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# Origin of transition metal clustering tendencies in GaAs based dilute magnetic semiconductors

Priya Mahadevan, J. M. Osorio-Guillén, and Alex Zunger[a)]
*National Renewable Energy Laboratory, Golden, Colorado 80401*

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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 $\mu_M$) and use it to replace Ga atoms in GaAs, placing the ejected Ga atom in its own reservoir (of energy $\mu_{Ga}$):

$$E_{sub}(n) = E(\mathrm{Ga}_{N-n}\mathrm{M}_n\mathrm{As}_N) - E(\mathrm{Ga}_N\mathrm{As}_N) - n\mu_M + n\mu_{Ga}, \quad (1)$$

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 $E_{sub}(1) = 0.6$ eV/cell for substitution into bulk GaAs, using the extreme values of $\mu_{In}$ and $\mu_{Ga}$. For substituting Mn in GaAs one similarly finds $E_{sub}(1) = 0.9$ eV/cell.[7] Thus, substitution costs energy relative to elemental metallic sources. The substitution energy $E_{sub}(n)$ is related to the formation enthalpy:

$$\Delta H(n) = E(\mathrm{Ga}_{N-n}\mathrm{M}_n\mathrm{As}_N) - nE(\mathrm{MAs}) - (N-n)E(\mathrm{GaAs}),$$

according to the relation $E_{sub}(n) = \Delta H(n) + nK$, where, $K = E(\mathrm{MAs}) - E(\mathrm{GaAs}) + \mu_{Ga} - \mu_M$. The calculated $\Delta H(1)$ 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:

$$\Delta^{(2)} = E(\mathrm{Ga}_{N-2}\mathrm{M}_2\mathrm{As}_N) + E(\mathrm{Ga}_N\mathrm{As}_N) - 2E(\mathrm{Ga}_{N-1}\mathrm{MnAs}_N). \quad (2)$$

For isovalent alloying of In in GaAs the calculated[6] repulsion was found to be $\Delta^{(2)} = 30$ meV/cell for nearest-neighbors along the (110) direction. However, for two Mn atoms in GaAs an attraction of the order $\Delta^{(2)} = -150$ 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)s

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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

$$\Delta^{n} = E\,\mathrm{Ga}_{N-n}\mathrm{M}_{n}\mathrm{As}_{N} - E\,\mathrm{Ga}_{N}\mathrm{As}_{N} - n\,E\,\mathrm{Ga}_{N-1}\mathrm{MAs}_{N} - E\,\mathrm{Ga}_{N}\mathrm{As}_{N} \quad . \qquad 3$$

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]

soft pseudopotentials,[16]

proximation GGA[17]

implemented in the V

18W

p

v

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2

N

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 $4 \times 4 \times 4$, 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 GG

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 D 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 $t_2$