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Effects of Mn clustering on ferromagnetism in (Ga,Mn)As

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Abstract

The magnetic interactions of substitutional Mn clusters in (Ga,Mn)As are investigated using density-functional total-energy supercell calculations within the projector augmented-wave method. Magnetic coupling strength values are directly calculated from the parallel and antiparallel spin alignments, and then used to estimate the Curie temperature T_C. The magnetic interactions both inside the clusters and between consequent clusters are investigated. We find that the ferromagnetic coupling inside the clusters is considerably larger than the coupling between two distant clusters, and that therefore the cluster–cluster magnetic coupling strength will determine the T_C of the material. Our cluster–cluster T_C values agree closely with experimental ones.

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1. Introduction

Semiconductors can be turned magnetic by including transition metal atoms in the crystal [1]. $(Ga_{1-x}, Mn_x)As$, where Ga atoms are replaced with Mn ones, is an important prototype material because the magnetism is carrier (hole) mediated. The substitutional Mn provides both local magnetic moments and delocalized holes. Semiconductor engineering can be used to manipulate the magnetism [2], but intrinsic semiconductor point defects hamper the magnetism. As antisite and interstitial Mn defects are known compensators that reduce both the hole concentration and the Curie temperature T_C [3–5]. However, by growth condition optimization and post-growth annealing harmful compensating defects can be removed. Therefore we limit our study on the substitutional Mn atoms, in particular on the clustering of the substitutional Mn atoms and the Mn clustering effects on the magnetic properties of (Ga,Mn)As.

To clarify the cluster distributions, we have calculated the average portions of different size clusters for random Mn substitution at relevant Mn concentrations x, given in Table 1. We find that for the random substitution the portion of dimers and trimers is significant. Total energy calculations have shown that the formation of As centered Mn clusters is energetically favorable [6–8], which indicates that even more Mn atoms are included in clusters. Small clusters have been observed experimentally [9]. This Mn clustering leads to anomalous exchange [6] and splitting of impurity bands [7,10,11], which in turn reduces free carrier (hole) concentration and changes finite temperature magnetic properties by decreasing T_C [7,10–12]. We investigate the cluster formation, magnetic interactions inside the clusters and also cluster–cluster interactions using density-functional total energy supercell calculations.

2. Methods

Total energies are calculated using the projector augmented-wave method together with the generalized gradient approximation for the exchange-correlation as implemented in the VASP code [13]. The Mn clusters are studied in supercells containing 64, 96 or 128 atoms, corresponding to $2 \times 2 \times 2$, $2 \times 2 \times 3$ and $2 \times 2 \times 4$ cubic zinc-blende unit cells, respectively. The calculations are described to more detail in Refs. [7,8,11].

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Table 1
The portions of different size clusters given for random Mn substitution at Mn concentration x

x	Monomer (%)	Dimer (%)	Trimer (%)	Tetramer (%)
0.02	89	9	1	0
0.04	79	15	4	1
0.06	71	18	6	3
0.08	64	19	8	4

T_C can be roughly estimated using the Weiss molecular field theory as [11,14–16]

$$T_C = \frac{2}{3k_B}\frac{\Delta}{N}, \quad (1)$$

where Δ is the difference in total energy of the supercell between parallel and antiparallel spin alignments and N is the number of magnetic particles per supercell. In case of Mn–Mn interactions inside the clusters (intra-cluster) $N(\leqslant 5)$ is the number of Mn atoms per supercell. It is reasonable to treat the intra- and inter-cluster interactions separately, because we find that the intra-cluster interactions are considerably stronger than the inter-cluster ones, in agreement with Ref. [10]. Therefore, in case of inter-cluster interactions $N(=2)$ is the number of clusters per supercell.

3. Results and discussion

First we address the overall stability of the substitutional clusters. These clusters together with some other calculated configurations as well as the total energy values and spin-flip energies Δ are given in Fig. 1. The ferromagnetic high symmetry configurations of substitutional Mn atoms surrounding one and the same neighbor As atom are energetically most favorable [8].

We consider next the magnetic coupling strength inside the clusters. The ground state ferromagnetic configurations always have a magnetic moment of $4n$ Bohr magnetons (μ_B), where n is the number of Mn atoms in the supercell (e.g. a Mn tetramer thus has a magnetic moment of $16\mu_B$). The intra-cluster spin flip energies for small dimer, trimer, and tetramer clusters are rather large, typically around 200 meV or more, as seen in Fig. 1(a)–(g). The estimated critical temperatures T_C calculated using Eq. (1) are around 500 K or higher (Table 2). For the open chain trimers there are always two different anti-parallel configurations, $\uparrow\uparrow\downarrow$ and $\uparrow\downarrow\uparrow$. Of these alignments the $\uparrow\downarrow\uparrow$ one corresponds to a large critical temperature even around 1000 K, due to the coordination of the flipped spin. This also holds for the 60° trimers. For the tetramer there are two anti-parallel alignments, $\uparrow\uparrow\uparrow\downarrow$ and $\uparrow\uparrow\downarrow\downarrow$, of which the latter corresponds to a considerably larger T_C, as it involves flipping of two Mn spins. In the pentamer, where a single Mn is bound to a tetramer, there are 12 inequivalent spin configurations. When the single Mn spin is flipped with respect to the tetramer, the energy difference and the related T_C are lower than for the smaller clusters. This decrease is consistent with the anomalous exchange found in Ref. [6], where the pairwise exchange J_{ij} is shown to decrease as the cluster size increases. The compact high symmetry clusters up to and including the tetramer are stable both in structure (see Ref. [8] for calculated binding energies) and magnetically, while the pentamer binding energy and T_C are smaller.

We follow by interpreting the magnetic coupling in terms of p–d hybridization. As the Mn atoms form a cluster around one and the same As atom there is a strong increase in the p–d hybridization inside the cluster. Therefore both the bonding of these As-centered clusters and the magnetic interaction inside them are strong. In the pentamer, however, as a further Mn atom is added to a tetramer the bonding is more loose because there are two As sites between the tetramer and the additional Mn atom. Thus, in the pentamer there are two p–d hybridization centers between the tetramer and additional Mn atom instead of a single localization center, and here the p–d hybridization is less localized than in the compact As-centered clusters. Because of smaller localization both the binding and the magnetic coupling are weaker in the pentamer than in the small As-centered clusters.

To carry on, we consider the inter-cluster magnetic coupling. Here we include in the supercell two clusters consisting of 1–4 substitutional Mn atoms with the maximum separation. The total energies of the ferromagnetic ground state and the anti-parallel alignment are compared. These inter-cluster spin flip energies Δ give the estimated T_C values of around 250 K (Table 3) that are considerably smaller than the intra-cluster ones (Table 2). Naturally the lower inter-cluster values correspond to the experimentally observed Curie temperature.

We study in more detail the inter-cluster T_C values with the Mn concentration of $x = 6.3\%$. A uniform Mn monomer distribution has a high T_C value of 661 K, while any cluster configuration calculated gives a considerably lower value around 250 K (Table 3). This lowering of T_C is due to the following reasons: (i) the obvious increase of average cluster–cluster separation, and (ii) the strong p–d hybridization *inside* the clusters which leads to band splitting, and the formation of a deep strongly localized band. This band does not interact strongly with the semiconductor host material or distant Mn atoms/clusters. At this concentration of $x = 6.3\%$ even for a random Mn substitution in the Ga fcc sublattice with the coordination of 12, only $0.937^{12} \approx 46\%$ of the Mn atoms will be monomers (corresponding to the portion of 71% of all clusters as given in Table 1). Experiments have shown that the Mn monomer concentration is even less than expected for random substitution [9]. This reduced monomer concentration is in line with the theoretical predictions that clustering is energetically favorable, and at the same time that clustering has a tendency to decrease T_C [6–8]. Consistently, our T_C values that include clustering

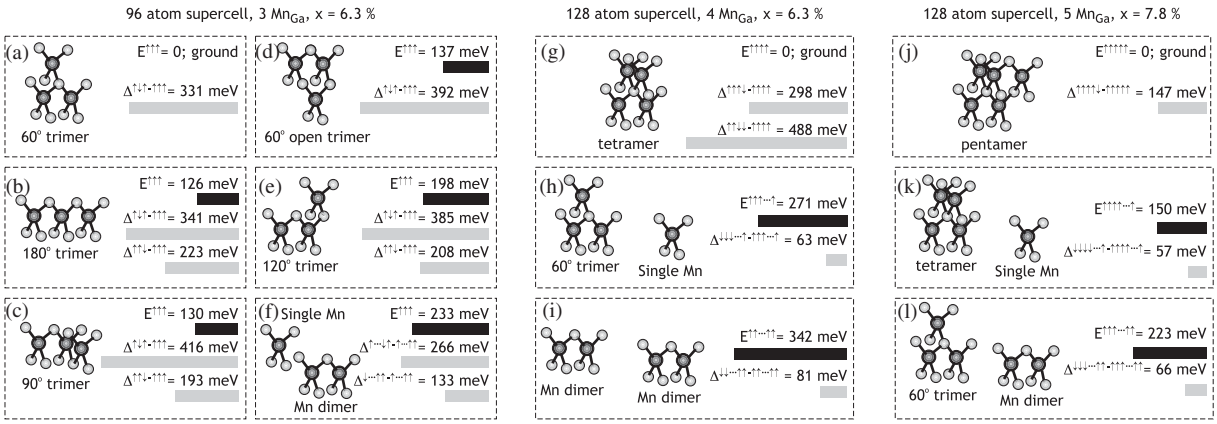

Fig. 1. Calculated cluster configurations and total energies. The Mn and As atoms are denoted with dark and light gray balls, respectively. The black vertical bars give the total energy with respect to the ground state cluster configuration for the given supercell. The gray vertical bars represent the energy difference Δ between ferromagnetic and anti-parallel spin alignments, as indicated with the arrow diagrams.

Table 2
Curie temperature T_C values for the clusters in Fig. 1 (a)–(g) and (j)

Configuration	T_C (K)			
Dimer[a]	816	↑↓		
60° trimer[b]	853	↑↓↑		
60° open trimer[b]	1011	↑↓↑		
90° trimer[b]	1073	↑↓↑	498	↑↑↓
120° trimer[b]	992	↑↓↑	536	↑↑↓
180° trimer[b]	879	↑↓↑	575	↑↑↓
Dimer + single Mn[b]	686	↑↓ · ↑		
Tetramer ($x = 6.3\%$)[c]	576	↑↑↑↓	943	↑↑↓↓
Pentamer ($x = 7.8\%$)[c]	227	↑↑↑↑↓		

[a]64 atom supercell (SC).
[b]96 atom SC.
[c]128 atom SC.

Table 3
Calculated T_C values related to inter-cluster spin flips, as indicated with the arrow diagrams

Configuration	T_C (K)	x (%)
Single Mn + Single Mn[a]	661 ↑ · ↓	6.3
Dimer + Single Mn[b]	514 ↑↑ · ↓	6.3
Single Mn + Single Mn[c]	220 ↑ · ↓	3.1
Dimer + Single Mn[c]	282 ↑↑ · ↓	4.7
60° Trimer + Single Mn[c]	244 ↑↑↑ · ↓	6.3
Dimer + Dimer[c]	313 ↑↑ · ↓↓	6.3
Tetramer + Single Mn[c]	220 ↑↑↑↑ · ↓	7.8
60° Trimer + Dimer[c]	255 ↑↑↑ · ↓↓	7.8

[a]64 atom supercell (SC).
[b]96 atom SC.
[c]128 atom SC.

agree closely with the experimental values of 159–173 K [17,18].

4. Conclusion

The magnetic coupling of substitutional Mn clusters in (Ga,Mn)As is calculated from density-functional calculations. Both intra and inter-cluster coupling strengths are calculated directly from spin flip energies in the supercell configurations investigated. We find a strong intra-cluster ferromagnetic coupling in the compact As-centered clusters up to and including the Mn tetramer. Here the strong intra-cluster interaction is due to increased hybridization between Mn d and center-As p orbitals. Consequently, for the compact As centered clusters the inter-cluster ferromagnetic interaction is weakened because of the p–d localization inside the clusters. However, in the case of pentamers an additional Mn atom is weakly bound to the tetramer, and the intra-cluster ferromagnetism of the pentamer is weaker than that of the compact As centered clusters. The Curie temperatures T_C of 220–313 K calculated from the inter-cluster magnetic coupling agree reasonably with experimental values of 159–173 K, while uniform monomer distributions give much higher T_C values (>600 K).

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