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The computational design of zinc-blende half-metals and their nanostructures

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Abstract

The influence of atomic disorder and heterointerfaces with III–V semiconductors on the electronic and magnetic properties of zinc-blende (ZB) CrAs is studied by *ab initio* calculations based on density-functional theory. Antisite Cr spins are coupled antiferromagnetically with the Cr spins at the ordinary sites, while the ferromagnetic coupling between the Cr spins at the ordinary sites is robust against defect formation. The degree of spin polarization is not reduced significantly by the impurity bands formed in the minority spin energy gap. In the ZB CrAs/GaAs junction, relatively high spin polarization is retained even at the interface in contrast to usual half-metal/semiconductor heterojunctions. Complete spin polarization is also preserved throughout ZB CrAs/GaAs multilayers and it is insensitive to the substitutional disorder between Cr and Ga sites.

1. Introduction

Increasing numbers of investigations have been devoted to half-metallic ferromagnets due to their perfectly spin-polarized electronic band structure, which is metallic for one spin-state and semiconducting for the other. The degree of spin polarization is usually defined by

$$P = \frac{D_\uparrow - D_\downarrow}{D_\uparrow + D_\downarrow}, \tag{1}$$

where D_σ denotes the density of states (DOS) at the Fermi level for the spin-σ band. Half-metallic ferromagnets are expected to be exploited as potential materials for spintronic device applications, such as an electrode of magnetic tunnel junction [1], a source of spin injection into semiconductors [2], and new transistors proposed theoretically [3, 4].

The half-metallic materials proposed so far are as follows: $C1_b$-type Heusler alloys NiMnSb and PtMnSb [5], Fe_3O_4 (magnetite) [6], rutile-type CrO_2 [7], $L2_1$-type

Heusler alloys [8], perovskite manganites [9], double perovskites [10], diluted magnetic semiconductors (DMS) [11, 12], and so on. However, the spin polarization observed experimentally by tunnel magnetoresistance and Andreev reflection measurements is reduced substantially in most half-metals except for CrO_2 [13]. The reduction of the spin polarization has been attributed to the effects of atomic disorder [14, 15], surfaces [16], and/or interfaces with non-magnetic materials [17–19]. Recently, novel half-metallic ferromagnets compatible with III–V semiconductors, i.e. ZB MnAs, CrAs, and CrSb, have been designed theoretically on the basis of *ab initio* density-functional calculations [20–22]. After that, experimental attempts to fabricate these materials were motivated by the preceding theoretical prediction. Indeed, these materials have been successfully grown on III–V semiconductors by molecular-beam epitaxy (MBE) and they have been confirmed to exhibit ferromagnetic behaviour at room temperature [23–25]. Also, an increasing number of theoretical works have been published on ZB or wurtzite transition-metal pnictides and chalcogenides [26–52].

In this paper, our previous studies on ZB CrAs and related materials are reviewed, and then recent results, in particular on the influence of atomic disorder and heterointerfaces with III–V semiconductors, are reported. *Ab initio* electronic band structure calculations have been carried out by using density-functional theory within the local spin-density approximation (LSDA) or generalized gradient approximation (GGA) for the exchange–correlation energy and potential. A computational code based on the Korringa–Kohn–Rostoker (KKR) method with the use of the coherent potential approximation (CPA) [53] and the Vienna *ab initio* simulation package [54, 55] based on an ultrasoft pseudo-potential method with projector augmented waves [56, 57] have been utilized for investigating the influence of atomic disorder and heterointerfaces, respectively.

2. Zinc-blende half-metals

2.1. Electronic and magnetic properties

The original motivation is the theoretical design of new materials which are ferromagnetic at room temperature, compatible with III–V semiconductors like GaAs and InAs. In order to achieve this, we considered at first heavily Mn-doped GaAs and InAs, which led to a hypothetical material, i.e. ZB MnAs [20]. Then, we sought for related materials having higher Curie temperature, T_c, than ZB MnAs, by evaluating the total-energy difference between the ferromagnetic and antiferromagnetic states, ΔE, which is a measure of the magnetic coupling between the nearest neighbouring 3d transition-metal spins. As a result, ΔE was evaluated as 0.30 and 0.28 eV for ZB CrAs and CrSb, respectively. These values are significantly larger than those for other materials, including ZB MnAs. The strong ferromagnetic coupling between the neighbouring Cr spins is attributed to remarkable hybridization between Cr 3d and As 4p (or Sb 5p) orbitals as described below. Using the exchange coupling constant, J, between the nearest neighbouring Cr spins evaluated from ΔE, the T_c of ZB CrAs or CrSb is roughly estimated as 1600–1800 K on the basis of the mean-field approximation (MFA) of the Heisenberg model. Of course, it is well known that the MFA usually considerably overestimates T_c. It is necessary for a more accurate estimation of T_c to take the effect of spin-fluctuation into account. Such a calculation has been carried out by Kübler [40]. According to his work, the T_c of ZB CrAs is evaluated to be about 1000 K, which is higher than that of NiMnSb, i.e. about 700 K. It has also been confirmed that the value of T_c drops sharply when the Fermi level moves into the minority-spin conduction bands, as in the case of ZB MnAs with its lattice constant identical with that of GaAs. These results are consistent with the experimental observation; i.e. the T_c of ZB CrAs is over 400 K [23], while that of ZB MnAs is below room temperature [25].

It is found that both ZB CrAs and CrSb have the half-metallic band structure. In the minority-spin state, the Fermi level is located in an energy gap of about 2 eV, which is quite a bit larger than that of other half-metals. The wavefunctions near the top of the valence bands are constructed mainly from the As 4p (or Sb 5p) orbitals which hybridize with the Cr 3d orbitals, while those near the bottom of the conduction bands are from the Cr 3d non-bonding orbitals. In the majority-spin state, on the other hand, the conduction bands which cross the Fermi level are composed of the well-hybridized Cr 3d and As 4p (or Sb 5p) orbitals and have antibonding character. The conducting electrons in the hybridized bands could play an important role in stabilizing the ferromagnetic state of these materials from the viewpoint of the double-exchange mechanism [58, 59].

The magnetic moment is evaluated theoretically as 3 μ_B per formula unit for both ZB CrAs and CrSb, which agrees well with the saturation magnetic moments obtained experimentally [23, 24]. The result can be considered as evidence for these materials being half-metallic. According to recent angle-resolved photoemission spectroscopy measurements [60, 61], the Fermi edge has been clearly observed in ZB CrAs, reflecting the metallic character of this material. Weakly dispersive bands, which can be assigned to the majority-spin Cr 3d states, have also been found around 2 eV below the Fermi level in agreement with the theoretical results. It has been pointed out that the Cr-terminated surface of ZB CrAs is also highly spin-polarized [30]. It is expected that the high spin polarization of ZB CrAs can be detected by spin-resolved photoemission spectroscopy and/or spin-polarized scanning tunnelling microscopy measurements.

2.2. The influence of spin–orbit interaction

Once spin–orbit interaction is included in the band structure calculation, then mixing of both spin states takes place and the spin polarization is reduced from unity even in half-metals. For ZB CrAs and CrSb, however, quite high spin polarization is preserved as 0.998 and 0.983, respectively, even if the spin–orbit interaction is taken into account [62]. The reason why the spin polarization is almost unaffected by the spin–orbit interaction in ZB CrAs and CrSb is attributed to the large minority-spin energy gap ($\sim$2 eV), which is larger by an order of magnitude than the spin–orbit coupling constant for Cr 3d and As 4p (or Sb 5p) electrons ($\sim$0.1 eV). Recently, a similar result has been reported for the spin polarization, 0.996, of ZB CrAs by fully relativistic calculations based on the screened KKR method [50]. According to the theoretical work on electrical spin injection, these values of spin polarization are enough for ferromagnetic metals to inject detectable spin-polarized current into semiconductors even in a diffusive transport regime [2].

2.3. Influence of atomic disorder

We have investigated the influence of substitutional disorder between Cr and As sites on the electronic and magnetic properties of ZB CrAs [63]. Only stoichiometric ZB CrAs is considered here, i.e. the number of antisite Cr atoms is assumed to be equal to that of antisite As atoms. The total energy has been calculated for three different magnetic structures: ferromagnetic, ferrimagnetic, and spin-glass states. In the ferrimagnetic state, the antisite Cr spins are antiparallel to those of Cr spins at the ordinary sites, while all Cr spins are parallel to each other in the ferromagnetic state. In the spin-glass state considered here, half of the randomly distributed Cr atoms have their local magnetic moments along one direction, while the other Cr moments are along the opposite direction, so that the total magnetic moment vanishes. The local-moment disordered state has been treated within the framework of the single-site CPA [53, 59].

It is found that the ferrimagnetic state is the most favourable energetically, compared to the other magnetic states, when antisite defects are introduced in ZB CrAs. The total-energy difference between the ferrimagnetic and ferromagnetic states increases linearly as a function of the concentration of antisite defects. This implies that the antisite Cr spins are coupled antiferromagnetically with the nearest neighbouring Cr spins at the ordinary sites due to kinetic exchange interaction between 3d electrons on the neighbouring Cr atoms. On the other hand, the total-energy difference between the ferrimagnetic and spin-glass states is almost unaltered ($\sim$0.2 eV) on increasing the antisite defects. If the antisite defects weaken the ferromagnetic coupling between the Cr spins at the ordinary sites, the total-energy difference mentioned above would be decreased on increasing the antisite defects, and finally the spin-glass state would become the ground state of the system. Since this is not the case, however, for ZB CrAs, it is concluded that the ferromagnetic coupling between the Cr spins at ordinary sites is robust against the formation of antisite defects. When an As site is substituted by a Cr atom, which is denoted as Cr_{As} hereafter, the antisite Cr_{As} connects two Cr atoms at ordinary sites, i.e. a Cr–Cr_{As}–Cr bond is formed. Since the Cr–Cr_{As} coupling is antiferromagnetic, the effective exchange interaction between the ordinary Cr spins through the Cr–Cr_{As}–Cr path becomes ferromagnetic. Hence, no frustration is caused by the existence of antisite Cr_{As} spins. This is the reason why the ferromagnetic coupling between the Cr spins at ordinary sites is robust against the formation of antisite defects.

According to the DOS calculated for the energetically favourable ferrimagnetic state of ZB CrAs, there appear impurity bands composed mainly of antisite Cr 3d orbitals near the Fermi level in the minority-spin energy gap. The impurity bands, however, are completely occupied by electrons in the stoichiometric system considered here. Hence, the spin polarization is not noticeably reduced by the impurity band formation, at least for an antisite Cr concentration less than 5%.

3. Nanostructures

3.1. Heterojunctions

The electronic structure of the ZB CrAs/GaAs(001) junction has been investigated by considering a supercell composed of nine atomic layers of ZB CrAs and ten layers of GaAs slabs [64]. The interface geometry is chosen so that an As atomic layer is placed between Ga and Cr atomic layers, which actually shows stronger adhesive properties than the other interface composed of Cr and Ga atomic layers. It turns out that relatively high spin polarization is retained well even at the interface of the ZB CrAs/GaAs(001) junction, in contrast to usual half-metal/semiconductor heterojunctions, in which the spin polarization at the interface reduces remarkably [17, 18]. The highly spin-polarized interface obtained for the ZB CrAs/GaAs(001) junction results from the similarity in structural and chemical bonding characters between the constituents. Spin polarization is also induced for several atomic layers from the interface in the GaAs side, which means that the metal-induced gap states are also spin-polarized.

The Schottky barrier height at the ZB CrAs/GaAs(001) interface is evaluated as about 1 eV, which is almost the same as that at usual half-metal/GaAs(001) interfaces [18]. The Schottky barrier formed at the interface would be an origin of the high electrical resistance measured at ZB CrAs surfaces. Indeed, relatively flat island structures, whose typical diameters are 200–300 nm, separated from each other by valleys have been observed at ZB CrAs surfaces by *ex situ* atomic force microscopy [65]. Recently, efficient electrical spin injection into semiconductors has been demonstrated through an Fe/AlGaAs Schottky barrier contact [66], following a preceding theoretical proposal [67]. Thus, higher efficiency in spin injection can be achieved for ZB CrAs/GaAs junctions by adjusting the width of the Schottky barrier.

3.2. Multilayers

It is difficult to grow ZB CrAs films thicker than a critical value (∼3 nm) [23]. Recently, we have proposed digital ZB CrAs/GaAs structures for realizing films containing net ZB CrAs layers thicker than the critical thickness [68]. The short period ZB CrAs/GaAs multilayers, where n-monolayer (ML) ZB CrAs and n ML GaAs ($n = 2, 4$) are stacked alternately in the [001] direction, have been successfully fabricated by the MBE technique [68, 69]. It is noted that the DOS calculated from first principles reveals that complete spin polarization is preserved throughout the multilayer [64, 70, 71]. It has been confirmed theoretically that the spin polarization is insensitive to substitutional disorder between Cr and Ga sites [64]. Since there is a dispersive band crossing the Fermi level along the [001] direction, highly spin-polarized electrons can be conducting in the ZB CrAs(001) plane as well as along the direction perpendicular to the plane. Therefore, the multilayer is considered as a new material having a half-metallic band structure, which can be exploited as an efficient spin filter in spintronic devices.

4. Summary

The electronic and magnetic properties of ZB CrAs and CrSb have been studied using *ab initio* calculations based on density-functional theory. It has been found that antisite Cr spins are coupled antiferromagnetically with the Cr spins at ordinary sites. However, the ferromagnetic coupling between the Cr spins at ordinary sites is robust against the formation of antisite defects, and the degree of spin polarization is not reduced significantly by atomic disorder. High spin polarization is retained even at the interface of ZB CrAs/GaAs(001) junctions in contrast to usual half-metal/semiconductor heterojunctions. The Schottky barrier height at the ZB CrAs/GaAs(001) interface is evaluated as about 1 eV, which is almost the same as that at usual metal/GaAs(001) interfaces. It has been confirmed that complete spin polarization is preserved throughout digital ZB CrAs/GaAs(001) multilayers, and it is insensitive to the substitutional disorder between Cr and Ga sites. In conclusion, ZB CrAs/GaAs heterojunctions and/or multilayers can be promising candidates for the source of highly spin-polarized current utilized in various spintronic device applications.

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