energy cutoff of 300 eV, Vosko–Wilk–Nusair interpolation scheme for the gradient term in the exchange functional and accurate precision in VASP. This gave $\Delta^{(2)}$ of −179, −8, −87, and −130 meV for first, second, third, and fourth neighbor Mn. In both cases, the internal coordinates were optimized to minimize the forces, while the lattice constant of the supercell was kept fixed at the GGA optimized lattice constant of 5.728 Å for GaAs. The total energies were

computed for ferromagnetic as well as antiferromagnetic arrangements of the transition metal atoms and the lowest energy configuration was chosen while evaluating the clustering energy. Unless otherwise stated, the calculations have been performed for the neutral charge state of the defect.

Table I shows our calculated $M–M$ pair interaction energies $\Delta^{(2)}$ for nearest neighbor atoms [at (0,0,0) and $(a/2,a/2,0)$, where a is the GaAs lattice constant], as well as $\Delta^{(4)}$ for four M atoms located at the vertices of the tetrahedron formed by four nearest neighbor Ga atoms in a zincblende lattice located at (0,0,0), $(a/2,a/2,0)$, $(a/2,0,a/2)$, and $(0,a/2,a/2)$. We also give in the table the electronic configuration of a single M impurity, showing occupation of e-like and t_2-like levels.[14] This shows that:

(i) Cr and Mn, having *partially occupied* (t_2-like) levels at the Fermi energy as well as Fe with *fully occupied* (t_2-like) levels have large attractive pair energies, $\Delta^{(2)}$, while V having *fully occupied* (e-type) levels show significantly reduced tendency to cluster. Similar tendencies are seen in $\Delta^{(4)}$. This suggests that the tendency to cluster reflects the nature of the occupied orbitals on the two impurity atoms.

(ii) The pair interaction energy $\Delta^{(2)}$ does not correlate with the magnetic state, as evidenced by the fact that Cr and Mn pairs are ferromagnetic while Fe pairs are antiferromagnetic, yet they both show a strong tendency for clustering. This conclusion contrasts with that of Alvarez and Dagotto[12] who associated the clusters with breakdown of long-range ferromagnetism. By associating the formation of clusters with shallow acceptors, Timm[13] also indirectly associated the existence of clusters with the ferromagnetic state, which is not supported by the present results.

(iii) The pair interaction $\Delta^{(2)}$ does not correlate with the existence of shallow acceptor levels, as evidenced by the fact (Table I) that Mn has a shallow acceptor in GaAs, but Cr has a deeper one, yet $\Delta^{(2)}$ is even more negative for Cr in GaAs. Similarly, the acceptor in GaN:Mn is extremely deep E_v +1.8 eV and $\Delta^{(2)}$ is found to be extremely negative.[10] This conclusion contrasts with that of Timm,[13] who suggest that long-ranged attractive Coulomb interactions produced by uncompensated shallow acceptor producing defects bring about the clustering. These shallow acceptor producing defects induce an attractive force between the nuclear core of M and the bound hole. As the Bohr radius for shallow acceptors is large, the wave function of the hole could overlap with that of another similarly bound hole about another M present. Hence the energy lowering is greater in the case when the acceptor level is shallower.

(iv) The pair interation $\Delta^{(2)}$ does not correlate with the J/t ratio. Indeed, the strength of the coupling t of d orbitals with e symmetry on neighboring TM atoms is weaker than

between orbitals with t_2 symmetry because in the zincblende structure, while the t_2 orbitals point to those on the neighboring atom, the e orbitals point at an angle of 45° to the line joining them.[1] As the magnitude of J is not expected to change across the series V–Fe, the ratio J/t is larger for V in GaAs, than it is for Cr–Fe in GaAs. However, Table I shows that the clustering tendencies do not follow the trend of the ratio J/t. The presence of clusters of 2–4 Mn atoms are difficult to detect. Our results suggest that the tendencies for TM clustering in GaAs is intrinsic. It is difficult to suppress clustering during growth (as *interstitial* Mn can be suppressed by annealing of a *thin* film), as the substitutional clusters are not mobile at annealing temperature.

(v) We have also performed calculations to examine clustering tendencies in the charged states of the defects. Recent experiments[19] find a tendency of such defects to anticluster. Considering the case of two Mn_{Ga}^{-1} defects that are stable when the Fermi energy is above the acceptor level at $E_v + 0.1$ eV, we find that $\Delta^{(2)}$ for nearest neighbor pairs is reduced to −70 meV from −256 meV for Mn_{Ga}^0 pairs. The reduction could have two origins. The first being that the repulsion between the charged Mn_{Ga}^- units destabilizes the formation of clusters. The second is that the antiferromagnetic state associated with the pair of Mn_{Ga}^- atoms occupying nearest neighbor Ga positions is weakly stabilized (~ 120 meV/cell).

What are the energetics favoring clustering? Clustering in the FM state is favored by the formation of energy-lowering bonds between the overlapping, partially-occupied t_2 orbitals on adjacent Mn sites. This interaction localizes the hole states in a smaller volume while lowering the total energy. The strong dependence of clustering on the symmetry of the highest occupied orbital suggests that the large values of the intraatomic exchange interaction strength J in comparison with the bonding strengths t are certainly not the origin. The dependence on the symmetry arises because the hopping interaction strength t between two transition metal atoms are different for e and t_2 symmetries. The states with e symmetry on the TM atom have no counterparts on the host lattice to couple to, so the TM(e)–TM(e) coupling is rather weak. In contrast the states with t_2 symmetry on the TM can couple to host states of the same symmetry available at the same energy range, so strong *indirect* TM(t_2)-host(t_2)-TM(t_2) effective coupling exists.

The coupling between states with t_2 symmetry will be largest for two TM atoms occupying lattice positions along the zincblende bonding chain, i.e., joined by the translation vector $(a/2, a/2, 0)$, while it would be the smallest when the translation vector is $(a, 0, 0)$. On the other hand, for states with e symmetry, the hopping matrix elements would be largest when the lattice vector joining the atoms is along the $(a, 0, 0)$ direction, and smallest along the $(a/2, a/2, 0)$ direction. Consequently nearest-neighbor Ga-substitutional positions will not be favored when the highest occupied level has e symmetry. We make quantitative estimates of this aspect of clustering by considering pairs of transition metal atoms with

the first atom at the origin and the second at $(a/2, a/2, 0) \equiv NN1$; or $(a, 0, 0) \equiv NN2$, or $(a/2, a/2, a) \equiv NN3$, or $(a, a, 0) \equiv NN4$ being the NN-th neighbor. The clustering/pairing energy were evaluated and the results are plotted in Fig. 1.

We see indeed that: (i) the results for Cr, Mn, and Fe indicate that the strengths of the hopping matrix elements are largest when the atoms can be joined by the vector along the (1 1 0) direction. (ii) It is not just nearest neighbor lattice positions that are mutually attractive, but even farther neighbor Mn pairs show substantially negative $\Delta^{(2)}$. (iii) Clustering is favored by the magnetic ground state whether FM (Cr, Mn) or AFM (Fe), whereas magnetically *excited* states (AFM-Cr, AFM-Mn, or FM-Fe) have weaker clustering tendencies. This is because a substantial portion of the energy favoring clustering comes from the energy stabilizing the observed magnetic ground state. The clustering energy is not equal to the magnetic stabilization energy as there is an energy cost brought about by the additional perturbation of the host lattice in bringing two or more impurity atoms close to each other compared to when they are far separated.

We conclude that clustering is produced by the tendency of t_2 orbitals on each TM to couple, thus lowering the energy of the system. This tendency is maximal for bond-oriented $M-M$ pairs. Note that the magnetism itself is stabilized by the same bonding interaction. Thus, systems with weak clustering (e.g., V) also have weak magnetism.

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