High Curie temperatures in (Ga,Mn)N from Mn clustering

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Abstract

The effect of microscopic Mn cluster distribution on the Curie temperature ($T_C$) of (Ga,Mn)N is studied using density-functional calculations together with the mean field approximation. We find that the calculated $T_C$ depends crucially on the microscopic cluster distribution, which can explain the abnormally large variations in experimental $T_C$ values from a few K to well above room temperature. The partially dimerized Mn$_2$–Mn$_1$ distribution is found to give the highest $T_C > 500$ K, and in general, the presence of the Mn$_2$ dimer has a tendency to enhance $T_C$. The lowest $T_C$ values close to zero are obtained for the Mn$_4$–Mn$_1$ and Mn$_4$–Mn$_3$ distributions.
The discovery of ferromagnetism in (In,Mn)As \cite{1} sprouted a family of III-V based diluted magnetic semiconductors. According to the mean-field Zener theory (Ga,Mn)N should have the highest Curie temperature $T_C \approx 400$ K among these prospective III-V spintronics materials \cite{2}. However, the experimental $T_C$ values for (Ga,Mn)N range from 10 to 940 K \cite{3,4,5,6}. First principles calculations combined with the mean field approximation have given rather high $T_C$ values of about 270-350 K \cite{7,8,9}, while more sophisticated statistical approaches including percolation effects and/or magnetic fluctuations give significantly lower Curie temperatures \cite{10,11,12,13}. The substantial variation of the experimental $T_C$ values is suggested to be due to clustering of Mn atoms \cite{6,14} and the formation of giant magnetic moments at the Mn clusters \cite{15}. Consistently with this, it is found that it is energetically favourable for substitutional Mn atoms to cluster around N atoms \cite{15,16}. Also, Mn clusters are observed directly at high Mn concentrations \cite{17,18,19}. Although in many theoretical calculations Mn clustering is generally found to decrease $T_C$’s in III-V materials \cite{2,10,20,21,22}, we show in this Letter by using first principles calculations and the mean field theory that Mn clustering may also act beneficially by increasing $T_C$. More generally, we find that the stability of the ferromagnetic order depends crucially on the microscopic cluster distribution: small Mn$_2$ clusters may increase $T_C$ whereas Mn$_4$ clusters may reduce $T_C$ down to a few Kelvins (by an Mn$_i$ cluster with $i = 2, 3, 4$ we mean $i$ Mn atoms surrounding the same central neighbouring N atom).

The presence of Mn clusters in (Ga,Mn)N is unavoidable at the Mn concentrations that give high $T_C$ values. This is obvious from Table I where Mn cluster distributions are given when the Ga atoms are substituted randomly by the Mn atoms at various relevant Mn concentrations. Already at $x = 0.02$ (counting single Mn atoms as Mn$_1$ clusters) the Mn$_2$ cluster portion exceeds 10 % and grows fast up to 40 % with increasing $x$. Also the Mn$_3$ portion increases markedly with increasing $x$ whereas the Mn$_4$ cluster portion remains less than 0.5 % even for highest Mn concentration of $x = 0.14$. To investigate the microscopic cluster distribution effects on the Curie temperature we perform spin-polarized total energy density-functional calculations using the projector augmented wave method as implemented in the VASP code \cite{23}. Our supercells contain two Mn$_i$ clusters ($i = 1, 2, 3, 4$) at maximum separation, thus representing a uniform distribution of clusters. The exchange-correlation is approximated as follows. In the first approach we use the generalized gradient approximation (GGA-PW91). In the second approach we use the local spin density approximation plus
$U (L + U)$ with $U$ chosen as 3 eV and used only for Mn. The second approach tries to compensate the self-interaction which is present in the local density approximation and which is known to be substantial in (Ga,Mn)N $^{24}$. The plane-waves cut-off is 425 eV. We use supercells of 48, 72, or 108 atoms ($3 \times 2 \times 2$, $3 \times 3 \times 2$, or $3 \times 3 \times 3$ primitive wurzite unit cells, respectively) and the $4 \times 6 \times 4$, $4 \times 4 \times 4$ or $4 \times 4 \times 3$ $\vec{k}$-meshes for the Brillouin zone sampling, respectively. We use throughout the same lattice parameters $a = 3.217 \, \text{Å}$ and $c : a = 1.631$ obtained from geometry optimization of the wurzite GaN crystal. The atomic positions are fully relaxed in the 48 and 72 atom supercells, and in the 108 atom supercells the atomic positions are fixed to the respective ones of the smaller relaxed supercells. The $T_C$ values are roughly estimated from the mean-field expression $^{8, 25, 26}$

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

where $N$ is the number of Mn clusters in the supercell fixed to 2, and $\Delta$ is the difference in supercell total energy between the anti-parallel and parallel alignments.

First we find, in agreement with Ref. $^{16}$, that the Mn$_i$ cluster ($i = 2, 3, 4$) is energetically the most stable configuration of $i$ Mn atoms. This suggests that the Mn$_2$, Mn$_3$, and Mn$_4$ cluster portions may in reality be even larger than the ones based on random substitution given in Table I. We also find in agreement with Refs $^{15, 16}$ that large stable magnetic moments are formed at the clusters, and therefore intercluster interactions determine the ferromagnetic order.

We now address the clustering effects on the Curie temperature within the GGA and the mean field approximation. In the case of the (nearly) uniform distribution of the single Mn atoms, when the Mn concentration $x$ increases from 0.056 to 0.083 (and the shortest Mn - Mn distance decreases from 7.65 to 6.15 Å) the calculated $T_C$ increases sharply from 39 to 355 K, as seen in the first two rows of Table II. The increased magnetic Mn - Mn coupling is reflected in the density of states (DOS) (given in Fig. (a)) where the width of the midgap Mn $d$ type majority spin DOS increases from 0.5 to 1 eV (see the inset in Fig. (a)). Next we allow partial dimerization at the same concentration of $x = 0.083$. Two thirds of the Mn atoms are allowed to form Mn$_2$ clusters in the plane perpendicular to the $c$ axis. This causes a further increase of $T_C$ up to 514 K given in Table II. In Fig. (b) for $x = 0.083$ the partial dimerization is seen to cause further broadening of the midgap majority spin DOS into a 1.7 eV wide joined structure.
with an increased $p-d$ hybridization. This atomic configuration offers the highest $T_C$ we have found. In more detail, the DOS of a uniform Mn$_2$ distribution for $x = 0.056$ is given in the inset in Fig. 1(b), and comparison with this inset shows that the structure in the DOS is mainly determined from the Mn$_2$ DOS.

To see whether clustering from Mn$_2$ to Mn$_3$ could raise the Curie temperature further, above 514 K, we add a third atom to the Mn$_2$ cluster in the plane perpendicular to the c axis. However, in this case the clustering decreases $T_C$ to 294 K in agreement with earlier experience [7, 10, 20, 21, 22]. The midgap DOS splits into four distinct subbands (with three gaps) still with a clear $p-d$ hybridization. When the distance between the Mn$_3$ cluster and the single Mn atom is increased (the distance between the central N atom of the cluster and the single Mn atom grows from 5.90 to 9.08 Å) $T_C$ decreases further to 128 K (see Table II), as expected.

Finally, we complete the Mn$_3$ cluster to a symmetric Mn$_4$ tetramer cluster and find that $T_C$ diminishes down to 27 K (Table III). The corresponding DOS shown in Fig. 2(a) consists of the narrow peak of about 0.5 eV at the Fermi level and of several other separated peaks. The total width of the original majority spin midgap DOS of 0.5 eV has grown to 2.1 eV which exceeds the calculated gap. The upper part overlaps with the minority spin conduction band edge. The reason for the low $T_C$ may be understood by comparing with the DOS of a uniform Mn$_4$ distribution ($x = 0.093$) shown in Fig. 2(b). It is immediately obvious that the essential $p-d$ hybridization is completely missing from the narrow peak at the Fermi level. The central narrow subband is of purely Mn $d$ type because the N $p$ orbitals are mainly used for the Mn$_4$ intracluster bonding which makes the magnetic coupling of the Mn$_4$ clusters to other Mn clusters (in this case to Mn$_1$) weak. Summarizing, we find that the presence of the Mn$_4$ clusters leads to a low Curie temperature. This explains also why in the Mn$_4$-Mn$_3$ case $T_C$ drops to 4 K although the Mn concentration is as high as $x = 0.13$ (Table III). On the other hand, the presence of the Mn$_2$ clusters has a tendency to increase $T_C$.

The L + U results differ from the GGA ones mainly in shifting the midgap Mn $d$ type DOS towards the valence band maximum by 0.5 eV. In the partial dimerization the Mn $d$ type DOS merges with the top of the valence band causing a growth of $T_C$ up to 618 K (Table III). This behaviour begins to resemble that in (Ga,Mn)As and might be assigned to the $p-d$ type hole mediated ferromagnetic coupling. In the Mn$_3$-Mn$_1$, and especially
in the Mn$_4$-Mn$_1$ case, the $p$ - $d$ type empty peak splits off decreasing $T_C$ to 453 and 39 K, respectively (Table II), similarly as for (Ga,Mn)As in Ref. [22]. All in all it seems that the previous conclusions on clustering effects on the Curie temperature hold also in the case when further corrections to the electronic correlation beyond $L + U$ are included.

The mean field approximation used in this work is known to overestimate Curie temperatures [10, 11, 12, 13], i.e. the dependence of $T_C$ on the total energy difference $\Delta$ may not be linear as in Eq. (1). Nevertheless, high $\Delta$ will imply high $T_C$, and thus the general trends presented for different microscopic cluster configurations should hold. It is interesting to remark that a recent study considering dimerization effects beyond the mean field approximation [14] leads to a similar conclusion as the present work.

In conclusion, we find that the calculated Curie temperature depends crucially on the microscopic cluster distribution. The partially dimerized Mn$_2$-Mn$_1$ distribution is found to give the highest $T_C$. This suggests that the presence of the Mn$_2$ dimer provides a mechanism to enhance $T_C$. On the other hand, low $T_C$ values are obtained for the Mn$_4$-Mn$_1$ and Mn$_4$-Mn$_3$ distributions. Thus we have shown that different cluster distributions may explain the abnormally large variations in experimental Curie temperatures.

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TABLE I Spin-flip energies (Δ) and Curie temperatures (T_C) for two clusters in the supercell. The fourth and fifth columns are GGA calculations, the sixth and seventh columns L+U calculations (denoted by the index “+U”). \( d \) is the minimum distance between the Mn atoms belonging to the different centers.

TABLE II Spin-flip energies (Δ) and Curie temperatures (T_C) for two clusters in the supercell. The fourth and fifth columns are GGA calculations, the sixth and seventh columns L+U calculations (denoted by the index “+U”). \( d \) is the minimum distance between the Mn atoms belonging to the different centers.

FIG 1 Densities of states together with Mn \( d \) and N \( p \) orbital projections for most likely cluster arrangements in (Ga,Mn)N. (a) Uniform Mn distribution for \( x = 0.056 \), in the inset for \( x = 0.083 \). (b) Partially dimerized Mn \(_2\) - Mn \(_1\) for \( x = 0.083 \), in the inset a uniform Mn \(_2\) distribution for \( x = 0.056 \).

FIG 2 Densities of states for (Ga,Mn)N. (a) Mn \(_4\) - Mn \(_1\) for \( x = 0.111 \). (b) Uniform Mn \(_4\) distribution for \( x = 0.093 \). For further information see the caption of Fig. 1.
TABLE I: Mn cluster distribution as a function of $x$ when the Ga atoms are substituted randomly by the Mn atoms. The portions are given in units of $\%$ (counting single Mn atoms as Mn$_1$ clusters).

| $x$  | Mn$_1$ | Mn$_2$ | Mn$_3$ | Mn$_4$ |
|------|--------|--------|--------|--------|
| 0.02 | 89     | 11     | 0      | 0      |
| 0.06 | 71     | 27     | 2      | 0      |
| 0.10 | 58     | 37     | 5      | 0      |
| 0.14 | 49     | 42     | 9      | 0      |
TABLE II: Spin-flip energies ($\Delta$) and Curie temperatures ($T_C$) for two clusters in the supercell. The fourth and fifth columns are GGA calculations, the sixth and seventh columns L+$U$ calculations (denoted by the index “+$U$”). $d$ is the minimum distance between the Mn atoms belonging to the different centers.

| System  | $x$ (%) | $d$ (Å) | $\Delta$ (meV) | $T_C$ (K) | $\Delta^{+U}$ | $T^{+U}_C$ |
|---------|---------|---------|----------------|----------|----------------|------------|
| Mn$_1$ - Mn$_1$ $^a$ | 5.6 | 7.65 | 10 | 39 | 1 | 4 |
| Mn$_1$ - Mn$_1$ $^b$ | 8.3 | 6.15 | 92 | 355 | - | - |
| Mn$_2$ - Mn$_1$ $^a$ | 8.3 | 6.13 | 133 | 514 | 160 | 618 |
| Mn$_3$ - Mn$_1$ $^a$ | 11.1 | 6.13 | 76 | 294 | 117 | 453 |
| Mn$_3$ - Mn$_1$ $^c$ | 7.4 | 9.28 | 33 | 128 | - | - |
| Mn$_4$ - Mn$_1$ $^c$ | 9.3 | 7.66 | 7 | 27 | 10 | 39 |
| Mn$_4$ - Mn$_3$ $^c$ | 13.0 | 6.19 | 1 | 4 | - | - |

$^a$ 72 atoms/supercell (SC), $^b$ 48 atoms/ SC, $^c$ 108 atoms/SC
FIG. 1:
