PHYSICAL REVIEW B **66**, 184435 (2002)

Half-metallic ferromagnetism of MnBi in the zinc-blende structure

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(Received 7 July 2002; published 27 November 2002)

The full-potential augmented plane wave plus local orbital method within density-functional theory is used to predict that MnBi in the zinc-blende structure is a true half-metallic ferromagnet with a magnetic moment of $4.000\mu_B$ per formula unit. This contrasts with the zinc-blende phase of MnAs, which is only a nearly half-metallic ferromagnet. This half-metallic ferromagnetic behavior of zinc-blende MnBi is found to be robust against compressive volume changes of up to 15%, its stability being enhanced by the relativistic shift of the valence *s* state energy levels. Zinc-blende MnBi could possibly be grown epitaxially on the important binary semiconductors such as InSb or CdTe, although it remains to be seen whether epitaxially it retains its half-metallic ferromagnetic state.

DOI: 10.1103/PhysRevB.66.184435 PACS number(s): 75.90.+w, 75.30.−m

I. INTRODUCTION

Spin-based electronics, or spintronics, is currently a hot topic,[1,2] which offers opportunities for a new generation of multifunctional devices combining traditional charge-based microelectronics with spin-dependent effects. As ideal components for such devices, half-metallic ferromagnets are receiving more and more attention around the world, because they have only one electronic spin direction at the Fermi energy.[3] Since de Groot *et al.* first predicted half-metallic ferromagnetism in Heusler compounds[4] in 1983, several half-metallic magnets have been theoretically predicted and experimentally found. Half-metallic ferromagnetism has been observed in NiMnSb,[5] CrO_2,[6] Fe_3O_4,[7] and the colossal magnetoresistance manganate materials.[8] Half-metallic systems have unique properties since only one spin-channel is metallic and these are currently being investigated both experimentally[9] and theoretically.[10] In addition, great effort is being made to find new members of this family of half-metallic magnets.

Recently, so-called nearly half-metallic ferromagnetism was predicted in the zinc-blende phase of MnAs with full-potential density-functional calculations.[11] In this case, the Fermi level not only crosses the energy bands of the spin-up electrons but also touches the bottom of the conduction bands of the spin-down electrons, rather than lying in the energy gap between the spin-down conduction and valence bands, as in a typical half-metallic magnet. This zinc-blende phase of MnAs has now been realized experimentally with the growth of ferromagnetic MnAs nanodots on a sulfur-passivated GaAs substrate.[12] These nanodots have an average height and diameter of 30 Å and 160 Å, respectively. They are found to undergo a 0.7% lattice expansion parallel to the surface compared to the GaAs substrate. However, it has not been possible to grow a complete film of zinc-blende MnAs on GaAs due to the large lattice mismatch of 5.8%, which is expected between bulk zinc-blende MnAs and GaAs.[12] This is in contrast to CrAs where zinc-blende films and multilayers have been grown on GaAs substrates,[13] since the lattice mismatch is only 2–3%.[14] It was shown by an accurate density-functional method that the zinc-blende CrSb is a robust half-metallic ferromagnet.[15] Theoretically, full half-metallic ferromagnetism would be achieved by expanding the lattice constant by some 10%.[16] Therefore, it is natural to ask the question: Is the zinc-blende phase of MnBi, which has a larger equilibrium atomic volume than that of MnAs, a full half-metallic ferromagnet? MnBi in the NiAs phase has been intensively studied during the last ten years for possible magnetic recording and magneto-optical applications,[17–19] but there are no reports on the zinc-blende phase of MnBi, of which we are aware.

In this paper we study the zinc-blende phase of MnBi with the full-potential augmented plane wave plus local orbitals method[20] within density-functional theory, predicting that it is a full half-metallic ferromagnet with a magnetic moment of $4.000\mu_B$ per formula unit. This full half-metallic behavior is robust against compressive volume changes of up to 15%. Although being metastable, this MnBi phase could possibly be grown epitaxially on appropriate substrates such as InSb or CdTe, for which the lattice mismatch is small. It remains to be seen, however, whether epitaxially it retains its half-metallic ferromagnetic state.

II. HALF-METALLIC FERROMAGNETISM OF ZINC-BLENDE MnBi

A. Computational details

The Vienna package WIEN2K[20] for the full-potential augmented plane wave plus local orbitals (FAPWLO) method within density functional theory[21] was used for all our calculations. For the exchange-correlation potential, we took the generalized gradient approximation (GGA) proposed in 1996 by Perdew, Burke and Ernzerhof (PBE96). Because Bi is a heavy atom we have performed both relativistic and nonrelativistic calculations for comparison. We have found that the spin-orbit interaction does not influence the half-metallic ferromagnetism and we have, therefore, neglected it in the relativistic calculations discussed here, which include only the Darwin shift and mass velocity term. The ground state of MnBi is the hexagonal NiAs phase with the experimental

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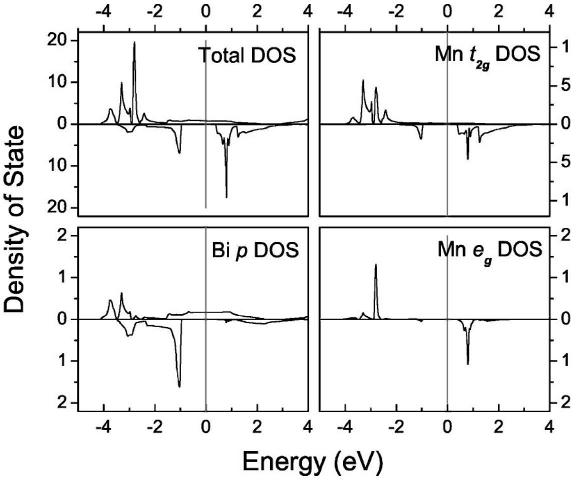

FIG. 1. The total and three main partial DOS of zinc-blende MnBi at the predicted equilibrium lattice constant 6.399 Å. There is a clear gap of approximately 1.0 eV width about the Fermi energy for the spin-down electrons.

lattice constants $a=4.170$ Å and $c=5.755$ Å. The metastable zinc-blende phase of MnBi has the same crystalline structure as the sp-valent octet semiconductors GaAs, InAs, GaSb, InSb, and CdTe. Its lattice constant was determined from the predicted binding energy curve. The radius R_{mt} of the muffin tins was taken as 2.4 bohr (1.27 Å) for both Bi and Mn and $R_{\mathrm{mt}}\ K_{\mathrm{max}}$ taken as 8.0. For all our calculations we took 3000 k points in the Brillouin zone. The self-consistent calculations were considered to be converged only when the integrated magnitude of the charge density difference between input and output [i.e., $\int|\rho_{n+1}(\vec{r})-\rho_n(\vec{r})|d\vec{r}$] was less than 0.000 01, a very strict standard.

B. Half-metallic ferromagnetism in zinc-blende MnBi

We predict that zinc-blende MnBi would be a true half-metallic ferromagnet at its equilibrium lattice constant. Figure 1 shows the spin-dependent density of states (SDOS) of zinc-blende MnBi at the predicted equilibrium lattice constant of 6.399 Å in GGA.[22] It is clear that the spin-up electrons are metallic whereas there is an energy gap of about 1.0 eV about the Fermi energy in the bands for the spin-down electrons, as illustrated in Fig. 1. We see, therefore, that zinc-blende MnBi is a typical half-metallic ferromagnet. In Fig. 2 we present the corresponding spin-dependent energy bands along high-symmetry directions in the Brillouin zone. There are three bands crossing the Fermi energy. One of them is almost fully filled, but the other two are approximately half-filled. The unfilled sections are around the Γ point for all the three bands. The charge carriers of the almostfully filled band are holelike, but those of the remaining two are electronlike. The total magnetic moment is $4.000\mu_B$ per formula unit. This is in contrast with the $3.75\mu_B$ per formula unit of the zinc-blende MnAs.[16] Therefore, we have established with accurate FAPWLO calculations that zinc-blende MnBi would be a true half-metallic ferromagnet at equilibrium.

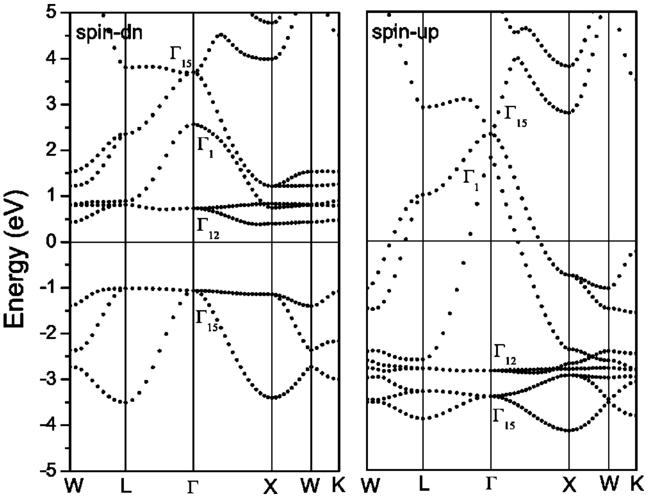

FIG. 2. The band structure of zinc-blende MnBi at the predicted equilibrium lattice constant. Note that the valence band arising from the s orbitals on Bi sites is not plotted since it falls around -11 eV.

C. Is half-metallic ferromagnetism robust against volume change?

Although we have shown that bulk zinc-blende MnBi would be a true half-metallic ferromagnet at its equilibrium volume, in practice we expect to stabilize this metastable phase by growing it as a thin film on a zinc-blende substrate with an appropriate lattice constant. We must, therefore, investigate the sensitivity of this half-metallic state to small

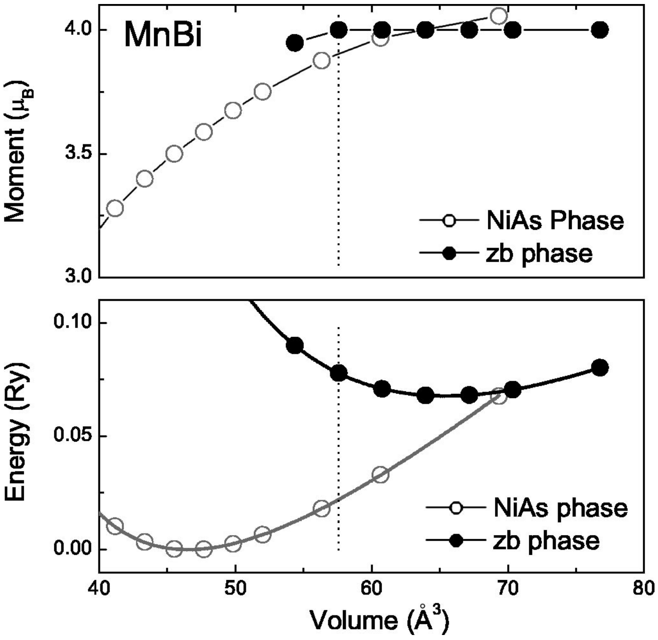

FIG. 3. The magnetic moment and binding energy (in the cohesive energy of the NiAs ground state) as a function of the volume per formula unit for MnBi with respect to the zinc-blende (solid circles) and NiAs (open circles) phases. The minimum energy of the zinc-blende phase corresponds to the equilibrium lattice constant of 6.399 Å.

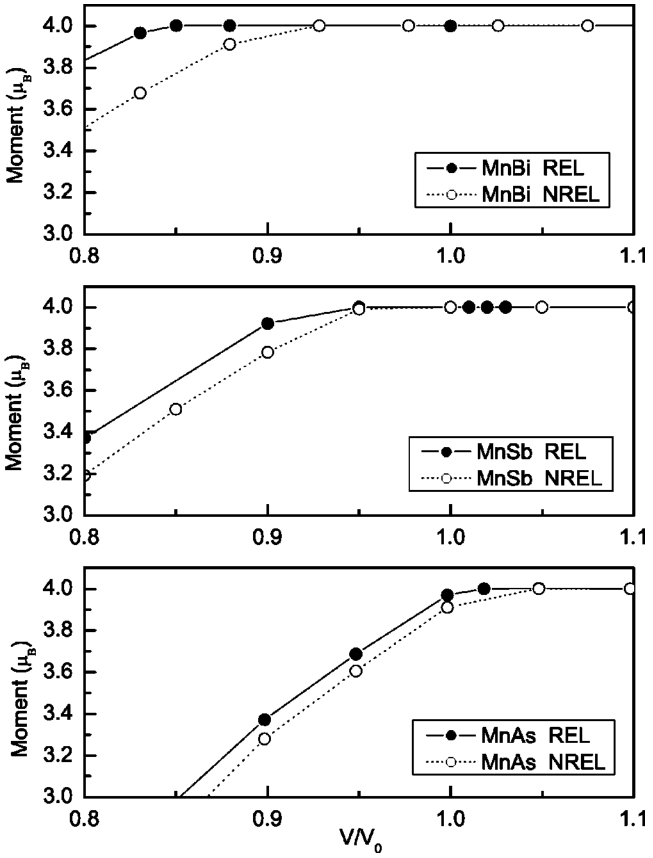

FIG. 4. The volume dependence of the magnetic moments of zinc-blende MnBi, MnSb, and MnAs with (REL) and without (NREL) relativistic effects included in the calculations, where V_0 is the predicted equilibrium volume of the particular Mn pnictide from the relativistic calculations. As expected, the influence of relativistic effect on half-metallic ferromagnetism decreases from MnBi to MnSb and MnAs.

changes in lattice constant. In the upper panel of Fig. 3 we plot the volume dependences of the magnetic moment per formula unit for MnBi in the zinc-blende and NiAs phases. The lower panel shows the corresponding binding energy curves, taking the cohesive energy of the ground state NiAs phase as reference. As expected, we find that the NiAs phase is about 1 eV per formula unit more stable than the zinc-blende phase, with a predicted equilibrium volume of 46.5 Å^3 which is within 7% of experiment. The zinc-blende phase has the much larger equilibrium volume of 65.4 Å^3. We see from the upper panel that zinc-blende MnBi can be compressed by up to 15% in volume before the full half-metallic ferromagnetic state is lost. Thus, we expect this state to be robust against small local strain fields which are induced during film growth.

III. RELATIVISTIC EFFECTS ON THE HALF-METALLIC FERROMAGNETISM

The difference in behavior of the half-metallic ferromagnetic state across the Mn pnictides is illustrated in Fig. 4 for both relativistic (full curves) and nonrelativistic (dashed curves) calculations. We see that as previously predicted,[11,16] MnAs is only a nearly half-metallic ferromagnet with a moment of $3.95\mu_B$ at equilibrium. The lattice needs to be expanded by 10% before the onset of full half-metallic ferromagnetism. We predict both MnSb and MnBi to be full half-metallic ferromagnets at equilibrium. An earlier calculation[16] had found MnSb to be a nearly half-metallic ferromagnet with a moment of $3.77\mu_B$. This disagreement with our results is probably due to either an insufficient number of k points or too low an energy cutoff in their plane-wave expansion, both of which can effect the position of the Fermi energy with respect to the energy gap. A comparison of the full and dashed curves in Fig. 4 demonstrates the importance of relativistic effects for the heavy element Bi. We see that the relativistic calculations predict that full half-metallic ferromagnetism persists up to 15% compression, whereas it only persists up to 9% for the nonrelativistic case.

Relativistic effects influence the states with s-like character, since they have nonvanishing weight at the atomic centers. The Γ_1 state in Fig. 2 has to be orthogonal with the low-lying Γ_1 state at -11 eV (not drawn), which is associated with the valence s orbitals on the Bi sites. Turning off the relativistic effect causes this low-lying Γ_1 state to increase in energy by about 2.1 eV with a corresponding shift in the upper Γ_1 state due to orthogonality repulsion. The net effect is that the Γ_1 dispersion branches in Fig. 2 are pushed up beyond the Γ_{15} branches. This drags up the Fermi energy towards the top of the spin-down energy gap and reduces the range of stability of the full half-metallic ferromagnetic state.

We can understand why relativistic effects increase the range of stability of the full half-metallic ferromagnetic state in zinc-blende MnBi. Figure 2 shows the relativistic band structure of MnBi at its equilibrium volume. Consider the right-hand panel for the spin-up electrons. Γ_{12} and Γ_{15} label the zone-center values of the e_g and t_{2g} Mn d bands with their fairly narrow dispersion. These bands are then followed by the much broader sp bands that terminate at Γ_1 and Γ_{15}, where Γ_1 has pure s-type symmetry. The left-hand panel for the spin-down electrons shows the same behavior except that the pure d state at Γ_{12} has been shifted upwards by about 3.5 eV due to the weaker exchange field seen by the minority spin electrons. This is consistent with the Stoner model of band magnetism where the local exchange splitting is simply Im with the Stoner exchange integral I taking a value of about 1 eV for 3d transition metals such as Mn,[23] and the magnetic moment m taking the full half-metallic value of $4\mu_B$.

IV. THE MECHANISM BEHIND THE HALF-METALLIC FERROMAGNETISM

The origin of the half-metallic ferromagnetism can be understood using the following simple argument which was initially put forward by de Groot *et al.*[4] in 1983. First, as discussed in the preceding section, the Mn d states undergo a large exchange splitting of about 3.5 eV due to the magnetic moment of $4.000\mu_B$ per formula unit. Second, the t_{2g} d states with Γ_{15} symmetry interact strongly with the Bi p states with the same symmetry. For the case of the majority band, the low-lying d states mutually repel the Bi p states to energies about the Fermi energy, thereby giving rise to the metallic conduction band. For the case of the minority band, however, the Mn *d* states lie above the Bi *p* band, so that their mutual repulsion simultaneously drives the *d* band up above the Fermi energy and the *p* band down below the Fermi energy, thereby opening up a gap with semiconducting behavior. The resultant minority valence band, therefore, looks very similar to that expected for a typical *sp*-valent III-V semiconductor such as GaAs (see Fig. 2 of Ref. 4). Thus, the metal-semiconductor asymmetry of half-metallic ferromagnets is driven by the interplay between the exchange splitting of the Mn *d* states and the interaction of the Mn t_{2g} states with neighboring Bi *p* states.

The Mn e_g *d* states, on the other hand, play an important role in determining the difference between the nearly versus full half-metallic ferromagnetism that is predicted across the zinc-blende Mn pnictides (from MnAs, MnSb, to MnBi). As Sanvito and Hill[11] first emphasized, this is driven by the width of the Mn e_g *d* band, which is centered on Γ_{12}. This is sensitive to the lattice spacing: for small volumes the width is sufficiently great for the spin-down e_g band to intercept the Fermi energy from above, whereas for larger volumes the width is sufficiently small for the Fermi energy to break free into the gap. This is in accord with our findings in Fig. 4. The zinc-blende phase of MnAs has an equilibrium volume of 46 Å^3 and displays nearly half-metallic ferromagnetism, whereas zinc-blende MnBi and MnSb have equilibrium volumes of 65 Å^3 and 59 Å^3, respectively, and display full half-metallic ferromagnetism. It is very interesting that the exchange splitting in all these cases and in the zinc-blende Cr pnictides[15] is consistent with the Stoner theory.

V. DISCUSSION AND SUMMARY

Can zinc-blende MnBi be realized? To answer this question, let us look at some binary semiconductors in the zinc-blende phase. Most famous and important are GaAs, InAs, GaSb, InSb, and CdTe. It has recently been demonstrated that MnAs, CrAs, and CrSb can be grown as nanodots[12] and thin films or multilayers[13] on a GaAs substrate in the zinc-blende phase,[16] even though in the bulk they form either the NiAs or related MnP structure as the ground state. It should, therefore, be possible to grow zinc-blende MnBi epitaxially on CdTe or InSb, for example, because of the quite small lattice mismatches. With modern epitaxial growth technique becoming more and more powerful,[24] zinc-blende MnBi should be able to be realized, at least as thin films or nanostructures on appropriate substrates with appropriate crystalline structures and lattice constants. However, recent theoretical and experimental research on Mn-doped GaAs has shown that the defects and the relative positions of the Mn ions and As antisites have a strong effect on the exchange between the Mn spins and therefore changes the magnetic properties in these materials.[25,26] Lattice defects and impurities in real materials make it more difficult to confirm experimentally a theoretical prediction based on ideal crystalline structures. However, in contrast with the Mn-doped GaAs and zinc-blende MnAs, which is only a nearly half-metallic ferromagnetic phase, zinc-blende MnBi is typical of full half-metallic ferromagnets even under relative cell volume changes of up to 15%. Hopefully, it should be more robust in surviving the impurities and defects in the real environment. Compared to other half-metallic magnets, zinc-blende MnBi shares the same crystalline structure as the important *sp*-valent octet semiconductors. It should therefore, be much easier to combine with them for future spintronic devices.[27]

In summary, we have studied the zinc-blende phase of MnBi using the full-potential augmented plane wave plus local orbitals method within density-functional theory. The results of the density of states, energy bands, and magnetic moment clearly demonstrated that it is a typical half-metallic ferromagnet with a magnetic moment of $4.000\mu_B$ per formula unit. This phase of MnBi is robust against compressive volume changes of up to 15%. Although it is metastable, it could be realized, at least as thin films or nanostructures, through epitaxial growth on appropriate substrates of important semiconductors such as InSb and CdTe. It remains to be seen, however, whether it retains its half-metallic properties in epitaxial form.

ACKNOWLEDGMENTS

This work was supported in part by the China National Key Projects of Basic Research (Grant No. G1999064509), by the Natural Science Foundation of China, and by the British Royal Society under a collaborating project with the Chinese Academy of Sciences.

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[1] 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 (2002); I.S. Osbourne, *ibid.* **294**, 1483 (2001).

[2] D.D. Awschalom and J.M. Kikkawa, Phys. Today **52** (6), 33 (1999).

[3] W.E. Pickett and J.S. Moodera, Phys. Today **54** (5), 39 (2001).

[4] R.A. de Groot, F.M. Mueller, P.G. van Engen, and K.H.J. Buschow, Phys. Rev. Lett. **50**, 2024 (1983); R.A. de Groot, Phys. Rev. B **172**, 45 (1991).

[5] J.W. Dong, L.C. Chen, C.J. Palmstrom, R.D. James, and S. McKernan, Appl. Phys. Lett. **75**, 1443 (1999).

[6] S.M. Watts, S. Wirth, S. von Molnar, A. Barry, and J.M.D. Coey, Phys. Rev. B **61**, 9621 (2000).

[7] F.J. Jedema, A.T. Filip, and B. van Wees, Nature (London) **410**, 345 (2001); S. Soeya, J. Hayakawa, H. Takahashi, K. Ito, C. Yamamoto, A. Kida, H. Asano, and M. Matsui, Appl. Phys. Lett. **80**, 823 (2002).

[8] J.M.D. Coey, M. Viret, and S. von Molnr, Adv. Phys. **48**, 169 (1999).

[9] T. Akimoto, Y. Moritomo, A. Nakamura, and N. Furukawa, Phys. Rev. Lett. **85**, 3914 (2000).

[10] I. Galanakis, P.H. Dederichs, and N. Papanikolaou, Phys. Rev. B **66**, 134428 (2002).

[11] S. Sanvito and N.A. Hill, Phys. Rev. B **62**, 15 553 (2000).

[12] K. Ono, J. Okabayashi, M. Mizuguchi, M. Oshima, A. Fujimori, and H. Akinaga, J. Appl. Phys. **91**, 8088 (2002).

[13] H. Akinaga, T. Manago, and M. Shirai, Jpn. J. Appl. Phys., Part 2 **39**, L1118 (2000); M. Mizuguchi, H. Akinaga, T. Manago, K. Ono, M. Oshima, M. Shirai, M. Yuri, H.J. Lin, H.H. Hsieh, and C.T. Chen, J. Appl. Phys. **91**, 7917 (2002); J.-H. Zhao, F. Matsukura, K. Takamura, E. Abe, D. Chiba, and H. Ohno, Appl. Phys. Lett. **79**, 2776 (2001).

[14] M. Shirai, Physica E (Amsterdam) **10**, 143 (2001).

[15] B.-G. Liu, cond-mat/0206485 (unpublished).

[16] A. Continenza, S. Picozzi, W.T. Geng, and A.J. Freeman, Phys. Rev. B **64**, 085204 (2001).

[17] J.B. Yang, K. Kamaraju, W.B. Yelon, W.J. James, Q. Cai, and A. Bollero, Appl. Phys. Lett. **79**, 1846 (2001); S. Saha, M.Q. Huang, C.J. Thong, B.J. Zande, V.K. Chandhok, S. Simizu, R.T. Obermyer, and S.G. Sankar, J. Appl. Phys. **87**, 6040 (2000).

[18] P.M. Oppeneer, V.N. Antonov, T. Kraft, H. Eschrig, A.N. Yaresko, and A. Ya. Perlov, J. Appl. Phys. **80**, 1099 (1996).

[19] K.-U. Harder, D. Menzel, T. Widmer, and J. Schoenes, J. Appl. Phys. **84**, 3625 (1998).

[20] P. Blaha, K. Schwarz, P. Sorantin, and S.B. Trickey, Comput. Phys. Commun. **59**, 399 (1990).

[21] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L.J. Sham, *ibid.* **140**, A1133 (1965).

[22] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[23] O. Gunnarsson, J. Phys. F: Met. Phys. **6**, 587 (1976).

[24] For example, G.H. Cocoletzi and N. Takeuchi, Phys. Rev. B **61**, 15 581 (2000); E. Alphandery, R.J. Nicholas, N.J. Mason, S.G. Lyapin, and P.C. Klipstein, *ibid.* **65**, 115322 (2002); V.K. Dixit, Bhavtosh Bansal, V. Venkataraman, H.L. Bhat, G.N. Subbanna, K.S. Chandrasekharan, and B.M. Arora, Appl. Phys. Lett. **80**, 2102 (2002); K. Kanisawa, H. Yamaguchi, and Y. Hirayama, *ibid.* **76**, 589 (2000); S.J. Chung, M.A. Ball, S.C. Lindstrom, M.B. Johnson, and M.B. Santos, J. Vac. Sci. Technol. B **18**, 1583 (2000); T.W. Kim, H.C. Bae, and H.L. Park, Appl. Phys. Lett. **74**, 380 (1999); J. Huerta, M. Lopez, and O. Zelaya-Angel, J. Vac. Sci. Technol. B **18**, 1716 (2000).

[25] S. Sanvito and N.A. Hill, Appl. Phys. Lett. **78**, 3493 (2001); Phys. Rev. Lett. **87**, 267202 (2001).

[26] B. Grandidier, J.P. Nys, C. Delerue, D. Stievenard, Y. Higo, and M. Tanaka, Appl. Phys. Lett. **77**, 4001 (2000); S.J. Potashnik, K.C. Ku, S.H. Chun, J.J. Berry, N. Samarth, and P. Schiffer, *ibid.* **79**, 1495 (2001).

[27] K.C. Cadien, J.L. Zilko, A.J. Eltoukhy, and J.E. Greene, J. Vac. Sci. Technol. **17**, 441 (1980); J.L. Zilko and J.E. Greene, J. Appl. Phys. **51**, 1549 (1980); J.L. Zilko and J.E. Greene, *ibid.* **51**, 1560 (1980).