On origin of room temperature ferromagnetism in wide gap semiconductors

Anna Korbecka and Jacek A. Majewski

Institute of Theoretical Physics & Interdisciplinary Center for Modeling of Materials University of Warsaw,
ul. Hoza 69, 00-681 Warszawa, Poland
E-mail: Jacek.Majewski@fuw.edu.pl

The emerging field of semiconductor spintronics would be dramatically boosted if a semiconductor exhibiting room-temperature ferromagnetism could be found. Here, we discuss the recent stage of the research, paying particular attention to the understanding of observed room temperature ferromagnetism in wide band semiconductors, GaMnN and ZnMnO. Since the spinodal decomposition has been observed in these structures, we consider the possibilities to influence density fluctuations of the alloys to obtain ferromagnetic semiconductors with required functionalities. We contrast these compounds with (In,Mn)As and (Ga,Mn)As, where the ferromagnetism is well understood, albeit well below room temperature.

1. Introduction

The idea of a spin transistor [1] has given rise to spintronics — a new emerging field of solid state physics [2], where the central theme is the active manipulation of spin degrees of freedom in solid-state, and/or molecular systems [3], in addition to the degrees of freedom connected to the electron charge. This offers new opportunities for novel devices that could combine standard electronics with the spin dependent effects that arise from the interaction between spin of the carriers and the magnetic properties of the material. It is hoped that the advantages of these new devices would be, among others, nonvolatility, increased data processing speed, decreased electric power consumption, and increased integration densities. The vision of the spintronic systems and the main directions of the future development have been formulated in Ref. 2. The actual stage of research has been already described in a series of reviews [4–6], monographs [7,8] and even a text book [9]. The spintronics involves an intensive search for virtually all possible materials allowing the effective realization of spintronics devices. In this search, the materials that combine semiconducting behavior with robust magnetism are of particular interest, since they could allow the fabrication of all semiconductor devices.

2. Ferromagnetism in diluted magnetic semiconductors

2.1. Ferromagnetism in homogeneous DMSs

The first attempts to create material systems that could be simultaneously semiconducting and magnetic range to the late seventies [10], where the magnetic ions carrying local magnetic moments have been introduced into well known semiconductors. In this way, a new class of semiconductors has emerged so-called diluted magnetic semiconductors (DMSs). Later on, it has been shown that InAs and GaAs heavily doped with Mn become ferromagnetic with Curie temperatures of the order of 100 K [11]. It has been also shown that Mn ion in these compounds acts simultaneously as the source of local moments and an acceptor. This implies that the originating ferromagnetism in this type of DMSs could be mediated by free carriers, and is in principle described by the so-called Zener's kinetic exchange or indirect-exchange mechanism [12]. In the case of (In,Mn)As or (Ga,Mn)As compounds, the coupling of the local d-shell moments is mediated by p-band valence electrons (i.e., holes). Based on Zener's model, the theoretical explanation of the ferromagnetism in (III,Mn)V compounds with homogeneous distribution of substitutional Mn ions in III–V cubic lattice has been provided by Dietl et al. [13], however, it turned out that the details of the electronic structure of the valence band play an important role. This mean field theory explains experimentally observed

thermodynamic, micro-magnetic, transport, and optical properties of DMS with delocalized holes. The problem of ferromagnetism in (III,Mn)V DMSs has been extensively studied both theoretically and experimentally (the summary of these studies can be found in an excellent review of Jungwirth et al. [14]), and nowadays is considered to be well understood. The Zener's like mechanism can account also for ferromagnetism in II–VI compounds doped with transition metal ions [15]. In all these cases, the Curie temperature T_C, in agreement with theoretical predictions, is well below the room temperature, with the highest observed up to now value of T_C being 173 K [16]. In the view of spintronic applications, the ferromagnetic materials with T_C below room temperature are obviously not satisfactory. Therefore, it is a strong research effort to find a ferromagnetic semiconductor with T_C above 300 K. It seems that one of the direct ways to reach this goal would be increase the Mn concentration. However, it turns out that T_C saturates with Mn concentration, as can be seen in Fig. 1. The main reason of this behavior is the fact that at higher concentrations Mn ions built in the interstitial positions of the III–V lattice. There they do not act as the acceptors (actually they act as double donors and each interstitial Mn ion compensates two substitutional Mn acceptors) and actually diminish the hole concentration and as a consequence Curie temperature [14].

2.2. Ferromagnetism in wide band gap DMSs

However, the theoretical prediction of Dietl et al. [17] (based on Zener's model of ferromagnetism) that Mn-doped ZnO and GaN would be ferromagnetic at room temperature provided the hole density would be large enough, and a report of ferromagnetism in Co-doped TiO_2 [18] gave the hope that Co- and Mn doped oxides and nitrides may indeed be useful for spintronics. In addition, the theoretical calculations appeared [19] showing that ZnO doped with several 3d transition metal ions such as V, Cr,
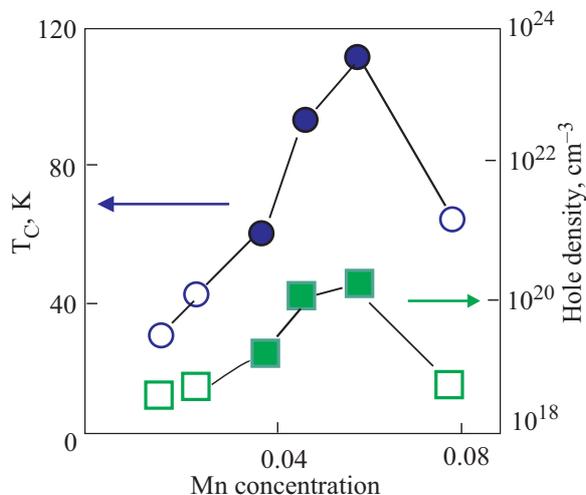

Fig. 1. Dependence of the Curie temperature and the hole density in (Ga,Mn)As on the Mn concentration.

Fe, Co and Ni may exhibit ferromagnetic ordering. This made the wide band gap materials very promising candidates for spintronic materials and induced enormous research effort devoted to these materials.

Many authors reported ferromagnetism above room temperature in Co- and Mn-doped ZnO [20], whereas other found magnetization only at low temperatures or even no ferromagnetism at all [21], showing that the magnetic properties of these systems are best described by a Curie–Weiss type behavior. In these systems, many other magnetic phases have been reported indicating that the growth conditions play decisive role in magnetic properties of these materials. These contradictory findings concerning ferromagnetism in transition metal doped ZnO led some authors to question the usefulness of these systems for spintronics [21]. These pessimistic conclusions were supported also by theoretical calculations [22], which excluded robust ferromagnetism in Mn and Co-doped ZnO, at least unless the additional sources of holes were provided, as predicted by Dietl et al. [17].

The studies of ferromagnetism in transition metal doped GaN (and other nitrides) have been also not very conclusive [23]. In 2001 successful growth of GaMnN films showing room temperature ferromagnetism and p-type conductivity has been reported [24]. The estimated Curie temperature was 940 K at 5.7% of Mn, which is highest among diluted magnetic semiconductors ever reported. However, the physical origin of ferromagnetism in this material remains still controversial. Other authors also found room temperature ferromagnetism in GaMnN layers of p-type [25], whereas some saw room temperature ferromagnetism and n-type layers [26] or did not observe ferromagnetism at all [27,28]. All these layers were obtained in different growth processes, clearly indicating the decisive role of growth conditions and rising question about homogeneity of the layers. Also the question of the role of external dopants has been addressed. In some cases, additional p-type codoping (with Mg in the case of GaN) should lead to enhancement of the carrier mediated ferromagnetism [29], whereas theoretical studies concluded that extrinsic doping of p-type generating defects in Mn doped GaN reduce the stability of the ferromagnetic state [30]. Hence, according to them, p-type conditions are not suitable for high temperature ferromagnetism in Mn doped GaN [30].

These studies revealed that the physical mechanisms of magnetism in the wide band gap DMSs (like GaN and ZnO) can be very complicated in comparison to the situation in III–V compounds (exemplified by (Ga,Mn)As and (In,Mn)As). The latter are systems with homogeneous distribution of Mn ions, and their ferromagnetism can be explained by mean field Zener's type model. In contrary, more accurate theoretical studies clearly demonstrated that the Curie temperature in the homogeneous wide band

gap semiconductors GaMnN and ZnMnO can reach only few K [31], in agreement with experimental data [32]. Therefore, at present it is commonly believed that the ferromagnetism in GaMnN and ZnMnO can originate from the inhomogeneous character of these materials [33]. There is no universal theory of magnetism, and the magnetic order observed in various compounds can have quite different origins that cause the coupling of localized moments in the solid. A useful starting point for developing a model of magnetism is achieving a full understanding of the electronic structure of a single Mn impurity in the host lattice. Here, we discuss the energy level diagrams for Mn impurity substituted on Ga site in GaAs and GaN lattices, depicted in Figs. 2 and 3, proposed by many authors on the basis of first-principles calculations (see e.g., the reference [34]). In both cases the hole is ascribed to the state lying in the energy gap. However, in GaAs Mn 3*d*-levels have lower energy than the anion dangling bond states and the states in the gap are strongly hybridized, which corresponds to the delocalized hole. In GaN, Mn 3*d*-levels lie higher in energy than the anion dangling bond states and, therefore, the states in the gap are weakly hybridized and have mostly *d*-like character. In result, the hole has the same *d*-like character and is strongly localized on the Mn site. If many Mn ions are substituted into the crystal, the levels will spread in the bands that conserve their character. One can expect narrow 3*d*-like impurity band in the energy gap of the GaN, whereas in GaAs the delocalized hole states will overlap with the valence band of the crystal. It is now clear that the physical mechanism leading to the ferromagnetism in (Ga,Mn)As (i.e., Zener's like model) cannot work in the case of
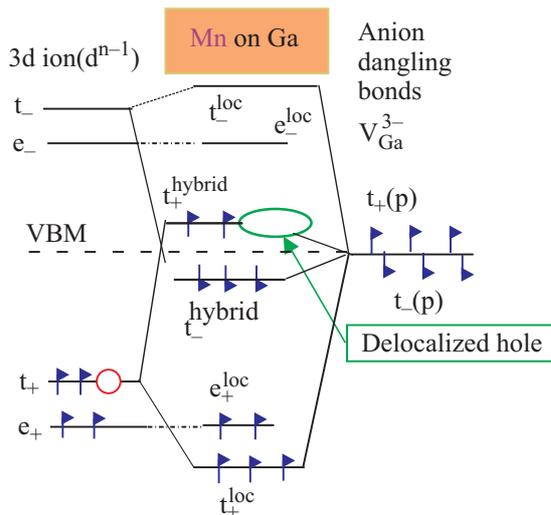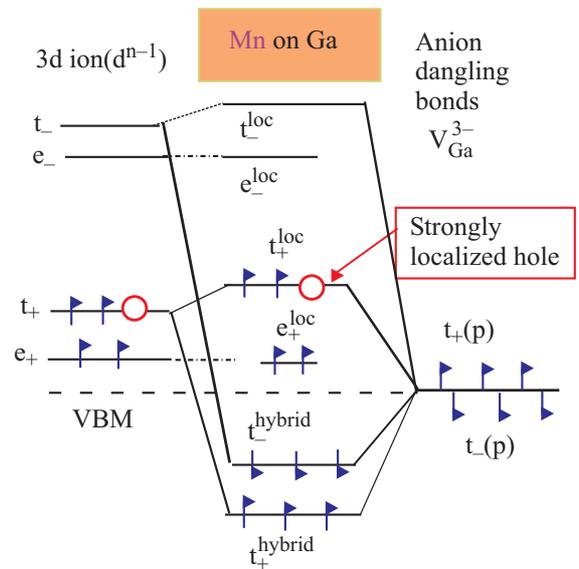

Fig. 3. The schematic energy level diagram for the hybridized levels of Mn 3*d*-states and the neighboring anion dangling bonds in GaN. The 3*d* Mn ion levels are split by the crystal-field and exchange interactions in the solid. In the (Ga,Mn)N *d* levels are energetically deeper than the dangling bond levels.

(Ga,Mn)N, where narrow band magnetism could be rather expected.

Further theoretical studies revealed further differences between (Ga,Mn)As and (Ga,Mn)N. It turns out that the hole mediated interactions between Mn ions are long ranged in GaAs, but are short ranged in GaN [31]. Therefore, usage of mean field theory to calculate Curie temperature is completely not justified in the case of GaN. This was the reason of false values of T_C obtained in earlies theoretical calculations for GaN [18]. Since the ZnO resembles to some extend GaN, the physics of transition metal impurities in this material is similar to that of GaN. The correct Monte Carlo calculations for (Ga,Mn)N and (Zn,Mn)O homogeneous alloys give T_C that is order of magnitude lower than 300 K. Obviously, the room temperature ferromagnetism observed in wide gap semiconductors must originate in different physical phenomena.

2.3. Spinodal decomposition and ferromagnetism in wide gap DMSs

In the moment it is believed that the spinodal decomposition in the GaMnN alloy can lead to its ferromagnetic behavior [33]. It is well know that in the alloys exhibiting the solubility gap in a certain concentration range the spinodal decomposition occurs into regions with high and low concentration of constituents. In some cases it may lead to coherent nanoregions embedded in the majority component. Such phenomenon is known to occur in GaInN alloy [35], where In rich nanoscale regions are embedded in the In low concentration regions. DMSs have particularly strong tendency to form inhomogeneous alloys. According to the pioneering *ab initio* work of van Schilfgaarde and Mryasov

Fig. 2. The schematic energy level diagram for the hybridized levels of Mn 3*d*-states and the neighboring anion dangling bonds in GaAs. The 3*d* Mn ion levels are split by the crystal-field and exchange interactions in the solid. In (Ga,Mn)As *d* levels are energetically deeper than the dangling bond levels.

[36] and others [37] bringing two Ga-substitutional Mn atoms together gives energy gain of 120 meV in GaAs and 300 meV in GaN, and in the case of Cr pair in GaN the energy gain reaches even 350 meV [36].

The spinodal decomposition generally does not involve a precipitation of another crystallographic phase. It is, therefore, not so easy detectable experimentally. Nevertheless, the electron transmission microscopy (TEM) experiments [38,39] found coherent zinc-blende Mn-rich (Mn,Ga)As nanocrystals in (Ga,Mn)As. It is believed that these regions were responsible for the apparent Curie temperature up to 360 K [39]. Furthermore, coherent hexagonal and diamond-type Mn-rich nanocrystals were detected by spatially resolved X-ray diffraction in (Ga,Mn)N [40] and by transmission electron microscopy in (Ge,Mn) [41], respectively. The nanoregions with higher concentration of magnetic moments, lead to ferromagnetic ordering of them at temperatures usually higher than 300 K. Recent simulations to large extend confirm this picture and are even able to provide hints for effective epitaxial growth of ferromagnetic compounds [37,42].

In order to obtain robust ferromagnetism, it may be worthwhile to investigate the effect of co-doping of samples with other cations to induce additional charge carriers, or samples with defect-induced carriers. It has been demonstrated that in this way one can control the charge state of the magnetic ions, and, therefore, their tendency to cluster, just influencing the magnetic order in the system. It has been demonstrated in the case of (Zn, Cr)Te alloy [43].

The ferromagnetism of (Zn, Cr)Te and the associated magnetooptical and magnetotransport functionalities, are dominated by the formation of Cr-rich (Zn,Cr)Te metallic nanocrystals embedded in the Cr-poor (Zn, Cr)Te matrix. Importantly, the formation of these nanocrystals can be controlled by manipulating the charge state of the Cr ions during the epitaxy. These findings provide insight into the origin of the ferromagnetism in a broad range of semiconductors and oxides, and indicate possible functionalities of these composite systems. Furthermore, they demonstrate a bottom-up method for self-organized nanostructure fabrication that is applicable to any system in which charge state of a constituent depends on the Fermi-level position in the host semiconductor [43].

A new route toward high temperature ferromagnetism in semiconductors is the idea of the so-called «subsurfactant epitaxy», i.e., optimal doping control of magnetic semiconductors in the process of epitaxial growth. Subsurfactant epitaxy has been proposed first theoretically [44]. The authors proposed the doping Mn into Ge in such a way that takes advantage of the energetic and kinetic characteristics of Mn at the growth front of Ge (100). It has been confirmed experimentally later on [45]. The resulting doping levels would normally be considered too low for ferromagnetic ordering. However, GeMn structures grown using this method exhibit the Curie temperature that exceeds room temperature by a comfortable margin [45].

This clearly demonstrates that deep understanding of the self-organized growth can be utilized to obtain ferromagnetic materials of required functionalities.

3. Conclusions

The emerging field of semiconductor spintronics would be dramatically boosted if a semiconductor exhibiting room-temperature ferromagnetism could be found. Therefore, the discovery of ferromagnetism first in diluted magnetic semiconductors such as (In,Mn)As and later in (Ga,Mn)As came as a landmark achievement. In these materials, substitutional divalent Mn ions (with concentration of several per cent) provide localized spins and function as acceptor centers that provide holes which mediate the ferromagnetic coupling between the parent randomly distributed Mn spins. The ferromagnetism of these systems is well understood and can be explained within the $p-d$ Zener's exchange mechanism and the Luttinger–Kohn kp theory of the valence band. This mean field theory explains experimentally observed thermodynamic, micromagnetic, transport, and optical properties of DMS with delocalized holes. However, in spite of the huge technological and experimental efforts, the highest possible Curie temperature that was possible to accomplish up to now lies in the range of 173 K.

Stimulated partly by the theoretical predictions, search for carrier-induced ferromagnetism in other types of semiconductors containing Mn and other transition metal ions begun and several observations of room temperature ferromagnetism in wide-gap semiconductors have been reported, e.g., in GaN:Mn, ZnO:Mn, and ZnO:Co. However, it is now known fairly well that the exchange interactions in wide-gap II–VI and III–N (nitrides) DMSs is dominated by Zener's double exchange mechanism and is short range. Therefore, the mean field theory applied to (Ga,Mn)As is invalid in this case. Monte Carlo simulations of Curie temperature give very low values of T_C (few Kelvin) and have been also confirmed in GaN:Mn samples grown by molecular beam epitaxy. It became clear that the room temperature ferromagnetism is impossible in uniformly alloyed wide-gap compounds.

Therefore, a question arises, where the room temperature ferromagnetism in wide-gap semiconductors comes from? The most serious candidate is spinodal decomposition in the moment, i.e., the appearance of regions with higher concentration of one species of an alloy. Theoretical works confirm the strong tendency of wide-gap DMSs to form strongly nonrandom alloys. Since spinodal decomposition does not usually involve a precipitation of another crystallo-graphic phase, it is rather difficult to detect it experimentally. However, the Mn rich nanocrystals have been observed in (Ge,Mn), (Ga,Mn)N, and (Ga,Mn)As.

One could expect that such spinodal decomposition is a generic property of a number of DMSs. Further, the suitable control of growth process could lead to fabrication of ferromagnetic semiconductors at room temperature.

1. S. Data and B. Das, *Appl. Phys. Lett*. **56**, 665 (1990).
2. S.A.Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S. von Molnar, M.L. Roukes, A.Y. Chtchelkanova, and D.M. Treger, *Science* **294**, 1488 (2001).
3. D. Gatteschi, R. Sessoli, and J. Villain, *Molecular Nanomagnets*, Oxford University Press (2006).
4. I. Zutic, J. Fabian, and S. Das Sarma, *Rev. Mod. Phys*. **76**, 323 (2004).
5. C. Felser, G.H. Fecher, and B. Balke, *Angew. Chem. Int. Ed*. **46**, 668 (2007).
6. R. Hanson, L.P. Kouwenhoven, J.R. Petta, S. Tarucha, and L.M.K. Vandersypen, *Rev. Mod. Phys*. **79**, 1217 (2007).
7. *Concepts in Spin Electronics*, Sadamichi Maekawa (ed.) Oxford University Press (2006).
8. *Spintonic Materials and Technology*, Y.B. Yu and S.M. Thompson (eds.) Taylor & Francis, Boca Raton (2007).
9. Mathias Getzlaff, *Fundamentals of Magnetism,* Springer–Verlag, Berlin (2008).
10. J.A. Gaj, J. Ginter, and R.R. Galazka, *Phys. Status Solidi* **B89**, 655 (1978).
11. H. Ohno, H. Munekata, T. Penney, S. von Molnar, and L.L. Chang, *Phys. Rev. Lett*. **68**, 2664 (1992); H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto, and Y. Iye, *Appl. Phys. Lett*. **69**, 363 (1996).
12. C. Zener, *Phys. Rev*. **81**, 440 (1951a).
13. T. Dietl, H. Ohno, and F. Matsukura, *Phys. Rev*. **B63**, 195205 (2001).
14. T. Jungwirth, J. Sinova, J. Masek, J. Kucera, and A.H. MacDonald, *Rev. Mod. Phys*. **78**, 809 (2006).
15. T. Dietl, A. Haury, and Y. Merle d'Aubigne, *Phys. Rev*. **B55**, R3347 (1997); T. Dietl, M. Sawicki, Le Van Khoi, J. Jaroszynski, P. Kossacki, J. Cibert, D. Ferrand, S. Tatarenko, and A. Wasiela, *Phys. Status Solidi* **B229**, 665 (2002).
16. K.Y. Wang, R.P. Campion, K.W. Edmonds, M. Sawicki, T. Dietl, C.T. Foxon, and B.L. Gallagher, *Proc. ICPS 2004*, American Institute of Physic (2005).
17. T. Dietl, H. Ohno, F. Matsukura, J. Cibert. and D. Ferrand, *Science* **287**, 1019 (2000).
18. Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S.-Y. Koshihara, and H. Koinuma, *Science* **291**, 854 (2001).
19. K. Sato and H. Katayama–Yoshida, *Jpn. J. Appl. Phys*. **39**, L555 (2000).
20. see e.g., S.A. Chambers and R.F. C. Farrow, *MRS Bull*. **28**, 729 (2003) and W. Prellier, A. Fouchet, and B. Mercey, *J. Phys.: Condens. Matter* **15**, R1583 (2003), and the references therein.
21. C.N.R. Rao and F.L. Deepak, *J. Mater. Chem*. **15**, 573 (2005).
22. N.A. Spaldin, *Phys. Rev*. **B69**, 125201 (2004).
23. C. Liu, F. Yun, and H. Morko з, *J. Mater. Science: Materials in Electronics* **16**, 555 (2004).
24. S. Sonoda, S. Shimizu, T. Sasaki, Y. Yamamoto, and H. Hori, *J. Cryst. Growth*. **237**–**239**, 1358 (2002); H. Hori, S. Sonoda, T. Sasaki, Y. Yamamoto, S. Shimizu, K. Suga, and K. Kindo, *Physica* **B324**, 142 (2002).
25. K.H. Kim, K.J. Lee, D.J. Kim, H.J. Kim, Y. E. Ihm, D. Djayaprawira, M. Takahashi, C.S. Kim, C.G. Kim, and S.H. Yoo, *Appl. Phys. Lett*. **82**, 1775 (2003).
26. S.J. Pearton, C.R. Abernathy, M.E. Overberg, G.T. Thaler, D.P. Norton, N. Theodoropoulou, A.F. Hebard, Y.D. Park, F. Ren, J. Kim, and L.A. Boatner, *J. Appl. Phys*. **93**, 1 (2003).
27. M. Zajac, J. Gosk, M. Kaminska, A. Twardowski, T. Szyszko, and S. Podsiadlo, *Appl. Phys. Lett*. **79**, 2432 (2001).
28. Y.L. Soo, G. Kioseoglou, S. Kim, S. Huang, Y.H. Kao, S. Kuwabara, S. Owa, T. Kondo, and H. Munekata, *Appl. Phys. Lett*. **79**, 3926 (2001).
29. K.H. Kim, K.J. Lee, D.J. Kim, H.J. Kim, Y.E. Ihm, C.G. Kim, S.H. Yoo, and C.S. Kim, *Appl. Phys. Lett.* **82**, 4755 (2003).
30. Priya Mahadevan and S. Mahalakshmi, *Phys. Rev*. **B73**, 153201 (2006).
31. K. Sato, P.H. Dederichs, and H. Katayama–Yoshida, *J. Superconduc*. **18**, 33 (2005).
32. M.E. Overberg, C.R. Abernathy, S.J. Pearton, N.A. Theodoropoulou, K.T. McCarthy, and A.F. Hebard, *Appl. Phys. Lett*. **79**, 1312 (2001).
33. T. Dietl, *Physica* **E35**, 293 (2006).
34. Priya Mahadevan and A. Zunger, *Phys. Rev*. **B69**, 115211 (2004).
35. M. Farhat and F. Bechstedt, *Phys. Rev*. **B65**, 075213 (2002).
36. M. van Schilfgaarde and O.N. Mryasov, *Phys. Rev*. **B63**, 233205 (2001).
37. K. Sato, H. Katayama-Yoshida, and P.H. Dederichs, *Jpn. J. Appl. Phys*. **44**, L948 (2005).
38. M. Moreno, A. Trampert, B. Jenichen, L. Daeweritz, and K.H. Ploog, *J. Appl. Phys*. **92**, 4672 (2002).
39. M. Yokoyama, H. Yamaguchi, T. Ogawa, and M. Tanaka, *J. Appl. Phys*. **97**, 317 (2005).
40. G. Martinez-Criado, A. Somogyi, S. Ramos, J. Campo, R. Tucoulou, M. Salome, J. Susini, M. Hermann, M. Eickhoff, and M. Stutzmann, *Appl. Phys. Lett*. **86**, 131927 (2005).
41. M. Jamet, A. Barski, T. Devillers, V. Poydenot1, R. Dujardin, P. Bayle–Guillmaud, J. Rotheman, E. Bellet–Amalric, A. Marty, J. Cibert, R. Mattana, and S. Tatarenko, *Nature Mat*. **5**, 653 (2006).
42. T. Fukushima, K. Sato, H. Katayama-Yoshida, and P.H. Dederichs, *Jpn. J. Appl. Phys*. **45**, L416 (2006).
43. S. Kuroda, N. Nishizawa, K. Takita, M. Mitome, Y. Bando, K. Osuch, and T. Dietl, *Nature Mat*. **6**, 440 (2007).
44. W.G. Zhu, H.H. Weitering, E.G. Wang, E. Kaxiras, and Z. Zhang, *Phys. Rev. Lett*. **93**, 126102 (2004).
45. C. Zeng, Z. Zhang, K van Benthem, M.F. Chrisholm, and H.H. Weitering, *Phys. Rev. Lett*. **100**, 066101 (2004).