

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

Teemu Hynninen, Hannes Raebiger,^{a)} and J. von Boehm

COMP/Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, 02015 HUT, Finland

Andrés Ayuela

Donostia International Physics Centre (DIPC), P.O. Box 1072, 20018 Donostia - San Sebastian, Spain

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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 Mn₂-Mn₁ distribution is found to give the highest $T_C > 500$ K, and in general, the presence of the Mn₂ dimer has a tendency to enhance T_C . The lowest T_C values close to zero are obtained for the Mn₄-Mn₁ and Mn₄-Mn₃ distributions. © 2006 American Institute of Physics. [DOI: 10.1063/1.2188036]

The discovery of ferromagnetism in (In,Mn)As¹ 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 (≈ 400 K) among these prospective III-V spintronics materials.² However, the experimental T_C values for (Ga,Mn)N range from 10 to 940 K.³⁻⁶ First principles calculations combined with the mean field approximation have given rather high T_C values of about 270–350 K,⁷⁻⁹ while more sophisticated statistical approaches including percolation effects and/or magnetic fluctuations give significantly lower Curie temperatures.¹⁰⁻¹³ The substantial variation of the experimental T_C values is suggested to be due to clustering of Mn atoms^{6,14} and the formation of giant magnetic moments at the Mn clusters.¹⁵ Consistently with this, it is found that it is energetically favorable for substitutional Mn atoms to cluster around N atoms.^{15,16} Also, Mn clusters are observed directly at high Mn concentrations.¹⁷⁻¹⁹ Although in many theoretical calculations Mn clustering is generally found to decrease T_C 's in III-V materials,^{7,10,20-22} 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 Mn₂ clusters may increase T_C , whereas Mn₄ 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 neighboring 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 Mn₁ clusters) the Mn₂ cluster portion exceeds 10% and grows fast up to 40% with increasing x . Also the Mn₃ portion increases markedly with increasing x , whereas the Mn₄ 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.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 cutoff 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 $4 \times 4 \times 3$ \mathbf{k} meshes for the Brillouin zone sampling, respectively. We use throughout the same lattice parameters $a=3.217$ 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}

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

where N is the number of Mn clusters in the supercell fixed to 2, and Δ is the difference in supercell total energy between the antiparallel and parallel alignments.

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 Mn₁ 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

^{a)} Author to whom correspondence should be addressed; electronic mail: hra@fyslab.hut.fi

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.

System	x (%)	d (Å)	Δ (meV)	T_C (K)	Δ^{+U}	T_C^{+U}
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

^a72 atoms/supercell (SC).

^b48 atoms/SC.

^c108 atoms/SC.

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 Mn₂, Mn₃ and Mn₄ 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 and 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, qualitatively in agreement with Ref. 7. The increased magnetic Mn-Mn coupling is reflected in the density of states (DOS) [given in Fig. 1(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. 1(a)]. Next we allow partial dimerization at the same concentration of $x=0.083$. Two thirds of the Mn atoms are allowed to form Mn₂ 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.1(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 Mn₂ distribution for $x=0.056$ is

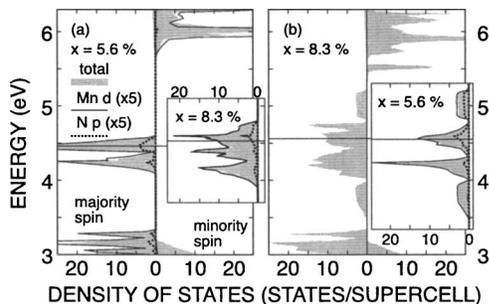


FIG. 1. Densities of states together with Mn d and N p orbital projections for most likely cluster arrangements in (Ga,Mn)N. (a) Uniform Mn distribution for $x=0.056$, in the inset for $x=0.083$. (b) Partially dimerized Mn₂-Mn₁ for $x=0.083$, in the inset a uniform Mn₂ distribution for $x=0.056$.

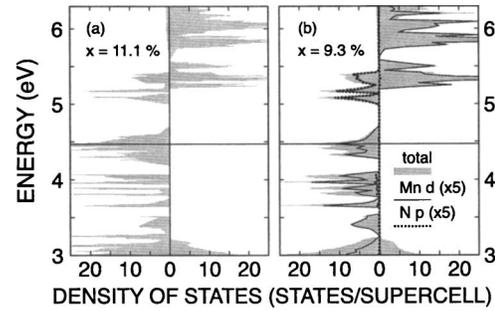


FIG. 2. Densities of states for (Ga,Mn)N. (a) Mn₄-Mn₁ for $x=0.111$. (b) Uniform Mn₄ distribution for $x=0.093$. For further information see the caption of Fig. 1.

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 Mn₂ DOS.

To see whether clustering from Mn₂ to Mn₃ could raise the Curie temperature further, above 514 K, we add a third atom to the Mn₂ 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.^{7,10,20-22} The midgap DOS splits into four distinct subbands (with three gaps) still with a clear p - d hybridization. When the distance between the Mn₃ 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 Mn₃ cluster to a symmetric Mn₄ tetramer cluster and find that T_C diminishes down to 27 K (Table II). 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 Mn₄ 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 Mn₄ intracenter bonding which makes the magnetic coupling of the Mn₄ clusters to other Mn clusters (in this case to Mn₁) weak. Summarizing, we find that the presence of the Mn₄ clusters leads to a low Curie temperature. This explains also why in the Mn₄-Mn₃ case T_C drops to 4 K, although the Mn concentration is as high as $x=0.13$ (Table II). On the other hand, the presence of the Mn₂ 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 II). This behavior begins to resemble that in (Ga,Mn)As and might be assigned to the p - d -type hole mediated ferromagnetic coupling. In the Mn₃-Mn₁, and especially in the Mn₄-Mn₁ 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,^{10–13} i.e., the dependence of T_C on the total energy difference Δ may not be linear as in Eq. (1). Nevertheless, high Δ 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 approximation¹⁴ 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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¹H. Munekata, H. Ohno, S. von Molnar, A. Segmüller, L. L. Chang, and L. Esaki, *Phys. Rev. Lett.* **63**, 1849 (1989).

²T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, *Science* **287**, 1019 (2000).

³M. E. Overberg, C. R. Abernathy, S. J. Pearton, N. A. Theodoropoulou, K. T. McCarthy, and A. F. Hebard, *Appl. Phys. Lett.* **79**, 1312 (2001).

⁴T. Sasaki, S. Sonoda, Y. Yamamoto, K. Suga, S. Shimizu, K. Kindo, and H. Hori, *J. Appl. Phys.* **91**, 3473 (2002).

⁵G. T. Thaler, M. E. Overberg, B. Gila, F. Frazier, C. R. Abernathy, S. J.

Pearton, J. S. Lee, S. Y. Lee, Y. D. Park, Z. G. Khim, J. Kim, and F. Ren, *Appl. Phys. Lett.* **80**, 3964 (2002).

⁶S. Dhar, O. Brandt, A. Trampert, L. Däweritz, K. J. Friedland, K. H. Ploog, J. Keller, B. Beschoten, and G. Güntherodt, *Appl. Phys. Lett.* **82**, 2077 (2003).

⁷L. M. Sandratskii, P. Bruno, and S. Mirbt, *Phys. Rev. B* **71**, 045210 (2005).

⁸K. Sato, P. H. Dederichs, and H. Katayama-Yoshida, *Europhys. Lett.* **61**, 403 (2003).

⁹L. M. Sandratskii, P. Bruno, and J. Kudrnovský, *Phys. Rev. B* **69**, 195203 (2004).

¹⁰J. L. Xu, M. van Schilfgaarde, and G. D. Samolyuk, *Phys. Rev. Lett.* **94**, 097201 (2005).

¹¹L. Bergkvist, O. Eriksson, J. Kudrnovský, P. Korzhavyi, and I. Turek, *Phys. Rev. Lett.* **93**, 137202 (2004).

¹²K. Sato, W. Schweika, P. H. Dederichs, and H. Katayama-Yoshida, *Phys. Rev. B* **70**, 201202(R) (2004).

¹³G. Bouzerar, T. Ziman, and J. Kudrnovský, *Europhys. Lett.* **69**, 812 (2005).

¹⁴G. Bouzerar, T. Ziman, and J. Kudrnovský, *Appl. Phys. Lett.* **85**, 4941 (2004).

¹⁵B. K. Rao and P. Jena, *Phys. Rev. Lett.* **89**, 185504 (2002).

¹⁶M. van Schilfgaarde and O. N. Mryasov, *Phys. Rev. B* **63**, 233205 (2001).

¹⁷R. Giraud, S. Kuroda, S. Marcet, E. Bellet-Amalric, X. Biquard, B. Barbara, D. Fruchart, D. Ferrand, J. Gibert, and H. Mariette, *Europhys. Lett.* **65**, 553 (2004).

¹⁸Y. Shon, Y. H. Kwon, Sh. U. Yuldashev, Y. S. Park, D. J. Fu, D. Y. Kim, H. S. Kim, and T. W. Kang, *J. Appl. Phys.* **93**, 1546 (2003).

¹⁹G. Martínez-Criado, A. Somogyi, M. Hermann, M. Eickhoff, and M. Stutzmann, *Jpn. J. Appl. Phys., Part 2* **43**, L695 (2004).

²⁰L. M. Sandratskii and P. Bruno, *J. Phys.: Condens. Matter* **16**, L523 (2004).

²¹H. Raebiger, A. Ayuela, and R. M. Nieminen, *J. Phys.: Condens. Matter* **16**, L457 (2004).

²²H. Raebiger, A. Ayuela, and J. von Boehm, *Phys. Rev. B* **72**, 014465 (2005).

²³G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996); G. Kresse and J. Furthmüller, *VASP the Guide* (Vienna University of Technology, Vienna, 1999) [<http://tph.tuwien.ac.at/~vasp/guide/vasp.html>]

²⁴A. Filippetti, N. A. Spaldin, and S. Sanvito, *Chem. Phys. Lett.* **309**, 59 (2004).

²⁵Ph. Kurz, G. Bihlmayer, and S. Blügel, *J. Phys.: Condens. Matter* **14**, 6353 (2002).

²⁶Ph. Kurz, J. Kudrnovský, G. Bihlmayer, and S. Blügel, *J. Phys.: Condens. Matter* **15**, 2771 (2003).