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## High Curie Temperature and Nano-Scale Spinodal Decomposition Phase in Dilute Magnetic Semiconductors

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We show that spinodal decomposition phase in dilute magnetic semiconductors (DMS) offers the possibility to have high Curie temperatures ( $T_C$ ) even if the magnetic exchange interaction is short ranged. The spinodal decomposition is simulated by applying the Monte Carlo method to the Ising model with realistic (*ab initio*) chemical pair interactions between magnetic impurities in DMS. Curie temperatures are estimated by the random phase approximation with taking disorder into account. It is found that the spinodal decomposition phase inherently occurs in DMS due to strong attractive interactions between impurities. This phase decomposition supports magnetic network over the dimension of the crystal resulting in a high- $T_C$  phase. [DOI: 10.1143/JJAP.44.L948]

KEYWORDS: dilute magnetic semiconductor, spinodal decomposition phase, concentration fluctuation, chemical pair interaction, percolation, Curie temperature

Following the pioneering theoretical work by Dietl *et al.*<sup>1)</sup> on ferromagnetism in dilute magnetic semiconductors (DMS), many theoretical efforts attempted to predict new DMS with high Curie temperatures ( $T_C$ ). In particular, wide band gap DMS such as (Ga,Mn)N, (Ga,Cr)N and (Zn,Co)O are proposed as good candidates for high- $T_C$  material.<sup>1–3)</sup> However, recent theoretical results pointed out that these predictions were inaccurate because of the inadequate treatment of disorder by the mean field approximation, and that the properly calculated  $T_C$  of wide band gap DMS are at low concentrations far below room-temperature due to the missing of magnetic percolation.<sup>4–6)</sup> In particular, this percolation effect is significant in wide band gap DMS, where magnetic exchange interactions are short ranged. This new theory predicts the  $T_C$  of (Ga,Mn)As in reasonable agreement with experiments and explains the low  $T_C$  phase in (Ga,Mn)N observed in experiments. However, this theory does not predict high- $T_C$  in wide gap DMS which are often observed in several experiments.<sup>7–14)</sup> The purpose of this Letter is to propose an idea which might solve this disagreement between experimental observations and theoretical predictions.

The idea is the following. In general, DMS systems exhibit a solubility gap and show phase separation in thermal equilibrium. As is known in alloy physics, in the quenching process for such systems spinodal decomposition occurs, i.e., local density fluctuations are amplified and finally lead to random patterns of high concentration regions which connect each other. We propose that in the decomposed phase magnetic network can be achieved and that high- $T_C$  values can occur in such phases. *Ab initio* calculations for such inhomogeneous disordered systems are difficult and no methods have been established yet. In this work, we take very simplified way. Our calculation procedure consists of four steps, i.e., (i) Calculation of the electronic structure for homogeneous DMS system with a random distribution of impurities, (ii) Calculation of the magnetic exchange and chemical pair interactions of two impurities in such an effective homogeneous effective medium, (iii) simulation of the spinodal decomposition using Monte Carlo method and

(iv) estimation of the Curie temperature of the spinodal phase. In the following, we present calculated results for (Ga,Mn)As and (Ga,Mn)N as typical examples of DMS.

The first part of our calculation procedure is the same as in our previous work.<sup>2,3)</sup> The electronic structures of (Ga, Mn)As and (Ga,Mn)N are calculated within the local density approximation (LDA) by using the Korringa–Kohn–Rostoker method. Mn atoms substitute Ga atoms randomly in the crystals. We assume a ferromagnetic arrangement of the local moments and a homogeneous distribution (no short-range and long-range order) of Mn in the host matrices. This kind of random substitutional disorder is well described by the coherent potential approximation (CPA). Our calculations use the MACHIKANEYAMA package developed by Akai.<sup>15,16)</sup> We refer our previous series of calculations regarding to calculational details.<sup>2,3)</sup> For the sake of simplicity, we assume zinc-blende structure (cubic) for both DMS.

The next step of our calculations is to calculate the effective magnetic exchange interactions and chemical pair interactions between Mn. We employ prescriptions formulated by Ducastelle and Gautier<sup>17)</sup> and Liechtenstein *et al.*<sup>18)</sup> for chemical and magnetic interactions, respectively. Both theories assume a CPA effective medium as a reference and calculate the effective interactions in the medium. For example, effective magnetic exchange interactions between site  $i$  and  $j$  ( $J_{ij}$ ) are calculated identifying the total energy change due to the rotation of two magnetic moments at  $i$  and  $j$  in the effective medium with the corresponding energy change of the classical Heisenberg model. Similarly, effective chemical pair interactions  $V_{ij}$  between Mn atoms at sites  $i$  and  $j$  are energy difference between Mn–Mn and Ga–Ga pairs and two Mn–Ga pairs in the effective medium, i.e.,  $V_{ij} = V_{ij}^{\text{Mn–Mn}} + V_{ij}^{\text{Ga–Ga}} - 2V_{ij}^{\text{Mn–Ga}}$  where  $V_{ij}^{\text{AB}}$  is the potential energy when sites  $i$  and  $j$  are occupied by A and B atoms, respectively. As is well known in this approach, positive (negative)  $V_{ij}$  means effective repulsive (attractive) interaction between Mn.

Figure 1 shows the calculated chemical interactions between Mn atoms in (Ga,Mn)As and (Ga,Mn)N. The electronic origin of the differences in the distance dependence in the pair interactions in two DMS will be discussed

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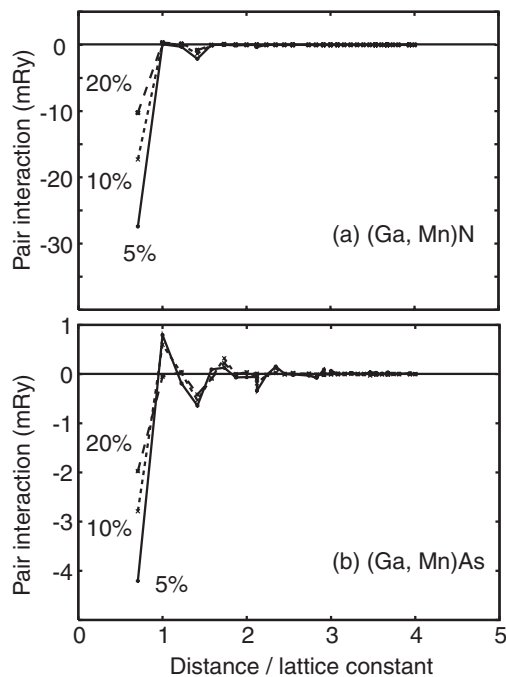


Fig. 1. Chemical pair interactions between Mn in (a) (Ga,Mn)N and (b) (Ga,Mn)As as a function of distance. Negative interactions mean effective attractive interactions between Mn.

elsewhere. In this work, we focus only on one common feature of chemical pair interactions in these DMS. As shown in Fig. 1, between the nearest neighbors strong attractive interaction occurs and most of the interactions are attractive in both compounds. The attractive interactions have been found also in the super-cell calculations.<sup>19)</sup> This means a strong tendency toward phase separation and is in line with the fact that DMS fabrication always requires sophisticated non-equilibrium crystal growth techniques and precise control of growth condition. Normally, the system in which the same kind of constituents experience attractive interactions undergo the phase separation known as spinodal decomposition during the quenching process below the critical spinodal temperature. Very fast passage from high temperature to low temperature does not allow the segregated phases to form simple way but results in complicated random pattern of high concentration regions which connect one another. Taking into account that the reason of the strong suppression of Curie temperatures in wide gap DMS with homogeneous impurity distributions is the missing of magnetic percolation path at low concentrations, we suggest that the spinodal decomposition might help to achieve magnetic percolation.

In order to see effects of spinodal decomposition on Curie temperatures of DMS, we try to include inhomogeneous impurity distribution in Curie temperature calculations. In the most of previous theoretical treatments, this kind of inhomogeneity has not been taken into account. First, we generate the spinodal decomposed phase by using Monte Carlo method. The DMS systems are now described by the Ising model, i.e., the Hamiltonian is written as  $H = -\frac{1}{2} \sum_{i \neq j} V_{ij} \sigma_i \sigma_j$ , where  $V_{ij}$  is effective pair interaction between impurities at site  $i$  and  $j$ ,  $\sigma_i$  is occupation number of impurity at site  $i$ . We use  $V_{ij}$  values calculated from first-

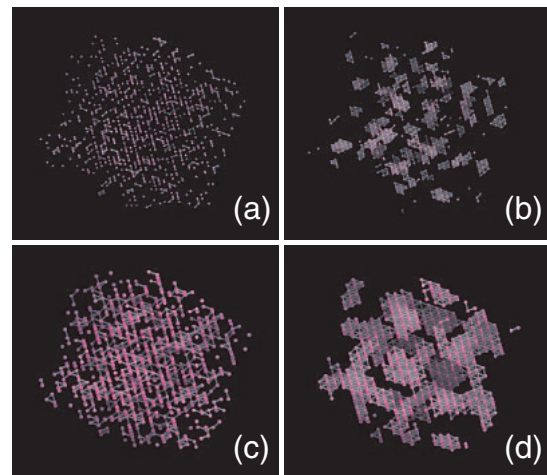


Fig. 2. Mn configuration in (Ga,Mn)N. (a) and (c) refer to completely random configurations (initial state corresponding to  $T = \infty$ ), (b) and (d) after 100 Monte Carlo steps (spinodal decomposition phase). Mn concentrations are 5% for (a) and (b), and 20% for (c) and (d). Nearest neighbor Mn-Mn pairs are connected by bars.

principles by using the prescription explained previously. Simulations are performed at scaled temperature of  $k_B T / V_{01} = 0.5$  for both cases. For example, real temperature  $T$  corresponds to 2164 and 332 K for (Ga,Mn)N and (Ga,Mn)As with 5% Mn, respectively. Starting from complete random distribution (configuration at  $T = \infty$ ), first we choose one impurity site, then try to move the impurity to one of the nearest neighbor sites which is chosen randomly. By obeying the Monte Carlo criterion, energy difference between original position and trial position decides if this trial is accepted or rejected. Visiting every impurity site counts one Monte Carlo step.

After starting Monte Carlo loop, the system relaxes towards the thermal equilibrium. We are not interested in the full relaxed thermal equilibrium Mn configuration but in a quenched and frozen in phase as a non-equilibrium transient state. Therefore, we interrupt the Monte Carlo sequence after 10, 20, 50 and 100 steps, and calculate Curie temperatures at these stages. Before discussing  $T_C$ , in Fig. 2, we show snapshots of simulated spinodal decomposition phases appear in our simulations. The figure shows Mn sites in (Ga,Mn)N after 0 (completely random) and 100 (spinodal decomposed phase) Monte Carlo steps for Mn concentrations of 5 and 20%. Each figure contains 1000 of Mn atoms ( $17 \times 17 \times 17$  and  $11 \times 11 \times 11$  conventional fcc cells, respectively). In the initial stages, Mn atoms are distributed randomly and the systems show overall homogeneity. The nearest neighbor percolation threshold is 20% for fcc structure, therefore both systems do not have any percolation path. At the later stages after 100 Monte Carlo steps, apparently we can find more nearest neighbor bonds however for 5% [Fig. 2(b)] it is still impossible to find a percolating path through the system. On the other hand, for 20% [Fig. 2(d)] we find characteristic patterns of a spinodal decomposition phase, i.e., high concentration regions (in this case the region is almost MnAs in zinc blende structure) with complicated random connecting pattern.<sup>20)</sup> We call this spinodal phase ‘three dimensional Dairiseki-phase’, where ‘Dairiseki’ means marble in Japanese. As shown in the figure, as a result of

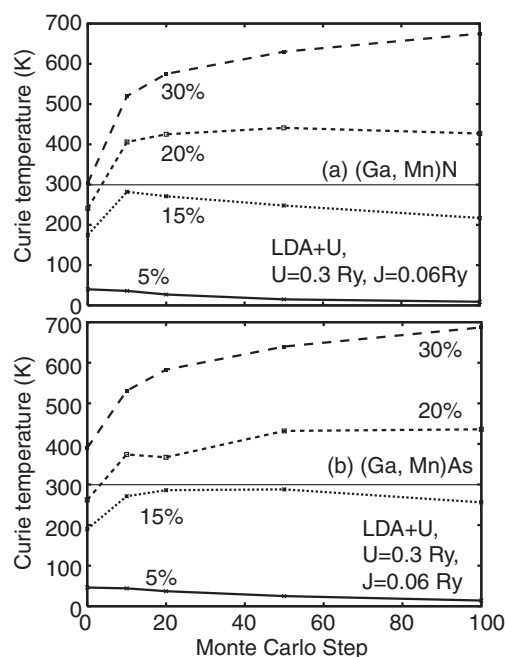


Fig. 3. Curie temperatures of (a) (Ga,Mn)N and (b) (Ga,Mn)As as a function of the number of Monte Carlo steps. Curie temperatures are calculated with corrected  $J_{ij}$  constants by LDA+U. Parameters used in the LDA+U corrections are indicated in the figures. We take 10 configurations for averaging.

spinodal decomposition, the percolating path is established and high- $T_C$  can be expected.

Finally, we discuss the Curie temperatures of the thus generated spinodal decomposition phases. The best way to calculate  $T_C$  of the DMS is using the Monte Carlo method.<sup>4–6)</sup> This method combined with the finite size scaling method in principles gives the exact value of  $T_C$ . However, the computational effort is huge and moreover we are not sure if the finite size scaling does work for inhomogeneous random systems like spinodal decomposition phases. In this work, we take another method proposed by Bouzerar *et al.*<sup>21)</sup> and Hilbert *et al.*<sup>22)</sup> They calculate  $T_C$  of DMS by the random phase approximation with taking the random Mn configurations explicitly into account. Thus, they succeeded to reproduce strong suppression of  $T_C$  for low concentrations due to the percolation effects. In Fig. 3, RPA-values of  $T_C$  are plotted as a function of the Monte Carlo steps for (Ga,Mn)N and (Ga,Mn)As with various Mn concentrations. The exchange interactions up to the 15-th neighbors are taken into account in the calculations. We use corrected effective exchange interactions by LDA+U (instead of LDA) in order to avoid an overestimation of anti-ferromagnetic superexchange interactions at higher concentrations. As progressing in the decomposition,  $T_C$  goes up. This behaviour can be understood as a consequence of the spinodal decomposition [Fig. 2(d)] which supports magnetic percolation. In this way, the spinodal decomposition phase could explain high- $T_C$  phase in wide gap DMS, for example (Ga,Mn)N and (Ga,Cr)N. However, this effect is remarkable only above the nearest neighbor percolation threshold and we can not see  $T_C$  enhancement for low concentrations. This is reasonable because attractive interactions between Mn only make isolated small clusters

[Fig. 2(b)] which cannot percolate. Therefore, in order for the spinodal decomposition to help ferromagnetism in wide gap DMS, first of all, high concentration regions ( $\geq 20\%$  in fcc lattice) should exist. In Fig. 3, for each concentration it seems that  $T_C$  values of (Ga,Mn)N and (Ga,Mn)As converge to the same value. However, this is accidental and in general  $T_C$  values depend on the host material.

In conclusion, we show that in (Ga,Mn)As and (Ga,Mn)N the effective chemical interactions between Mn are attractive and lead to the spinodal decomposition. It is shown that  $T_C$  goes up in the simulated decomposition process for concentrations approximately higher than the nearest neighbor percolation threshold, because the decomposition produces additional magnetic networks in the system. DMS systems are in general unstable against phase separation, therefore high- $T_C$  spinodal decomposition phases as proposed in this Letter should be generally found in DMS systems. Strong concentration fluctuations are recently observed in experiments.<sup>23)</sup> We strongly encourage experimentalists to seek nano-scale spinodal decomposition phase in DMS. This suggestion also opens a way to control the Curie temperatures of DMS by changing the annealing condition.

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- 1) T. Dietl, H. Ohno, F. Matsukura, J. Cibert and D. Ferrand: *Science* **287** (2000) 1019.
- 2) K. Sato and H. Katayama-Yoshida: *Semicond. Sci. Technol.* **17** (2002) 367.
- 3) K. Sato, P. H. Dederichs and H. Katayama-Yoshida: *Europhys. Lett.* **61** (2003) 403.
- 4) L. Bergqvist, O. Eriksson, J. Kudrnovský, V. Drchal, P. Korzhavyi and I. Turek: *Phys. Rev. Lett.* **93** (2004) 137202.
- 5) K. Sato, W. Schweika, P. H. Dederichs and H. Katayama-Yoshida: *Phys. Rev. B* **70** (2004) 201202(R).
- 6) T. Fukushima, K. Sato, H. Katayama-Yoshida and P. H. Dederichs: *Jpn. J. Appl. Phys.* **43** (2004) L1416.
- 7) S. Sonoda, S. Shimizu, T. Sasaki, Y. Yamamoto and H. Hori: *J. Cryst. Growth* **237–239** (2002) 1358.
- 8) N. Theodoropoulou, A. F. Hebard, M. E. Overberg, C. R. Abernathy, S. J. Pearton, S. N. G. Chu and R. G. Wilson: *Appl. Phys. Lett.* **78** (2001) 3475.
- 9) M. E. Overberg, C. R. Abernathy, S. J. Pearton, N. A. Theodoropoulou, K. T. McCarthy and A. F. Hebard: *Appl. Phys. Lett.* **79** (2001) 1312.
- 10) M. L. Reed, N. A. El-Masry, H. H. Stadelmaier, M. K. Ritums, M. J. Reed, C. A. Parker, J. C. Roberts and S. M. Bedair: *Appl. Phys. Lett.* **79** (2001) 3473.
- 11) G. T. Thaler, M. E. Overberg, B. Gila, R. 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** (2002) 3964.
- 12) K. H. Ploog, S. Dhar and A. Trampert: *J. Vac. Sci. Technol. B* **21** (2003) 1756.
- 13) M. Hashimoto, Y.-K. Zhou, M. Kamanura and H. Asahi: *Solid State Commun.* **122** (2002) 37.
- 14) L. Gu, S. Y. Wu, H. X. Liu, R. K. Singh, N. Newman and D. J. Smith: *J. Magn. Magn. Mater.* **290–291** (2005) 1395.
- 15) H. Akai and P. H. Dederichs: *Phys. Rev. B* **47** (1993) 8739.
- 16) H. Akai: <http://sham.phys.sci.osaka-u.ac.jp/kkr/>
- 17) F. Ducastelle and F. Gautier: *J. Phys. F* **6** (1976) 2039.
- 18) A. I. Liechtenstein, M. I. Katsnelson, V. P. Antropov and V. A.

- Gubanov: J. Magn. Magn. Mater. **67** (1987) 65.
- 19) M. van Schilfgaarde and O. N. Mryasov: Phys. Rev. B **63** (2001) 233205.
- 20) T. MacFarland, G. T. Barkema and J. F. Marko: Phys. Rev. B **53** (1996) 148.
- 21) G. Bouzerar, T. Ziman and J. Kudrnovsky: Europhys. Lett. **69** (2005) 812.
- 22) S. Hilbert and W. Nolting: Phys. Rev. B **71** (2005) 113204.
- 23) G. Martínez-Criado, A. Somogyi, S. Ramos, J. Campo, R. Tucoulou, M. Salome, J. Susini, M. Hermann, M. Eickhoff and M. Stutzmann: Appl. Phys. Lett. **86** (2005) 131927.