Half-metallic ferromagnetism in hypothetical wurtzite \( MBi (M=V, Cr, Mn) \)

Ming Zhang \(^a\)

Van der Waals-Zeeman Instituut, Universiteit van Amsterdam, Valckenierstraat 67, 1018XE Amsterdam, The Netherlands and State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People’s Republic of China

Ekkles Brück and Frank R. de Boer
Van der Waals-Zeeman Instituut, Universiteit van Amsterdam, Valckenierstraat 67, 1018XE Amsterdam, The Netherlands

Guangheng Wu
State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People’s Republic of China

(Apresented on 10 November 2004; published online 4 May 2005)

A theoretical study based on a first-principles band-structure calculation is carried out for the hypothetical wurtzite (WZ) \( MBi (M=V, Cr, Mn) \). The lattice parameters \( a \) and \( c \) are determined to be 0.4524 \( \text{nm} \)/0.7384 nm, 0.4496 \( \text{nm} \)/0.7352 nm, and 0.4508 \( \text{nm} \)/0.7367 nm for WZ VBi, CrBi, and MnBi, respectively. The total energy difference between wurtzite structure and NiAs phases are 0.95, 1.01, and 0.99 eV for VBi, CrBi, MnBi, respectively. WZ VBi and CrBi are found to be true half-metallic ferromagnets (HMFs) with the considerably wide half-metallic gap of 0.505 and 0.493 eV, but WZ MnBi is not HMF.

I. INTRODUCTION

Half-metallic ferromagnets (HMF) are expected to achieve high performance in spintronics, since they have only one electronic spin channel at the Fermi level and may show nearly 100\% spin polarization at quite high temperatures. \(^1\) After de Groot et al. \(^2\), predicted HMF in Heusler compounds in 1983, several HMFs have been theoretically predicted and experimentally fabricated in the laboratory. Some transition-metal oxides have also been predicted to be HMFs, i.e., \( \text{Fe}_2\text{O}_4 \), \( \text{CrO}_2 \) (Ref. 4) perovskites, \(^5\) and dilute magnetic semiconductors. \(^6\) Recently, it was found that zinc-blende (ZB) MnAs was a so-called nearly HMF, whereas MnSb, MnBi, CrAs, CrSb, and CrBi in the ZB structure were true HMFs. \(^7,8\) Therefore it is interesting to explore theoretically new HMFs with other structures. \(^9\)

In the present article, we systematically investigate \( MBi (M=V, Cr, Mn) \) in the wurtzite (WZ) structure by first-principles calculation within the density-functional theory (DFT). The calculations show that WZ VBi and CrBi are predicted to be robust half-metallic ferromagnets, but WZ MnBi does not show half-metallicity.

II. COMPUTATIONAL DETAIL

The first-principles electronic band-structure calculation in the present article is based on the density-functional theory (DFT) within the local spin density approximation for the exchange-correlation potential. \(^10\) We use the full-potential linearized augmented-plane-wave plus local orbitals method, \(^11,12\) where the potential and/or the charge density in the crystal are treated with no shape approximation. The relativistic effect is taken into account in the scalar style except for the spin-orbital coupling. Inside the atomic spheres the charge density and the potential are expanded in cubic harmonics up to \( l=6 \). The radial basis functions of each linearized augmented plane wave are calculated up to \( l=8 \) and the nonspherical potential contribution to the Hamilton matrix has an upper limit of \( l=4 \). The Brillouin-zone integration is done with a modified tetrahedron method \(^11\) and we use 3000 \( k \) points in the Brillouin zone. The density plane-wave cutoff is \( RK_{\text{max}} = 8.0 \). The self-consistency is better than 0.001 \( \text{me} /\text{a.u.} \) \(^3\) for charge density, and the stability is better than 0.01 mRy for the total energy per formula unit.

III. RESULTS AND DISCUSSIONS

In order to investigate the half-metallic ferromagnetism in WZ \( MBi (M=V, Cr, Mn) \), we optimize their lattice parameters by calculating the total energy as a function of the lattice parameter for the paramagnetic and ferromagnetic configurations. The predicted equilibrium lattice constants and the WZ and NiAs phases with the ferromagnetic states \( \Delta E_1 \), the paramagnetic states, and the ferromagnetic states for the WZ structure \( \Delta E_2 \) are tabulated in Table I. For WZ CrBi and MnBi the ferromagnetic phases are much more favorable in energy than the corresponding paramagnetic phases. But a quite small energy difference between the paramagnetic and ferromagnetic states is observed for WZ VBi, with \( \Delta E_2 \) reaching 0.71 eV. It is possible that the paramagnetic state is more favorable in practice.

All energy bands and density of states (DOS) are calculated with the optimized lattice parameters. Half-metallic ferromagnetism is found in WZ VBi and WZ CrBi. Due to the similarity of the electronic structure of WZ VBi and CrBi, for brevity, in the following we mainly focus on the computational electronic structure for WZ CrBi. Figure 1 shows the spin-dependent DOS for WZ CrBi. Majority-spin DOS between \( -4.2 \) and \( -1.5 \) eV and minority-spin DOS between

---

\(^a\)Electronic mail: zm_info@yahoo.com.cn
−3.8 and −0.5 eV originate mainly both from Bi 6p states, which also hybridizes with the Cr 3d states with the same symmetry. In the majority-spin component, Cr 3d states are mostly occupied; but in the minority-spin part, local and mostly nonhybridized Cr 3d states are found at around 1.2 eV above $E_F$.

Also, we can see from the energy bands of WZ CrBi, shown in Fig. 2, that the six minority-spin bands between −3.38 and −0.51 eV originate almost completely from Bi 6p states and most of the six majority-spin bands between −3.67 and 1.91 eV originate from the Bi 6p states. However, the narrow majority-spin bands between −1.3 and −0.4 eV are mainly of Cr 3d in character. It is clear that the majority-spin band is strongly metallic, while the minority-spin band shows a semiconducting gap, 1.332 eV, around $E_F$, and the half-metallic (HM) gap is 0.493 eV, which is determined as the minimum between the bottom energy of minority-spin conduction bands with respect to the Fermi level and the absolute values of the top energy of minority-spin valence bands. This gap is essential to a HMF. Xie et al.\textsuperscript{9} reported that for WZ structure the exchange splitting of the Cr $d$ bands could produce the ferromagnetism and further pushed the higher minority-spin bands above the Fermi energy, while the favorable DOS distribution of the majority-spin bands could make the Fermi energy to fell within the band gap, thus the HMF was formed.

Table I shows the spin-dependent DOSs of WZ VBi and MnBi. The band gaps, HM gaps, and spin magnetic moments are also tabulated in Table I. Since the Fermi level of WZ MnBi is located into the conduction bands, it does not show half-metallicity. It is worth noting that for WZ MnBi with expanding the volume of the unit cell, the real minority-spin gap can be obtained and the Fermi level can move toward lower energy, in other words, the half-metallicity can be obtained by expanding the volume of the unit cell to a very large extent. But WZ VBi is a true HMF with a considerably wide HM gap of 0.505 eV.

As seen in Fig. 1, the DOS of WZ CrBi is mainly characterized by the large exchange splitting of the Cr 3d states, which leads to the localized spin moment at the Cr site. In HMFs, the total magnetic moment should be an integer. As given in Table I, we notice that the total magnetic moments consist of three parts: the transition metal atoms, Bi atoms, and the interstitial regions, and the total moments contain integer Bohr magnetons of 2 and 3 $\mu_B$ for WZ VBi and CrBi.
The local moments at $M$ (V and Cr) and Bi atoms are antiparallel to each other. In addition, we also check the effects of the variation of the lattice parameter on the magnetic properties and furthermore the half-metallicity since the distortion of the lattice at the interface between the film and the substrate can often occur when this kind of materials are grown to be epitaxial films or heterostructures on the WZ semiconductors. The calculations show that the half-metallicity of WZ VBi and CrBi can be maintained when the volume of unit cell is contracted up to 10%, and the magnetic moments can be kept to be integer Bohr magnetons for a very large expansion (>20%) of the unit volume.

IV. SUMMARY

In this article, using an accurate full-potential density-functional method we explore systematically the hypothetical wurtzite (WZ) $MBi$ ($M$=V, Cr, Mn) in order to find half-metallic ferromagnets which can be fabricated as thin film with thickness large enough for spintronic applications. It is found from the total-energy calculation that the ferromagnetic state is more favorable than paramagnetic state for all compounds. The lattice parameters $a/c$ are 0.4524 nm/0.7384 nm, 0.4496 nm/0.7352 nm, and 0.4508 nm/0.7367 nm for WZ VBi, CrBi, and MnBi, respectively. WZ VBi and CrBi are found to be robust half-metallic ferromagnets with very large half-metallic gaps (0.505 and 0.493 eV), but WZ MnBi does not show half-metallicity. The magnetic moments for WZ VBi and CrBi are evaluated to be equal to 2 and 3 $\mu_B$ per formula unit as is expected for half-metallicity. The total energy difference between WZ VBi, CrBi and their ground-state phases are 0.95 and 1.01 eV, respectively. Since the wurtzite structure is compatible with III–V and II–VI semiconductors, these half-metallic ferromagnets of WZ VBi and CrBi would be useful in the spintronic applications if thin films of them can be grown epitaxially on the appropriate substrate.

ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China Grant Nos. 50271083 and 50201020, and also performed in the framework of the scientific exchange program between the People’s Republic of China and the Netherlands.


FIG. 3. Spin-dependent total DOSs of WZ VBi and MnBi at their predicted equilibrium lattice constants.