

## Half-metallic ferromagnetism in vanadium chalcogenides

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 5085

(<http://iopscience.iop.org/0953-8984/15/29/320>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.121

The article was downloaded on 19/05/2010 at 14:20

Please note that [terms and conditions apply](#).

# Half-metallic ferromagnetism in vanadium chalcogenides

Wen-Hui Xie and Bang-Gui Liu

Institute of Physics and Centre of Condensed Matter Physics, Chinese Academy of Sciences,  
Beijing 100080, People's Republic of China

E-mail: wenhui.xie@hotmail.com

Received 2 April 2003, in final form 11 June 2003

Published 11 July 2003

Online at [stacks.iop.org/JPhysCM/15/5085](http://stacks.iop.org/JPhysCM/15/5085)

## Abstract

Using an accurate density-functional method, we systematically explore vanadium chalcogenides in various crystal structures in order to find half-metallic (HM) ferromagnets which could possibly be fabricated as thin films with a thickness sufficient for real spintronic applications. The zincblende and wurzite (WZ) phases of VTe and the WZ phase of VSe are found to be HM ferromagnets with a magnetic moment of  $3.000 \mu_B$ /formula unit. Their HM gaps of, respectively, 0.31, 0.60, and 0.25 eV are 0.53, 0.56, and 0.52 eV higher in total energy/formula unit than the ground-state NiAs phase of VTe and therefore could possibly be realized in the form of films with great enough thickness. Their HM ferromagnetism persists even when the volume is compressed by 10, 20, and 5%. As they are compatible with the well-known binary semiconductors, these HM ferromagnetic phases, when realized experimentally, may be useful in spintronic applications.

## 1. Introduction

Half-metallic (HM) ferromagnets, in which one of the two spin channels is metallic, while the other has an energy gap around the Fermi energy, are attracting more and more attention because of their potential in spintronic applications [1, 2]. Since de Groot and co-workers first predicted in 1983 HM ferromagnetism in Heusler compounds NiMnSb [3, 4], HM ferromagnetism has also been found in mixed valence perovskites  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  [5], in ferromagnetic metallic oxides such as  $\text{Fe}_3\text{O}_4$  [6] and  $\text{CrO}_2$  [7], and in dilute magnetic semiconductors [8, 9]. Recently, binary Mn pnictides with zincblende (ZB) crystal structure have been intensively studied theoretically and experimentally for possible applications to spintronics [10–12]. It was found that ZB MnAs was a so-called ‘nearly HM’ ferromagnet [12], but MnSb, MnBi, CrAs, and CrSb in the ZB structure were true HM ferromagnets with a finite HM gap [13–17]. Although the ground-state phases of MnAs, CrAs, and CrSb have the NiAs structure [18, 19], the ZB phases of MnAs [11], CrAs [16, 20], and CrSb [21] have been successfully fabricated in the

form of thin films or nanostructures on III–V semiconductor substrates. There have even been some density-of-states (DOS) reports claiming HM ferromagnetism in other binary compounds with the ZB structure [17]. For spintronic applications, it is highly desirable to find new HM ferromagnets that, on the one hand, can be realized in the form of bulk or at least film and, on the other hand, are compatible with important III–V and II–VI binary semiconductors.

In this paper, we focus on a systematic study of vanadium chalcogenides in various crystal structures by means of the accurate full-potential (linear) augmented plane wave plus local orbitals (FLAPWLO) method within the density-functional theory. We shall show that the wurzite (WZ) and ZB phases of VTe and the WZ phase of VSe are found to be HM ferromagnets with a magnetic moment of  $3.000 \mu_B$ /formula unit. The HM gaps of the WZ VTe, ZB VTe and WZ VSe are 0.6, 0.31, 0.25 eV at their equilibrium lattices and persist even when compressed by 20, 10, or 5% in relative volumes, respectively. With our accurate systematic results we predict that it should be possible to fabricate the ZB and WZ VTe phases with true HM ferromagnetism in the form of films with sufficient thickness, because they are 0.53 and 0.56 eV higher in total energy/formula unit than the ground-state NiAs phase of VTe, respectively, and furthermore are harder than the ZB CrAs phase which has already been fabricated using the epitaxial technique. Since they are compatible with the binary III–V and II–VI semiconductors, they should be useful to spin electronics in the future.

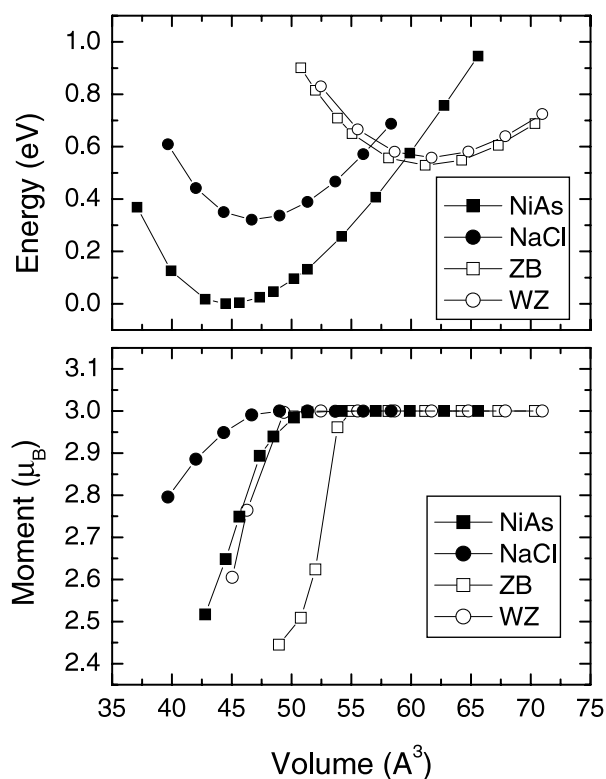
In the next section we present our calculation details. In section 3 we present our main theoretical findings. In section 4 we show the electronic structures of the four VTe phases. In section 5 we discuss the mechanism of HM ferromagnetism in these three phases. Finally, in section 6 we present our conclusion.

## 2. Calculation details

We make use of the Vienna package WIEN2k [22] for the FLAPWLO method within density-functional theory (DFT) [23] for all our calculations. We took the generalized gradient approximation (GGA) proposed in 1996 by Perdew, Burke and Ernzerhof (PBE96) [24]. The relativistic effect was taken into account in the scalar approximation, but the spin–orbit coupling was neglected in the results presented in this paper because the energy bands of the heavy atoms (Te and Se) are deep enough below the Fermi level so that the spin–orbit effect is very small in these cases. 3000  $k$ -points are used in the Brillouin zone for the NaCl and ZB structures and 1000  $k$ -points for NiAs and WZ. We took  $R_{\text{mt}} \times K_{\text{max}}$  as 8.0 and made the expansion up to  $l = 10$  in the muffin tins. The radii  $R_{\text{mt}}$  of the muffin tins was chosen to be 2.3 (V) and 2.5 (Te, Se) bohr, respectively.

## 3. Main findings

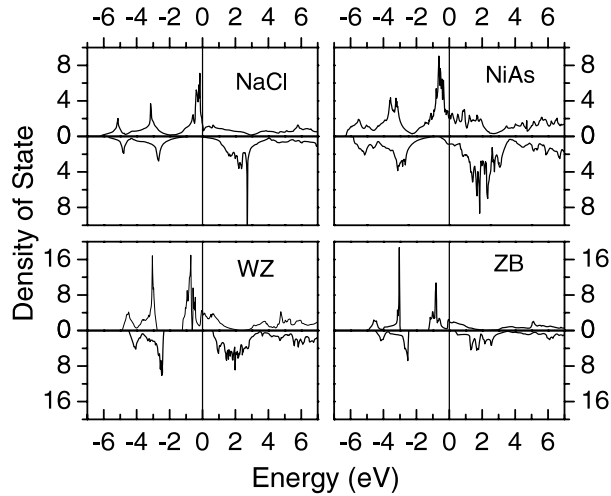
It was found that the WZ and ZB VTe and WZ VSe phases are HM ferromagnets. Since the VTe phases are better than the VSe phase, in the following we mainly present the computational results for VTe. The total energy of the four VTe phases as functions of formula volume are shown in the upper panel of figure 1. Only the ferromagnetic phases are presented because the nonmagnetic and antiferromagnetic phases are always higher in total energy. There has not yet been any experimental report on the ground-state phase of VTe. The total energy of the NiAs phase is lowest in energy among the four phases and is taken as the ground-state phase. The equilibrium lattice constants for the NiAs and WZ phases are  $a = 4.13 \text{ \AA}$ ,  $c = 6.07 \text{ \AA}$  ( $c/a = 1.47$ ), and  $a = 4.42 \text{ \AA}$ ,  $c = 7.28 \text{ \AA}$  ( $c/a = 1.65$ ), respectively, by means of systematical energy optimization. The optimized  $c/a$  value (1.47) for the NiAs phase is much



**Figure 1.** The total energy (upper panel) and the magnetic moments (lower panel)/formula as functions of the formula volume in the case of VTe. The solid squares, solid circles, open squares and open circles are for the NiAs, NaCl, ZB, and WZ phases, respectively. The optimized volumes (moments) are  $44.83 \text{ \AA}^3$  ( $2.65 \mu_B$ ),  $46.92 \text{ \AA}^3$ , ( $2.99 \mu_B$ ),  $61.65 \text{ \AA}^3$ , ( $3.000 \mu_B$ ), and  $61.77 \text{ \AA}^3$ , ( $3.000 \mu_B$ ) for the four phases, respectively.

smaller than the  $c/a$  value (1.633) in the perfect NiAs structure. The short  $c$ -axis originates from the interaction between metal layers of the hexagonal crystal structure. Predicted lattice constants for cubic NaCl and ZB phases are 5.73 and 6.27 Å, respectively. Relative to the NiAs phase, the NaCl phase is always 0.3 eV higher in energy/formula unit. The equilibrium volumes of the WZ and ZB VTe phases are almost the same, with their difference being only  $0.01 \text{ \AA}^3$ , while the difference in the equilibrium volumes of the NiAs and NaCl VTe phases is  $2 \text{ \AA}^3$ . The WZ and ZB phases are more favourable in energy when the cell volume goes beyond  $60 \text{ \AA}^3$ . The WZ and ZB phases of VTe are 0.56 and 0.53 eV higher in energy/formula unit than the ground-state NiAs phase of VTe.

The dependence of the magnetic moments on the formula volume is illustrated in the lower panel of figure 1. The moments are an integer, 3.000, in the units of  $\mu_B$  at the equilibrium volumes for WZ and ZB VTe, and remain unchanged down to 49 and  $55 \text{ \AA}^3$ , or  $-20$  and  $-10\%$  in relative volumes, respectively. The net moment of  $3.000 \mu_B$  results from the remaining three of the 3d plus 2s electrons of vanadium bonding with the four Te p electrons. The moments of NiAs and NaCl VTe are  $2.65$  and  $2.99 \mu_B$  at their equilibrium volumes, respectively. With increasing volume, the moments of the NiAs and NaCl VTe become integer at 52 and 49 Å, respectively. This implies that the HM magnetism can occur if the NaCl and NiAs VTe phases are realized with expanded lattices. The main properties of the four phases of VTe are summarized in table 1.



**Figure 2.** The spin-dependent total density of states (DOS,  $\text{eV}^{-1}/\text{formula unit}$ ) of the NaCl, NiAs, WZ, and ZB phases of VTe at their equilibrium volumes, respectively. In the upper part of every panel shown are the majority-spin DOS between  $-7$  and  $7$  eV and the lower part the minority-spin DOS. It is clear that the NaCl phase is of nearly HM ferromagnetism and the WZ and ZB phase are of true HM ferromagnetism.

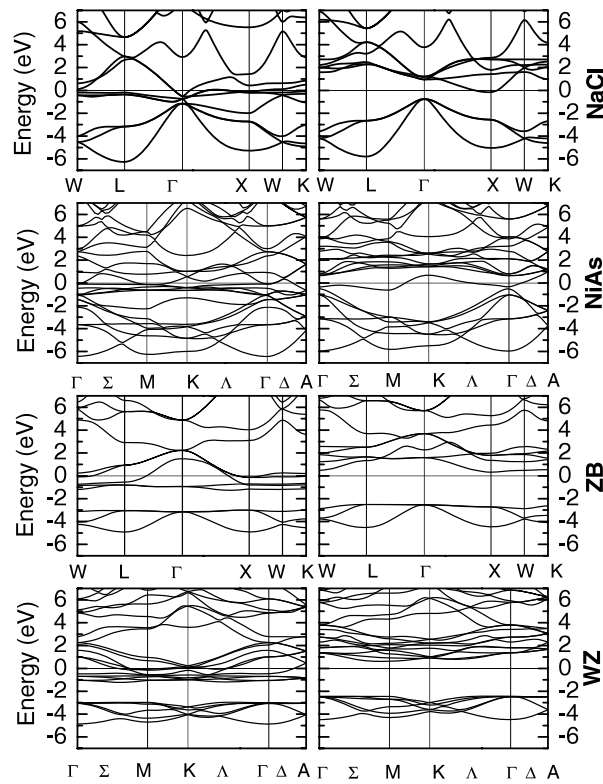
**Table 1.** The predicted equilibrium volumes/formula unit ( $V_0$ ), magnetic moment/formula unit ( $M$ ), HM gap ( $E_g$ ), and metastable energy/formula unit ( $E_t$ ) of the four phases of VTe and the WZ VSe phase at their equilibrium volumes.

Phase	$V_0$ ( $\text{\AA}^3$ )	$M$ ( $\mu_B$ )	$E_g$ (eV)	$E_t$ (eV)
NiAs VTe	44.83	2.65	—	0.00
NaCl VTe	46.92	2.99	—	0.32
ZB VTe	61.65	3.000	0.31	0.53
WZ VTe	61.77	3.000	0.60	0.56
WZ VSe	48.66	3.000	0.25	0.52

#### 4. Electronic structures of VTe

Figure 2 shows that the Fermi energy crosses majority-spin bands in all four VTe phases. The partly filled majority-spin bands provide the conductive electrons and at the same time contribute to the magnetic moment. The distribution of the ZB DOS is similar to that of the WZ DOS, and the NaCl DOS is also similar to the NiAs DOS. This results from the same local structure of the cubic ZB and the hexagonal WZ structure. A vanadium atom and its nearest Te construct a tetrahedron in the cases of the ZB and WZ structures, but a vanadium atom and its nearest Te construct an octahedron in the cases of the cubic NaCl and the hexagonal NiAs structures. The detailed partial DOS will show that the DOS distributions of the five d orbitals in the WZ VTe phase are similar to each other because of the more symmetrical coordination.

In the cubic crystal field, the anion p states have  $t_2$  ( $\Gamma_{25'}$ ) symmetry and the metal d states are split into a doublet with  $e$  ( $\Gamma_{12}$ ) symmetry and a triplet with  $t_2$  ( $\Gamma_{25'}$ ) symmetry. In the tetrahedral coordinated ZB phase, the  $e$  states are lower than the  $t_2$  states and there is no p-d hybridization between them, but the  $t_2$  states are lower than the  $e$  states in the octahedral coordinated NaCl phase. Furthermore, the  $t_2$  triplet states are split into singlet and doublet states in hexagonal NiAs and WZ phases because of their hexagonal crystal symmetry. In



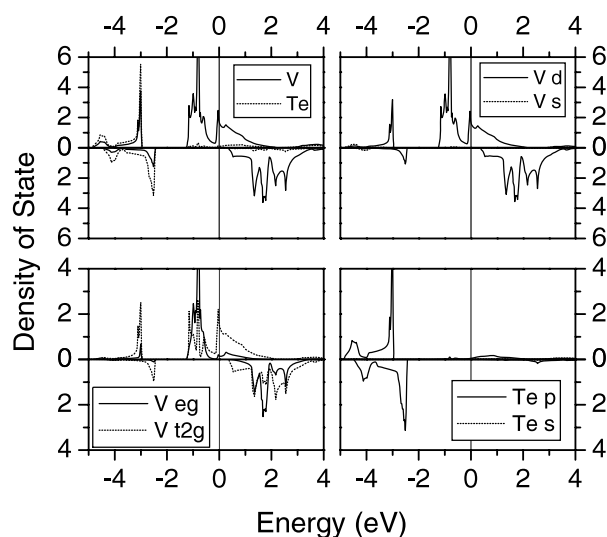
**Figure 3.** The spin-dependent energy bands in the high-symmetry directions of the equilibrium NaCl (top row panels), NiAs (second row), ZB (third row), and WZ (bottom row) phases. In the left panels are shown the majority-spin bands and in the right panels the minority-spin bands.

the NiAs structure, the singlet states ( $d_{z^2}$ ) are lower in energy than all the doublet states, corresponding to the interlayer interaction of metal atoms in the hexagonal structure. In the hexagonal WZ phase, the  $e$  doublet states are lower in energy than the  $t_2$  singlet and doublet states.

Figure 3 shows the spin-dependent bands of the four VTe phases. The ZB bands resemble those of the ZB transition-metal pnictides with HM ferromagnetism. Most important for the HM ferromagnetism are the spin exchange splitting of the  $d$  electrons and the strong interaction of the  $p$  electrons and the  $d$  electrons. However, the HM ferromagnetism is strongly dependent on the detailed band structure. In the NiAs phase, the Fermi level intersects the separated  $d_{z^2}$  singlet in the minority-spin bands, so that there is no HM ferromagnetism at the equilibrium volume. The NaCl phase has the so-called nearly HM ferromagnetism resulting from its expanded minority-spin  $t_{2g}$  bands. Both WZ and ZB phase are of robust HM ferromagnetism. The minimal energy gap for a spin-flip excitation, or the HM gap, is 0.60 and 0.31 eV for the WZ and ZB phases, respectively.

## 5. Mechanism of HM ferromagnetism

The larger the cell volumes become, the narrower the  $d$  bands are and the larger the spin-flip gaps of the phases with HM ferromagnetism. In the cases of the NaCl and NiAs VTe phases,



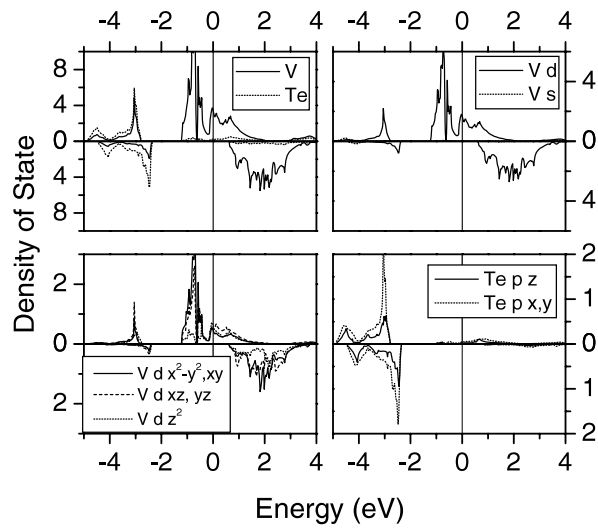
**Figure 4.** The spin-dependent partial DOS ( $\text{eV}^{-1}/\text{formula unit}$ ) of the HM ZB phase of VTe at the equilibrium volume. In every one of the four panels the upper part denotes the majority-spin DOS between  $-5$  and  $4$  eV and the lower part the minority-spin DOS.

d electrons transfer from minority-spin bands to majority-spin bands with increasing volume, so that their minority-spin bands are pushed to high energy and the p–d hybridization gap becomes wide, and then the true HM ferromagnetism appears when their volumes become large enough. Because the tetrahedral coordination results in a larger equilibrium volume than the octahedral coordination, the WZ and ZB phases have tight bands and therefore show true HM ferromagnetism. Moreover, the WZ phase shows more robust HM ferromagnetism than the ZB phase because its covalent band gap is  $0.1$  eV larger and its magnetic splitting is  $0.2$  eV larger than the ZB phase. Appropriate narrow d bands are important to the HM ferromagnetism.

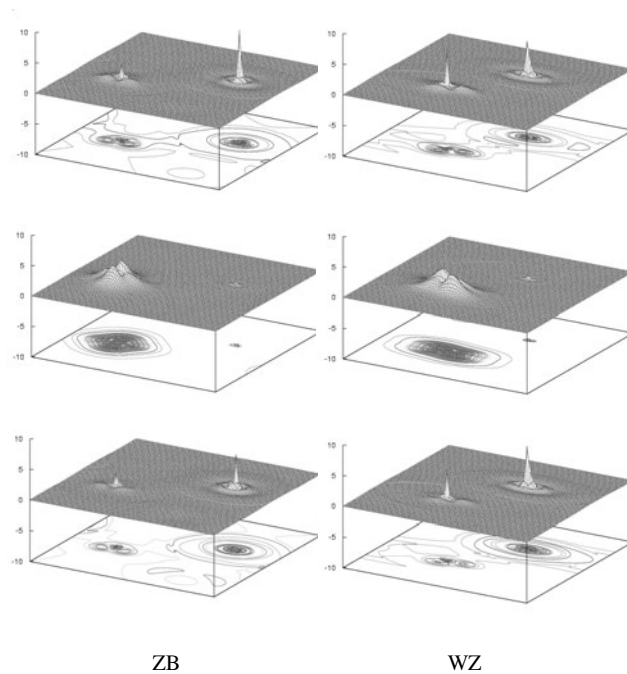
In order to understand the mechanism behind the HM ferromagnetism in the ZB and WZ phases of VTe, we present their detailed partial DOS in figures 4 and 5. It is clear that the partial DOS between  $-5$  and  $0$  eV can be divided into three parts for both ZB and WZ VTe phases. The first part, majority-spin DOS between  $-5$  and  $-2.7$  eV, originates mainly from Te p states. The second part, majority-spin DOS between  $-1.5$  and  $0$  eV, originates mainly from V d states, with the V s spectral weight being very small. The last part, minority-spin DOS between  $-4.5$  and  $-2$  eV, is mainly contributed by Te p states. The main features of the DOS results are shared by the two HM ferromagnetic phases of VTe. The spectral weight of vanadium s states between  $-2$  and  $0$  eV is reduced by the fact that vanadium s states are raised substantially in energy level because they have to be diagonal to the Te s states. These are supported by the spin-dependent charge distribution of the two phases of VTe with HM ferromagnetism, as demonstrated in figure 6. It is the spin exchange splitting that makes the ZB and WZ phases ferromagnets. The upward movement of minority-spin  $\Gamma_1$  bands mainly originating from V s states is also necessary to clean HM gaps in these phases.

## 6. Summary

In summary, our accurate DFT calculations show that the WZ VTe, ZB VTe, and WZ VSe phases are the metastable phases with HM ferromagnetism. In the case of VTe, all of the four phases studied here become HM ferromagnets at large enough volumes. This means that the



**Figure 5.** The spin-dependent partial DOS ( $\text{eV}^{-1}/\text{formula unit}$ ) of the HM WZ phase of VTe at the equilibrium volume. In every one of the four panels the upper part denotes the majority-spin DOS between  $-5$  and  $4$  eV and the lower part the minority-spin DOS.



**Figure 6.** The spin-dependent charge distributions of the ZB (left panels) and WZ (right panels) phases of VTe at their equilibrium volumes, respectively. In the top row panels are shown the charge distributions of the majority-spin bands around  $-3.5$  eV; in the middle row panels the majority-spin bands between  $-1.5$  and  $0$  eV; and in the bottom row panels the minority-spin bands around  $3$  eV.

HM ferromagnetism is not very dependent on specific crystal structures and therefore can be achieved in real environments where there are some lattice defects or impurities. However,



the total energies differences/formula unit, 0.56 and 0.53 eV, of the WZ VTe and ZB VTe phases from their ground-state phases are quite small with respect to that of the ZB CrAs phase (0.9 eV) [14]. On the experimental side, ZB CrAs and MnTe films have been fabricated successfully [25] using the epitaxial technique. Therefore, the two VTe phases with HM ferromagnetism could be fabricated in the form of films thick enough epitaxially on appropriate substrates, such as AlSb and ZnTe. Since they are compatible with the well-known binary semiconductors, these HM ferromagnets, when realized experimentally, should be useful in spin electronics and other applications.

### Acknowledgments

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

### References

- [1] Wolf S A, Awschalom D D, Buhrman R A, Daughton J M, von Molnár S, Roukes M L, Chtchelkanova A Y and Treger D M 2001 *Science* **294** 1488  
Osborne I S 2001 *Science* **294** 1483  
Awschalom D D and Kikkawa J M 1999 *Phys. Today* **52** 33
- [2] Pickett W E and Moodera J S 2001 *Phys. Today* **54** 39
- [3] de Groot R A, Mueller F M, van Engen P G and Buschow K H J 1983 *Phys. Rev. Lett.* **50** 2024
- [4] de Groot R A 1991 *Physica B* **172** 45
- [5] Coey J M D, Viret M and von Molnár S 1999 *Adv. Phys.* **48** 169
- [6] Yanase A and Sitarori H 1984 *J. Phys. Soc. Japan* **53** 312  
Soeya S, Hayakawa J, Takahashi H, Ito K, Yamamoto C, Kida A, Asano H and Matsui M 2002 *Appl. Phys. Lett.* **80** 823
- [7] Watts S M, Wirth S, von Molnár S, Barry A and Coey J M D 2000 *Phys. Rev. B* **61** 9621
- [8] Matsumoto Y, Murakami M, Shono T, Hasagawa T, Fukawara T, Kawasaki M, Ahmet P, Chikyow T, Koshihara S and Koinuma H 2001 *Science* **291** 854
- [9] Ohno H 1998 *Science* **281** 951
- [10] Plake T, Ramsteiner M, Kaganer V M, Jenichen B, Kästner M, Däweritz L and Ploog K H 2002 *Appl. Phys. Lett.* **80** 2523  
Sugahara S and Tanaka M 2002 *Appl. Phys. Lett.* **80** 1969
- [11] Ono K, Okabayashi J, Mizuguchi M, Oshima M, Fujimori A and Akinaga H 2002 *J. Appl. Phys.* **91** 8088
- [12] Sanvito S and Hill N A 2000 *Phys. Rev. B* **62** 15553  
Continenza A, Picozzi S, Geng W T and Freeman A J 2001 *Phys. Rev. B* **64** 085204  
Zhao Y J, Geng W T, Freeman A J and Delley B 2002 *Phys. Rev. B* **65** 113202
- [13] Xu Y-Q, Liu B-G and Pettifor D G 2002 *Phys. Rev. B* **66** 184435
- [14] Liu B-G 2003 *Phys. Rev. B* **67** 172411 (*Preprint cond-mat/0206485*)
- [15] Shirai M 2000 *Physica E* **10** 147  
Galanakis I, Dederichs P H and Papanikolaou N 2002 *Phys. Rev. B* **66** 134428
- [16] Akinaga H, Manago T and Shirai M 2000 *Japan. J. Appl. Phys.* **39** L1118
- [17] Galanakis I and Mavropoulos P 2003 *Phys. Rev. B* **67** 104417
- [18] Ravindran P, Delin A, James P, Johansson B, Wills J M, Ahuja R and Eriksson O 1999 *Phys. Rev. B* **59** 15680
- [19] Radhakrishna P and Cable J W 1996 *Phys. Rev. B* **54** 11940
- [20] Mizuguchi M, Akinaga H, Manago T, Ono K, Oshima M, Shirai M, Yuri M, Lin H J, Hsieh H H and Chen C T 2002 *J. Appl. Phys.* **91** 7917
- [21] Zhao J H, Matsukura F, Takamura K, Abe E, Chiba D and Ohno H 2001 *Appl. Phys. Lett.* **79** 2776
- [22] Blaha P, Schwarz K, Sorantin P and Trickey S B 1990 *Comput. Phys. Commun.* **59** 399
- [23] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864  
Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [24] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [25] Durbin S M, Han J, Sungki O, Kobayashi M, Menke D R, Gunshor R L, Fu Q, Pelekanos N, Nurmikko A V, Li D, Gonsalves J and Otsuka N 1989 *Appl. Phys. Lett.* **55** 2087  
Matsumoto T, Souno Y, Tatsuoka H, Nakanishi Y and Kuwabara H 2001 *Appl. Surf. Sci.* **169/170** 325