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First-principles Study on the Half-metallicity and Magnetism of a Full Heusler Alloy, Co_2HfSi, in Bulk State and at its (001) Surfaces

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The authors predicted that Co_2HfSi, a Co_2-based full Heusler alloy, is being a half-metallic ferromagnet by first-principles calculations using the all electron full-potential linearized augmented plane wave method which adopts the generalized gradient approximation. The integer value of the calculated total magnetic moment of 2.00 μ_B per formula unit and a spin gap of 0.69 eV in spin down state confirmed the half-metallicity of bulk Co_2HfSi. For the Co_2HfSi(001) surface, we considered two possible surface terminations, namely, Co terminated and HfSi terminated surfaces. It was found that half-metallicity was retained at the HfSi-terminated surface but not at the Co-terminated surface. The magnetic moment of surface Co atoms in the Co-terminated surface was slightly lower than that of Co atoms in deep inner-layers, whereas the magnetic moments of Hf and Si atoms at the HfSi-terminated surface were almost same as those in deep inner-layers.

Keywords : half-metallicity, electronic structures, magnetism, full-Heusler alloy

1. Introduction

Spintronics, which utilizes the spin degree of freedom of electrons, is a rapidly developing field in nano-technology. One of the crucial issues in spintronics is to enhance the efficiency of spin-injection, that is, the spin-polarized current from magnetic material into semiconductor [1, 2]. In this sense, half-metallic materials in which one spin channel is semiconducting while the other is metallic with perfect spin-polarization at the Fermi level, have attracted much attention because of their potential applications.

Since half-metallicity was first discovered in half Heusler NiMnSb alloy by de Groot *et al.* based on band structure calculations [3], another family of Heusler alloys, the full Heusler alloys, also has attracted particular interest because of their high Curie temperatures, relatively large magnetic moments, and structural similarities with the zinc-blende structure. Full-Heusler alloys have the chemical formula of X_2YZ, in which X and Y are transition metals and Z is a periodic table group III or IV element. Furthermore, these alloys crystallize to form the $L2_1$-type structure, shown in Fig. 1(a). Recently, Picozzi *et al.* [4], using the all-electron full-potential linearized augmented plane wave (FLAPW) method, found that the Co_2MnZ (Z=Si, Ge) alloys are half-metallic ferromagnets with integer magnetic moments per formula unit which satisfies the Slater-Pauling rule [5, 6]. Other theoretical studies have predicted half-metallicity in full-Heusler Co_2YSi (Y=Ti, V, Cr, and Fe) alloys [7, 8]. Furthermore, recently, Jin and Lee [9] investigated the electronic structures of full Heusler alloys containing 4*d* transition elements *T*, i.e., Co_2TSi (*T* = Y, Zr and Nb), using the FLAPW method, and found that Co_2ZrSi is a half-metallic ferromagnet with a large minority spin gap of about 0.94 eV, whereas Co_2YSi and Co_2NbSi alloys were not found to be half-metals. In this paper, we predict, based on first-principles band calculations, that Co_2HfSi, which includes a 5d transition element, is a half-metallic ferromagnet.

Contrary to theoretical predictions of half-metallic ferromagnets, measured spin-polarizations have shown that spin polarization is lower than 100% [10, 11] due to atomic disorder and surface effects [12-15]. First-principles investigations have found that many half-metallic ferromagnets lose half-metallicity at surfaces [16, 17]. Hashemifar *et al.* [17] performed *ab initio* band calculations on 15 different terminations of the Co_2MnSi(001) surface, and found the half-metallicity was retained at the pure Mn terminated surface due to strong surface-subsurface coupling but the half-metallicity was lost for the other 14 terminations.

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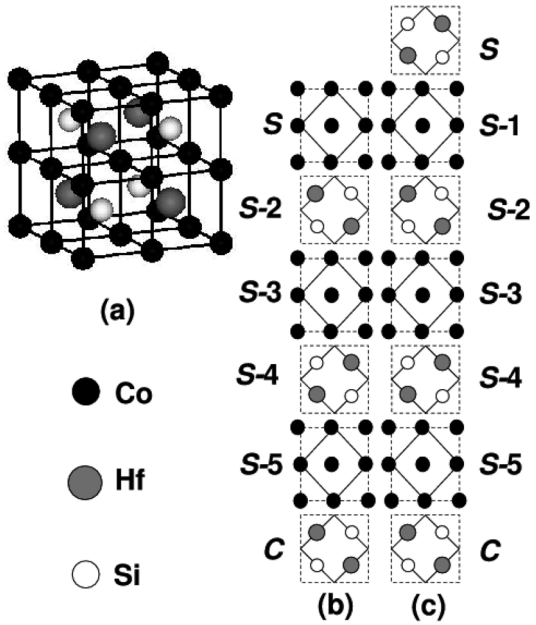

Fig. 1. Schematic representations of (a) full Heusler alloy, Co_2HfSi with a $L2_1$ structure, and the single slab models of (b) Co-terminated and (c) HfSi-terminated $Co_2HfSi(001)$ surfaces, respectively.

Based on FLAPW calculations, Jin and Lee [18] also found that half-metallicity was destroyed at the CrSi terminated surface of $Co_2CrSi(001)$ due to a surface state at the Fermi level, whereas half-metallicity was retained at the TiSi terminated surface of $Co_2TiSi(001)$. However, the minority spin gap was much reduced due to a surface state just below the Fermi level.

For practical applications, it is essential that we understand the electronic structures of half-metallic ferromagnets at their surfaces. In the present study, we investigated electronic structures, magnetism, and half-metallicity at the (001) surfaces of Co_2HfSi, by using the FLAPW method embodied in QMD-FLAPW [19] incorporating the generalized gradient approximation (GGA) [20]. In Sec. 2, we describe the calculation model and method used. Results and discussions are presented in Sec. 3, and a brief summary is given in Sec. 4.

2. Calculation Method

In order to check the half-metallicity of bulk Co_2HfSi and to find the equilibrium lattice constant, we performed spin-polarized band calculations by varying the lattice parameter. The calculated equilibrium lattice constant of the bulk Co_2HfSi is 11.32 atomic unit (a.u.) (5.99 Å). The parameters used in the bulk calculation were as follows. The muffin-tin (MT) radii for Co, Hf, and Si atoms used were 2.15, 2.50, and 2.00 a.u., respectively. Lattice harmonics with $l \leq 8$ were employed to expand charge density, potential, and wavefunctions inside the muffin-tin (MT) radius. We used a 210 Ry star function cut-off to depict charge density and potential in the interstitial region, and 14 Ry for the plane-wave cut-off.

In order to investigate the electronic structure at the Co_2HfSi (001) surface, we constructed two single slabs consisted of 11 and 13 atomic layers of Co atom terminated (Co-term) and HfSi atom terminated (HfSi-term) surfaces, as presented in Fig. 1(b) and (c), respectively. For these slabs the two-dimensional (2D) lattice constant was $\frac{\sqrt{2}}{2}a$=8.00 a.u. and the interlayer spacing was 2.83 a.u., which is a quarter of the calculated equilibrium lattice constant. We used the same MT radius value for each atom in the slab systems as used in the bulk system, and the same star function cut-off and plane wave cut-off parameters as used in the bulk system. Neither reconstruction nor relaxations were considered.

The Kohn-Sham equation [21] was solved self-consistently using the FLAPW method embodied in QMD-FLAPW adopting the GGA to the exchange-correlation potential. The 4*f* electrons of the Hf atom were treated as core electrons. All core electrons were treated fully relativistically, while valence states were treated scalar relativistically, *i.e.*, without spin-orbit coupling [22]. Self-consistency was assumed when the difference between input and output charge (spin) densities were less than 1.0×10^{-4} electrons/a.u.^{3}

3. Results and Discussions

We calculated the electronic structures and total energies of paramagnetic (PM) and ferromagnetic (FM) states for bulk Co_2HfSi alloy with a $L2_1$ structure by varying lattice constants. Total energy versus lattice constant curves

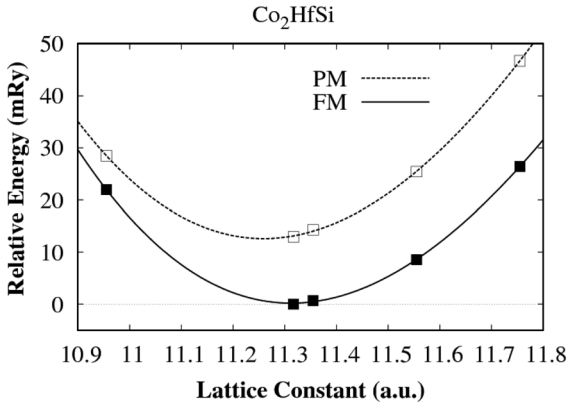

Fig. 2. Plot of total energies vs. lattice constants showing that the bulk Co_2HfSi has an equilibrium lattice constant of 11.32 a.u.

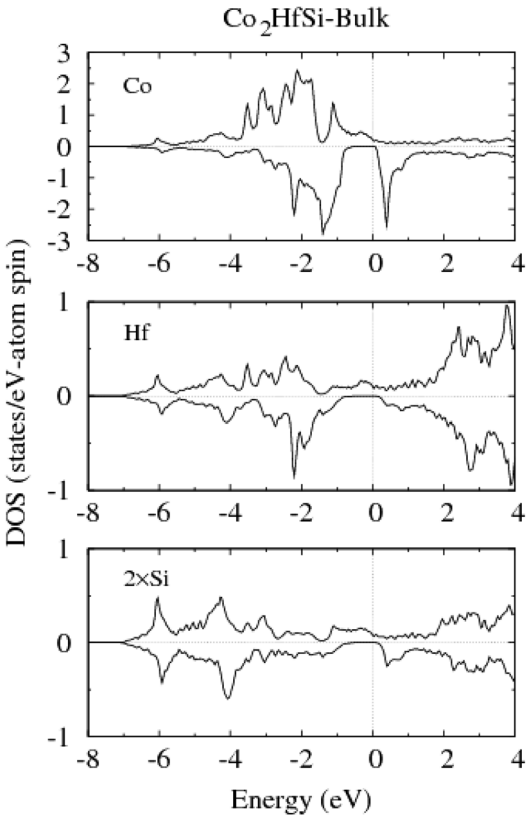

Fig. 3. Spin-polarized atom-resolved density of states for bulk Co_2HfSi. The DOS values of Si atoms are multiplied by 2 and the minority spin states are multiplied by –1. The Fermi levels are set to zero.

for the PM and the FM states of Co_2HfSi are given in Fig. 2. The equilibrium lattice constant of Co_2HfSi in a FM state was found to be 11.32 a.u. (5.99 Å), which is smaller than the 6.23 of isoelectronic Co_2HfSn alloy [23], but close to those of several zinc-blende structured semiconductors, such as, InP (5.87 Å), InAs (6.06 Å), and CdSe (6.05 Å).

We can confirm that bulk Co_2HfSi Heusler alloy is half-metallic based on the calculated atom-resolved density of states (DOSs) presented in Fig. 3. The positive and negative values of DOSs correspond to the majority- and minority-spin states, respectively. The DOS of Si was multiplied by a factor of 2 and the Fermi level was set to zero. We found no DOS at the Fermi level for minority-spin states and a gap of 0.69 eV, which is opened by localized t_{1u} and e_u states located at 0.56 eV below the Fermi level and at 0.13 eV above the Fermi level, respectively. Half-metallicity of Co_2HfSi was also evidenced from the value of its total magnetic moment (2.00 μ_B/f.u.), which satisfies the Slater-Pauling rule. The magnetic moment of the Co atom in the bulk Co_2HfSi is 1.05 μ_B, which is antiparallel to that of the Hf atom (–0.07 μ_B).

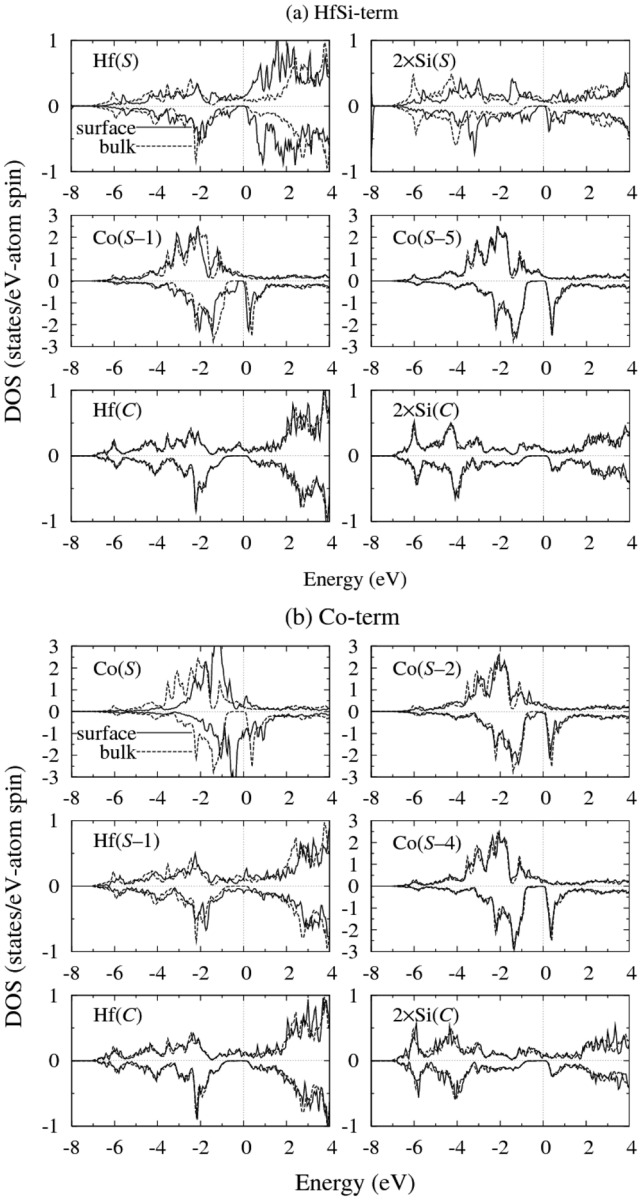

Fig. 4. Spin-polarized layer-projected atom-resolved DOS, denoted by the solid lines, for (a) the HfSi-term and (b) the Co-term of $Co_2HfSi(001)$ surfaces. DOS values of Si atoms are multiplied by 2 and minority spin states are multiplied by –1. The Fermi levels are set to zero. The DOSs for bulk Co_2HfSi, denoted by dotted lines, are also provided for comparison.

We now discuss the surface electronic structures of $Co_2HfSi(001)$ using the calculated spin-polarized layer-projected atom-resolved DOSs given in Fig. 4 for; (a) the HfSi-term and (b) the Co-term. We added the DOSs for bulk, denoted by the dotted lines, for comparison purposes. From the figures shown, we found that surface electronic structures were strongly dependent on surface terminations. We found that half-metallicity was retained

at the surface of HfSi-term, whereas the surface of Co-term lost its half-metallic character.

Regarding the HfSi-term (see Fig. 4(a)), which retains half-metallicity, the minority-spin band gaps (0.33 eV) of Hf(*S*) and Si(*S*) were much reduced with respect to that of central layers (0.69 eV) due to surface states at just below the Fermi level. This situation is similar to those of YSi (Y=Ti, Cr, and Mn) terminated surfaces of $Co_2YSi(001)$ [17, 18], in which the surface states arise from hybridizations between the surface Y *d*-, Si *sp*-states and the subsurface Co $d_{3z^2-r^2}$-states. Surface Hf (or Si) and subsurface Co atoms lose four nearest neighbor (n.n.) Co atoms and one next nearest neighbor (n.n.n.) Co atom, respectively. It was found that the unoccupied majority- and minority-spin states of Hf(*S*) were shifted to lower energy due to a reduced coordination number, but that the edge of the unoccupied minority-spin states still pinned just above Fermi level, as in the center layer. Due to hybridizations between surface and subsurface layers the minority-spin band gap of subsurface Co atoms was also reduced considerably, but the layer retained half-metallicity.

On the other hand, we found that the surface Co-term was no longer half-metallic since the localized t_{1u} and e_u states became dispersed due to symmetry breaking caused by surface termination. The bandwidths of majority- and minority-spin Co(*S*) 3*d*-states became narrower compared to that of Co(*S*-4), and the 3*d*-states of Co(*S*) were shifted to a higher energy region due to a reduced coordination number. Surface Co atoms lost two n.n., *i.e.*, Hf and Si, and one n.n.n., a Co atom. It was found that the subsurface also loses half-metallicity due to hybridizations between the minority-spin Hf(*S*-1) 4*d*-, Si(*S*-1) *sp*-states and the surface Co 3*d*-states. Even at the Co(*S*-2) layer, we found a small portion of 3*d*-states below the Fermi level, and the minority-spin e_u state of Co(*S*-2) just above Fermi level was slightly dispersed, which makes the (*S*-2)-layer near half-metallic. To our knowledge, the Co-terminated surfaces of Co_2-based full Heusler alloys, such as, Co_2YSi(Y=Ti, Cr, and Mn), Co_2TiSi, and Co_2CrAl, have similar behaviors, that is, all of them lose half-metallicity [17, 18].

The numbers of layer-projected *l*-decomposed majority and minority-spin electrons inside MT spheres and layer-by-layer magnetic moments are summarized in Table 1. It was found that the surface transition metal atoms (the Hf(*S*) of the HfSi-term and the Co(*S*) of the Co-term) lose some *sp*-like electrons which spill out into the vacuum region to screen the abrupt surface termination, while the *sp*-like electrons of Si(*S*) of the HfSi-term were increased with respect to that of the central layers. This difference

Table 1. Layer-projected *l*-decomposed majority and minority spin-electrons inside muffin-tin spheres, and layer-by-layer magnetic moments (μ_B) for relaxed systems.

(a) HfSi-term					
atom(layer)	*s* (↑/↓)	*p* (↑/↓)	*d* (↑/↓)	Total (↑/↓)	M
Hf(*S*)	0.13/0.14	0.08/0.08	0.61/0.65	0.84/0.89	−0.05
Si(*S*)	0.38/0.38	0.43/0.40	0.02/0.03	0.83/0.81	0.03
Co(*S*-1)	0.17/0.15	0.15/0.15	4.05/3.06	4.37/3.37	1.01
Hf(*S*-2)	0.15/0.16	0.13/0.14	0.66/0.72	0.97/1.05	−0.07
Si(*S*-2)	0.35/0.35	0.45/0.41	0.05/0.05	0.85/0.81	0.04
Co(*S*-3)	0.17/0.15	0.15/0.15	4.08/3.05	4.40/3.35	1.06
Hf(*S*-4)	0.15/0.16	0.13/0.13	0.67/0.72	0.97/1.04	−0.07
Si(*S*-4)	0.35/0.34	0.44/0.41	0.05/0.06	0.85/0.81	0.03
Co(*S*-5)	0.17/0.15	0.15/0.15	4.08/3.05	4.41/3.35	1.06
Hf(*C*)	0.15/0.16	0.13/0.13	0.67/0.72	0.97/1.04	−0.07
Si(*C*)	0.35/0.34	0.44/0.41	0.05/0.06	0.85/0.81	0.03
(b) Co-term					
Co(*S*)	0.15/0.14	0.07/0.08	4.05/3.07	4.27/3.29	0.98
Hf(*S*-1)	0.15/0.16	0.12/0.13	0.61/0.74	0.92/1.07	−0.15
Si(*S*-1)	0.35/0.35	0.42/0.41	0.04/0.05	0.82/0.82	0.00
Co(*S*-2)	0.17/0.15	0.15/0.15	4.02/3.12	4.34/3.42	0.92
Hf(*S*-3)	0.15/0.16	0.13/0.13	0.66/0.72	0.97/1.04	−0.07
Si(*S*-3)	0.35/0.34	0.44/0.41	0.05/0.05	0.85/0.81	0.03
Co(*S*-4)	0.17/0.15	0.15/0.15	4.07/3.06	4.39/3.36	1.03
Hf(*C*)	0.15/0.16	0.13/0.13	0.66/0.72	0.97/1.04	−0.07
Si(*C*)	0.35/0.34	0.44/0.41	0.05/0.05	0.85/0.81	0.03

was considered to arise from the different bonding characteristics of *sp*-like electrons, *i.e.*, the almost free-electron-like natures of transition metal bonding and the covalent bonding-like nature of Si atoms. In both slab systems, the numbers of *d*-like electrons in each of the Co and Hf atoms are almost constant at 7.13 and 1.39, respectively, with the exception of the surface Hf atom in the HfSi-term, where the number of *d*-like electrons is only 1.26. This implies that the 4*d*-electrons of Hf atoms were more delocalized than the 3*d*-electrons of Co atoms.

The magnetic moments of Co, Hf and Si atoms in the deep inner-layers are almost same as those of the bulk at 1.05, –0.07 and 0.03 μ_B, respectively, regardless of surface terminations. At the surface of the HfSi-term, the magnetic moments of Hf(*S*) and Si(*S*) atoms are not much different from those of the central layer atoms. On the other hand, for the Co-term the magnetic moment of the Co(*S*) atom is reduced slightly to 0.98 μ_B since the dispersed t_{2g} states occupy more of the minority bands. The magnetic moment of the Hf(*S*-1) atom was increased to –0.15 μ_B, which is considered to be due to *d*-*d* hybridization between the surface Co 3*d*- and subsurface Hf 4*d*-states. Furthermore, it was found that surface termination also affects the magnetic moment of Co(*S*-2), which was

reduced to 0.92 μ_B by hybridization between the Co(S) and Co(S-2) atoms, as shown in Fig. 4(b).

4. Summary

In the present study, we investigated the magnetism and half-metallicity of bulk Co_2HfSi and its (001) surfaces using the all electron full-potential linearized augmented plane wave (FLAPW) method which adopts the generalized gradient approximation (GGA). The calculated equilibrium lattice constant for bulk Co_2HfSi was 11.32 a.u. (5.99 Å). From calculated magnetic moments and density of states we confirm that bulk Co_2HfSi is a half-metallic ferromagnet with an integer magnetic moment of 2.00 μ_B/f.u, which follows the Slater-Pauling rule, and a minority spin gap of 0.69 eV, which is opened by t_{1u} and e_u states due to Co d – Co d hybridization.

At the HfSi-term Co_2HfSi(001) surface, half-metallicity was retained, but the minority spin-gap was much reduced to about 0.33 eV. On the other hand, the Co-terminated surface lost half-metallicity due to dispersed t_{1u} and e_u states caused by surface creation. Furthermore, the magnetic moment (0.98 μ_B) of surface Co atoms of the Co-term was slightly lower than that (1.06 μ_B) of the deep inner-layer due to the d-d hybridization between surface Co 3d- and subsurface Hf 4d-states.

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