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# Half-metallic ferromagnetism in zinc-blende CrBi and the stability of the half-metallicity of zinc-blende CrM (M = P, As, Sb, Bi)

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## Abstract

First-principles calculations within density-functional theory are used to investigate zinc-blende-structured CrBi. Our calculation predicts ZB-type CrBi to be a true half-metallic ferromagnet with a magnetic moment of  $3 \mu_B$  per formula. Its half-metallicity can be maintained over a relatively wide range of lattice constant (from  $-8$  to  $8\%$ ). The trends with varying lattice constant for the ZB-type half-metallic system CrM (M = P, As, Sb, Bi) are also studied.

## 1. Introduction

There has been increasing interest in highly spin-polarized ferromagnets since these materials recently showed potential for technical applications in spin-based electronic devices [1, 2] which offer opportunities for producing a new generation of multifunctional devices combining traditional charge-based microelectronics with spin-dependent effects. As ideal materials for use in such devices, the half-metallic ferromagnets are attracting more and more attention; the majority-spin band is metallic while the minority-spin band is semiconducting, leading to complete spin polarization at the Fermi level. The behaviour of half-metallic ferromagnets was first predicted by de Groot *et al* [3], based on band calculations for the  $C1_b$ -type Heusler alloys NiMnSb and PtMnSb. Various half-ferromagnets have been discovered and investigated, such as semi-Heusler and full-Heusler alloys [4, 5], CrO<sub>2</sub> [6], and transition metal perovskites [7, 8]. A great effort is now being made to find new members of this family of half-metallic ferromagnets.

Recently, Akinaga *et al* [9] found a new possibility, based on first-principles calculations, which suggested zinc-blende-type (ZB-type) CrAs was a half-metallic ferromagnet, and succeeded in fabricating film on a GaAs substrate. In a similar way, the ferromagnetism of ZB-type CrSb film was then investigated [10].

In the present paper, we have studied ZB-type CrBi, which has not been reported on yet, and predicted it to be a true half-metallic ferromagnet; the trends with varying lattice constant for the ZB-type half-metallic system CrM ( $M = \text{P, As, Sb, Bi}$ ) are also studied.

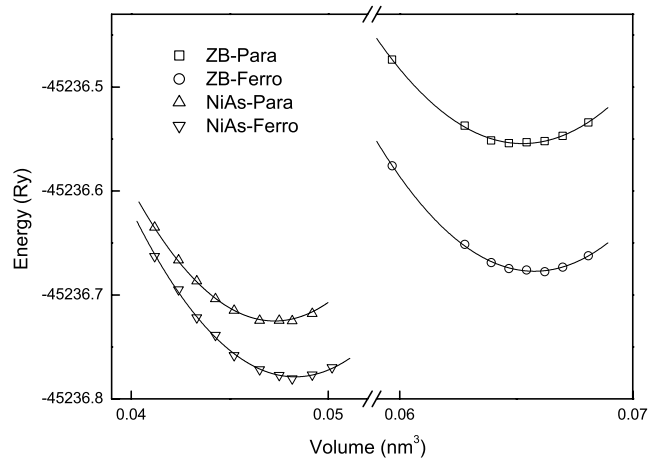
## 2. Half-metallic ferromagnetism

### 2.1. Computational details

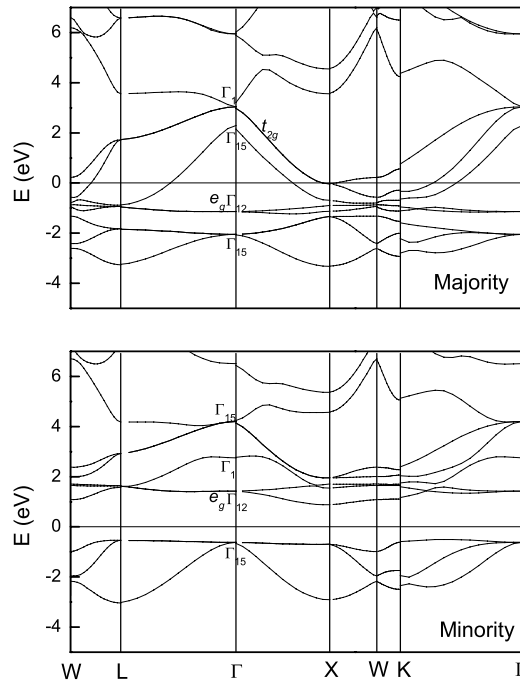
The first-principles electronic band-structure calculations in the present work are based on the local spin density approximation (LSDA) for the exchange–correlation potential. As reported by Galanakis *et al* [11], although the generalized gradient approximation (GGA) could give better results than the LDA as regards the lattice parameters [12], the LDA calculations are able to obtain the same results as the GGA ones for the gap and the position of the Fermi level if the same lattice parameter is adopted. Furthermore, as seen in the following results, it is found that half-metallic ferromagnetism can be maintained over a relatively wide range of lattice constants. So the use of the LSDA calculation should be considered adequate for accurately describing the situations considered here. We use the full-potential linear augmented-plane-wave plus local orbitals (FLAPWLO) method [12], where the potential and/or the charge density in the crystal are treated with no shape approximation. The muffin-tin sphere radii  $R$  used are 2.4 au for both Cr and M atoms. Inside the atomic spheres the charge density and the potential are expanded in crystal harmonics up to  $l = 6$ . The radial basis functions for each LAPW are calculated up to  $l = 10$  and the non-spherical potential contribution to the Hamilton matrix has an upper limit of  $l = 4$ . The Brillouin-zone integration is done with a modified tetrahedron method [13] and we use 60  $k$ -points in the first irreducible Brillouin zone (IBZ). The density plane-wave cut-off is  $RK_{\max} = 8.0$ . The relativistic effect is taken into account because of the heavy atom Bi, but the spin–orbital coupling is neglected in the results presented in this work because it does not influence the half-metallic ferromagnetism. The self-consistency is better than  $0.001 \times 10^{-3} e \text{ au}^{-3}$  for charge density and spin density, and the stability is better than 0.01 mRyd for the total energy per cell.

### 2.2. Half-metallic ferromagnetism in ZB-type CrM

**2.2.1. Lattice parameters and total energy.** Turning our attention to the structural properties, we calculate the total energy for NiAs-type and ZB-type CrBi as a function of the volume per formula unit, and the total energy for paramagnetic and ferromagnetic states as a function of the volume per formula unit is also obtained, as shown in figure 1. We find that the paramagnetic NiAs phase is about 2.2 eV per formula unit more stable than the paramagnetic ZB phase, with an equilibrium volume of  $0.0473 \text{ nm}^3$ . The equilibrium volume of paramagnetic ZB-type CrBi is  $0.0651 \text{ nm}^3$ ; and the ferromagnetic NiAs phase is about 1.3 eV per formula unit more stable than the ferromagnetic ZB phase, with an equilibrium volume of  $0.0483 \text{ nm}^3$ . ZB-type CrBi has the much larger equilibrium volume of  $0.0658 \text{ nm}^3$ . Hence, the equilibrium structures for the paramagnetic and ferromagnetic states of CrBi are both NiAs phases, and the ferromagnetic state of ZB-type CrBi is metastable. It is worth noting that there is a relatively large energy barrier and also a big difference in cell volume between the equilibrium and the ZB-type phases, which would be expected to have important effects on the applications. Here we must note that within the LDA the equilibrium lattice constant is known to be underestimated by a



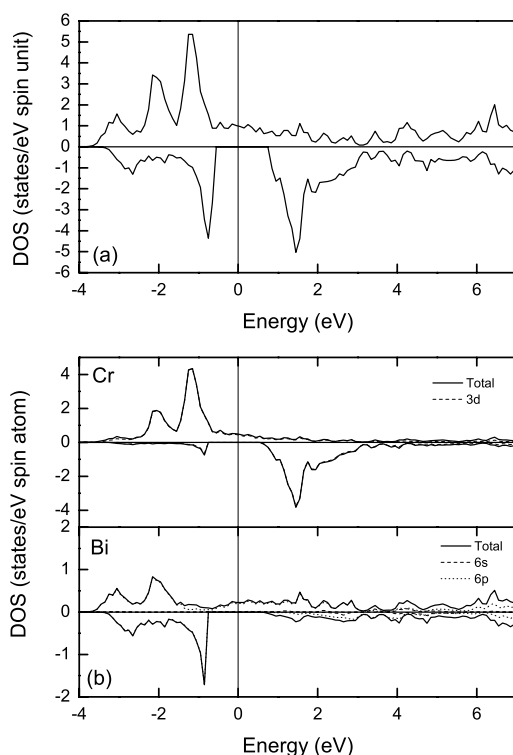
**Figure 1.** The structure optimization per formula as a function of the volume per formula. ‘ZB-Para’, ‘ZB-Ferro’, ‘NiAs-Para’, and ‘NiAs-Ferro’ stand for the ZB-type paramagnetic, ZB-type ferromagnetic, NiAs-type paramagnetic, and NiAs-type ferromagnetic phases, respectively.



**Figure 2.** The band structure of ZB CrBi at the predicted equilibrium lattice constant. Note that the valence band arising from the s orbitals on Bi sites is very low in energy and not presented.

few per cent [14] (the so-called overbinding); thus the real lattice constant of such materials would be as much as 3% larger.

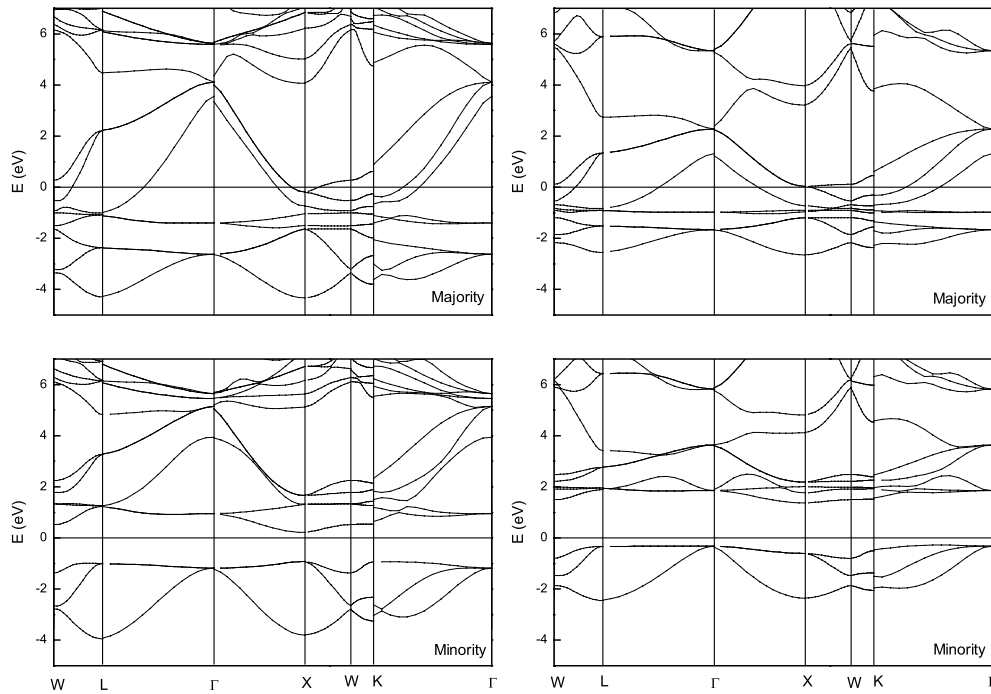
**2.2.2. Electronic structure.** In figure 2 we present the band structure at its equilibrium lattice constant for ferromagnetic CrBi with the ZB-type lattice structure. In the ZB structure [15],



**Figure 3.** The total (upper panel) and partial (lower panel) spin-resolved DOS of ZB CrBi at its predicted equilibrium lattice constant. There is a gap of approximately 1.38 eV width around the Fermi level for the minority-spin direction.

the tetrahedral environment allows its  $t_{2g}$  states ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$ ) to hybridize with the p states of the four first neighbours (Bi atoms). This creates a large bonding–antibonding splitting, with the low-lying bonding states being more of p character around the Bi neighbours, and the antibonding being rather that of the Cr atom ( $d_{z^2}$  and  $d_{x^2-y^2}$ ). The positions of the gap will be different for majority and minority electrons due to the exchange splitting. The s states of Bi are very low in energy and not presented in figure 2. As seen in figure 2, there are three minority-spin and five majority-spin fully filled bands above  $-5$  eV. The  $\Gamma_1$  bands, corresponding to the Cr s states, are pushed above the Fermi level by the interaction with the Bi s electrons [15]. The three fully filled minority-spin bands ( $\Gamma_{15}$ ) and the three fully filled majority-spin bands ( $\Gamma_{15}$ ) reflect the strong bonding between the Cr d and the Bi p electrons, and do not contribute to the total magnetic moment. The two narrow majority-spin bands ( $\Gamma_{12}$ ) around  $-1.1$  eV and minority-spin bands around  $+1.4$  eV are mainly of Cr d  $e_g$  character; these are separated from each other by 2.5 eV due to the exchange interaction and are quite flat, reflecting the fact that their hybridization with the states of Bi neighbours is weak (or even zero, at  $\mathbf{k} = 0$ , due to the symmetry [15]). Above them the substantially wider antibonding due to the Bi p and Cr d  $t_{2g}$  hybridization appears, starting from  $-0.8$  eV for majority bands and  $+2$  eV for minority bands. Their large bandwidth can be attributed to the strong hybridization and to their high energy position. In addition, the magnetic moment of  $3.0 \mu_B$  results from the remaining three Cr d electrons.

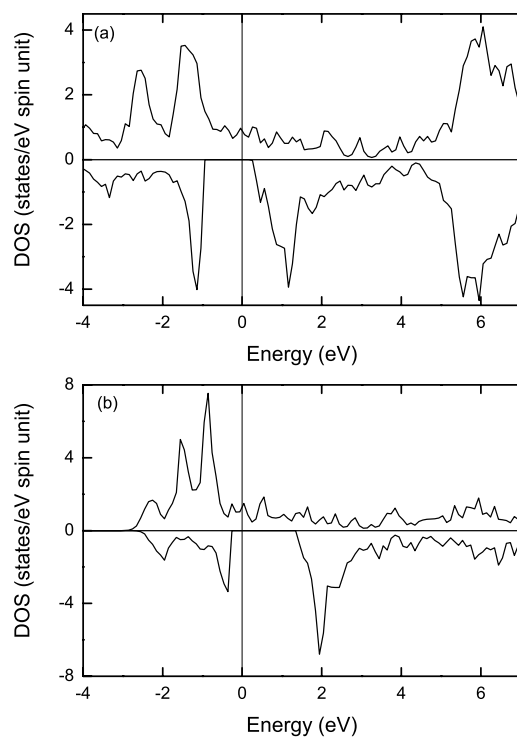
The spin-resolved total and partial DOS for ZB-type CrBi at its theoretical equilibrium lattice constant are shown in figure 3. It is obvious that the majority-spin bands are metallic



**Figure 4.** The band structure of ZB CrBi when we contract (left panel) or expand (right panel) the lattice constant by 8% with respect to its equilibrium value.

but the Fermi level is situated within an energy gap of 1.381 eV for the minority-spin bands. The bottom of the minority-spin conduction bands is located at +0.879 eV and the top of the minority-spin valence bands at  $-0.502$  eV. The gap for creating a minority-spin hole at the top of the minority-spin valence bands by exciting a minority-spin electron into the conducting majority bands is 0.502 eV, and the gap for a minority-spin electron at the bottom of the minority-spin conduction bands is +0.879 eV. As a result, the minimal energy gap for a spin-flip excitation is 0.502 eV. This non-zero spin-flip gap is the essential character for a true half-metallic ferromagnet. From comparing figures 3 and 2, it is known that two peaks around  $-2$  eV for the majority band and  $-0.7$  eV for the minority band result from the hybridization between the Bi p and Cr  $d_{2g}$  electrons, and another two peaks around  $-1.1$  eV for the majority-spin DOS and 1.4 eV for the minority-spin DOS originate from the Cr  $d_{e_g}$  states which cannot hybridize with Bi.

**2.2.3. Variation of lattice constants for the half-metallic system CrM ( $M = P, As, Sb, Bi$ ).** Compounds such as CrAs [9, 16], CrSb [10], MnAs [17], MnSb [18, 19], and MnBi [20] have been synthesized for various studies by the molecular beam epitaxy (MBE) method. Although we have shown that the bulk ZB-type CrBi could be a true half-metallic and metastable ferromagnet at its equilibrium lattice constant, in practice in order to find some synthesis technique for stabilizing its metastable phase, we must investigate the sensitivity of this half-metallic state to the lattice constant. To pursue this, we have performed calculations of the band structures (figures 4 and 5) when the lattice constant is contracted or expanded by 8%, and we have re-checked the lattice constant dependence of the magnetic moment, spin-flip gap, and energy gap for the half-metallic system CrM ( $M = P, As, Sb, Bi$ ) (figure 6). Moreover, the

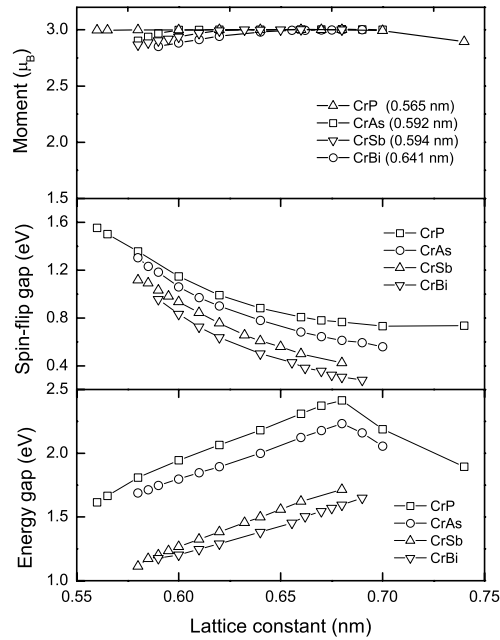


**Figure 5.** The total spin-resolved DOS of ZB CrBi when we contract (top panel) or expand (bottom panel) the lattice constant by 8% with respect to its equilibrium value.

equilibrium lattice constants for CrM ( $M = \text{P, As, Sb, Bi}$ ) have also been re-calculated, and they are marked in figure 6.

Comparing figures 2 and 4, upon contracting, the main feature is that the bandwidth of the three fully filled majority-spin bands and the  $e_g$  bands increases and the energy gap between them in the minority-spin band decreases somewhat. The position of the Fermi level will be moved higher in energy and the half-metallicity will be destroyed when the Fermi level moves into the minority  $e_g$  bands. In addition, it is worth noting that an energy gap can be presented even if the half-metallicity is destroyed upon contraction; i.e., for ZB-type CrAs the gap is 1.433 eV but the top of the gap is located at  $-0.123$  eV when the lattice constant is contracted by 8% with respect to the equilibrium value. This trend can be further demonstrated using the spin-resolved DOS calculation. Comparing figures 3 and 5, it is clear that either expansion or contraction results in a practically rigid shift of the bands with small rearrangements of the shape of the peaks to account for the charge neutrality. Expansion moves the Fermi level deeper in energy, i.e., closer to the minority occupied states, while contraction moves the Fermi level higher in energy. This can be understood on the basis of the behaviour of the p electrons of the Bi atom [11]. When we make an expansion, we expand mainly the delocalized p electrons of Bi, as the d electrons of the 3d transition metal Cr atom are well localized. So the Bi p states move deeper in energy compared to the d electrons of the transition metal Cr, and due to the charge neutrality the Fermi level also moves deeper in energy compared to the equilibrium lattice constant case.

In the middle and the lower panels of figure 6, the lattice constant dependences of the spin-flip gap and the energy gap are shown. The spin-flip gap decreases upon expanding, but the energy gap increases upon expanding at the beginning and afterwards decreases when



**Figure 6.** The lattice dependence of the magnetic moment (upper panel), spin-flip gap (middle panel), and energy gap (lower panel); the predicted equilibrium lattice constants of CrM ( $M = \text{P, As, Sb, Bi}$ ) are given in parentheses in the upper panel.

the lattice constant becomes larger than a critical value, i.e., 0.68 nm for CrP and CrAs. Furthermore, at the same lattice constant, the trend is that for the lighter sp atom the energy gap and the spin-flip gap are both larger than those of the heavier sp atoms, as can be seen in figure 6, for  $\text{CrP} > \text{CrAs} > \text{CrSb} > \text{CrBi}$ . In the upper panel of figure 6, the lattice constant dependence of the magnetic moment for ZB-type CrM ( $M = \text{P, As, Sb, Bi}$ ) is plotted. On the whole, the moments almost continue to be  $3 \mu_{\text{B}}$  although a slight decrease occurs when the lattice constant is contracted severely. From the band-structure calculation, we see that the half-metallicity can be retained for variation of the lattice constant from  $-4$  to  $30\%$  for CrP, from  $-5$  to  $18\%$  for CrAs, from  $-6$  to  $15\%$  for CrSb, and from  $-8$  to  $8\%$  for CrBi. In general, because of the physical errors in the LSDA potential, there would be some calculation errors, but the relative lattice constant error must be less than  $3\%$  in these accurate full-potential DFT calculations [14]. However, the LSDA-DFT calculation usually underestimates the gap by  $30\text{--}60\%$  [21]. Thus, we conclude that the ZB-type CrBi is unquestionably a true half-metallic ferromagnet, beyond any theoretical error. Furthermore, it is worth noting that in the present calculations the spin-orbital coupling is not taken into account, as it is expected to play an important role in the electronic structure. The spin-orbital coupling can lift the band degeneracy [11], but when the energy gap is sufficiently large, the spin-orbital coupling does not destroy the half-metallicity, as has been confirmed by [15, 21–23]. Hence, the spin-orbital coupling is neglected, since this would greatly complicate the plots and the discussion of the band structure without really changing the overall physics [22].

### 3. Summary and conclusions

We have investigated CrBi with the ZB structure in the ferromagnetic configuration, and predict it to be a true half-metallic ferromagnet with a magnetic moment of  $3 \mu_{\text{B}}$  per formula.



This behaviour is attributed to the strong hybridization between the Cr  $d_{t_2g}$  states and the Bi  $p$  states, conspiring with the large exchange splitting of the narrow and flat Cr  $e_g$  states which is very important for the formation of the ferromagnetism.

We have studied the trends with varying lattice constant for the ZB-type half-metallic system CrM ( $M = P, As, Sb, Bi$ ). The results show that the spin-flip gap increases upon contracting, and that the Fermi level moves upwards and finally would move into the minority  $e_g$  band and destroy the half-metallicity, but moves downwards with expansion. For all compounds of CrM ( $M = P, As, Sb, Bi$ ), their half-metallicity can be maintained over a relatively wide range of lattice constant, and it is clear that this property is very important for the film growth and applications. After taking the theoretical errors into consideration, ZB-type CrBi can be seen as a possible new half-metallic material. But we must also note that, according to our calculations, it seems very difficult to grow CrBi in the ZB phase as a half-metal, due to the relatively large energy barrier and big difference in cell volume between NiAs and the ZB phase.

### Acknowledgment

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### References

- [1] Wolf S, Awschalom D D, Buhrman R A, Daughton J M, von Molnar S, Roukes M L, Chtchelkanova A Y and Teger D M 2002 *Science* **294** 1488
- [2] Awschalom D D and Kikkawa J M 1999 *Phys. Today* **52** June 33
- [3] de Groot R A, Mueller F M, van Engen P G and Buschow K H J 1983 *Phys. Rev. Lett.* **50** 2024
- [4] Borca C N, Komesu T, Jeong H, Dowben P A, Ristoiu D, Hordequin C, Pierre J and Nozières J P 2000 *Appl. Phys. Lett.* **77** 88
- [5] Ambrose T, Krebs J J and Prinz G A 2000 *Appl. Phys. Lett.* **76** 3280
- [6] Brener N E, Tyler J M, Callaway J, Bagayoko D and Zhao G L 2000 *Phys. Rev. B* **61** 16582
- [7] Park J H, Vescovo E, Kim H J, Kwon C, Ramesh R and Venkatesan T 1998 *Nature* **392** 794
- [8] Soulen R J Jr, Byers J M, Osofsky M S, Nadgorny B, Ambrose T, Cheng S F, Broussard P R, Tanaka C T, Nowak J, Moodera J S, Barry A and Coey J M D 1998 *Science* **282** 85
- [9] Akinaga H, Manago T and Shirai M 2000 *Japan. J. Appl. Phys.* **39** L1118
- [10] Zhao J H, Matsukura F, Takamura K, Abe E, Chiba D and Ohno H 2001 *Appl. Phys. Lett.* **79** 2776
- [11] Galanakis I, Dederichs P H and Papanikolaou N 2002 *Phys. Rev. B* **66** 134428
- [12] Hohenberg P and Kohn W 1964 *Phys. Rev. B* **136** 864  
Blaha P, Schwarz K, Sorantin P and Tricky S B 1990 *Comput. Phys. Commun.* **59** 399
- [13] Blöchl P, Jepsen O and Andersen O K 1994 *Phys. Rev. B* **49** 16223  
Blugel S, Akai H, Zeller R and Dederichs P H 1987 *Phys. Rev. B* **35** 3271
- [14] Asato M, Settels A, Hoshino T, Asada T, Blugel S, Zeller R and Dederichs P H 1999 *Phys. Rev. B* **60** 5202
- [15] Galanakis I and Mavropoulos P 2003 *Phys. Rev. B* **67** 104417  
Xu Y Q, Liu B G and Pettifor D G 2002 *Phys. Rev. B* **66** 184435
- [16] Mizuguchi M, Akinaga H, Manago T, Ono K, Oshima M and Shirai M 2002 *J. Magn. Magn. Mater.* **239** 269
- [17] Tanaka M, Harbison J P and Rothberg J M 1994 *Appl. Phys. Lett.* **65** 1964
- [18] Miyanishi S, Akinaga H, Van Roy W and Tanaka K 1997 *Appl. Phys. Lett.* **70** 2046
- [19] Mizuguchi M, Akinaga H, Ono K and Oshima M 2000 *Appl. Phys. Lett.* **76** 1743
- [20] Hayashi R, Terayama K, Ishibashi T and Sato K 1999 *J. Magn. Soc. Japan* **23** 99
- [21] Liu B G 2002 *Preprint cond-mat/0206485*
- [22] Continenza A, Picozzi S, Geng W T and Freeman A J 2001 *Phys. Rev. B* **64** 085204
- [23] Sanvito S and Hill N A 2000 *Phys. Rev. B* **62** 15553