Electronic structures and the spin polarization of Heusler alloy Co$_2$FeAl surface

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Abstract. The electronic structures of the Heusler alloy Co$_2$FeAl surface are studied theoretically via first-principles calculations. The space localization of the surface states is the key effect on the electronic structures of the Co$_2$FeAl surface. At the surface, the lattice parameter shrinks to minimize the total energy, and the minority spin gap disappears and shows a metallic band gap character. However, with the depth increasing, the lattice parameter equals to that of bulk phase, and there shows an energy gap opening at the Fermi level in the minority spin states. As a result, the spin polarization at the surface is lower than that of the bulk Co$_2$FeAl, while it is close to that of bulk phase beneath the surface. According to the calculations, it is clear that the half-metallic property fading of the Co$_2$FeAl films is caused by the surface states. Therefore, it is important to minimize the lattice mismatch at the interface of Co$_2$FeAl in order to obtain a high tunneling magnetoresistance.

1. Introduction

Half-metallic ferromagnets (HMFs), which are metallic in the majority spin while insulating in the minority spin, have a theoretical spin polarization of 100%. Among all the HMFs, Co-based full-Heusler alloys are ideal materials for application as ferromagnets in spintronic devices, such as spin valves (SPVs) or magnetic tunnel junctions (MTJs), because of their high Curie temperature ($T_C$) and low coercivity ($H_C$). In recent years, Co-based Heusler alloys have attracted great interest. The application in MTJs as ferromagnetic layers can dramatically improve tunneling magnetoresistance (TMR). Okamura et al. [1] fabricated Co$_2$FeAl/Al-O$_x$/Co$_{75}$Fe$_{25}$ MTJ on a thermally oxidized Si substrate, and obtained a TMR of 47% at room temperature (RT). Co$_2$FeSi is also reported to be a HMF with high $T_C$ and magnetic moment, both experimentally and theoretically. [2, 3] The Fermi level lies at the top of the minority spin gap in Co$_2$FeSi, while at the bottom in Co$_2$FeAl. [4] So theoretically, the Co$_2$FeAl$_{1-x}$Si$_x$ ($0<x<1$) compound has perfect half-metallic electronic structures with the Fermi level locating in the middle of the minority spin gap. [5] It is also experimentally verified that the application of Co$_2$FeAl$_{1-x}$Si$_x$ in MTJs can improve TMR dramatically. [6] However, the TMR value varies in a wide range, even with the same HMFs electrodes and MgO barrier. [7, 8] The MTJs with HMFs electrodes are theoretically predicted to have an infinite TMR value. But till now, the highest TMR value realized experimentally is only a few hundred percent. This is due to different

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surface or interface structures that are essential to the performance of MTJs. Therefore, it is important to study the surface electronic structures of HMFs.

2. Calculations

Our density functional theory calculations are performed by using Vienna ab initio Simulation Package (VASP). [9] Exchange correlation interactions are described by the Perdew-Bruke-Ernzerhof (PBE) generalized gradient approximation (GGA). [10] The projector-augmented wave (PAW) method [11] is used for the treatment of core electrons. In addition, the GGA+U method is used to consider on-site correlation of 3\(d\) transition metals. The effective Coulomb-exchange interaction \(U_{\text{eff}} = U - J\) is used, where \(U\) and \(J\) are the Coulomb part and exchange part, respectively. The electronic structures are sensitive to the value of \(U_{\text{eff}}\), and a large \(U_{\text{eff}}\) results in a large band gap. Therefore, we select smaller values of \(U_{\text{eff}}\) to avoid overestimated band gap in the calculations (\(U_{\text{Co}} = 2.2\) eV, \(U_{\text{Fe}} = 2.1\) eV). In order to test the reliability of the calculations, we first calculate the electronic structures of bulk Co\(_2\)FeAl in \(L2_1\) phase. The positions of Al, Fe and Co are (0, 0, 0), (1/2, 1/2, 1/2) and (1/4, 1/4, 1/4), respectively. We employ an \(8\times8\times8\) mesh of special \(k\)-points to perform the summation over the Brillouin zone. The energy convergence criterion is set to \(10^{-3}\) eV and the criterion for charge convergence to \(10^{-5}\) electrons. The lattice parameter is 5.692 Å after optimization, which is close to the experimental value 5.730 Å. [12] The supercells to model the Co\(_2\)FeAl(001) surface are constructed by 3, 4, and 5 periodic unit cell of Co\(_2\)FeAl \(L2_1\) phase separated by a vacuum layer of 12 Å, which is named as 3, 4, and 5 layers, respectively. The model of 3 layers is presented in Figure 1. The lattice parameters are fixed, and the atoms are relaxed using the same convergence criterion as that of the bulk phase. A \(k\)-mesh of \(6\times6\times1\) is employed for geometry optimizations, while a \(6\times6\times6\) \(k\)-mesh for density of states (DOS) calculations. The kinetic cutoff energy is 335 eV in all calculations.

![Figure 1. Supercell of the Co\(_2\)FeAl(001) surface.](image1)

![Figure 2. Total DOS for the Co\(_2\)FeAl bulk phase and surface.](image2)

3. Results and discussion

The total DOS of the Co\(_2\)FeAl bulk phase and the (001) surface of 3, 4, and 5 layers are presented in Figure 2, in which the zero of energy denotes the Fermi level. The majority states of the bulk Co\(_2\)FeAl take on a metallic character, while the minority states have an energy gap about 1.0 eV with the Fermi level locating at the bottom of it. The electronic structures indicate that the bulk Co\(_2\)FeAl in \(L2_1\) phase is half-metallic, which is in consistent with the result of G. H. Fecher et al.. [4] For the total DOS of the Co\(_2\)FeAl(001) surface, it can be seen in all the three panels that both the majority and minority states
are metallic, which is the main difference between the bulk phase and the (001) surface causing the fading of half-metallic property.

To justify whether the calculation model is thick enough to describe the surface, we calculate the total energy and magnetic moment for each model. The total energy difference between 3 and 4 layers is 45.2 eV, which is close to the value of 45.3 eV between 4 and 5 layers. The energy fluctuation of 0.0125 eV per atom is within the calculation error. The magnetic moment increments from 3 to 4 layers and from 4 to 5 layers are 10.8 and 10.6 μB, respectively. The changes of energy and magnetic moment with the surface thickness are almost constant, which suggests the 3 layers model is thick enough to discuss the surface effect. Accordingly, we choose the 3 layers model to study detailed DOS.

In Figure 3, we present total DOS and partial density of states (PDOS) of Al, Fe, and Co atoms in the 3 layers model. The atoms at different depth as shown in Fig. 1 are sampled to reveal the evolitional electronic structures with the depth beneath the surface. From the total DOS shown in the first row of Fig. 3, it can be seen that both the majority and minority states are metallic for the atoms located at the positions numbered as ‘1’ in Fig. 1 (represented by solid lines in Fig. 3), which are exposed to vacuum at the surface of Co2FeAl. When the depth increases and the atoms locate at the positions numbered as ‘2’ (represented by dashed lines in Fig. 3), the majority states are still metallic and have no distinct change at the Fermi level, while the minority states of each atom decrease dramatically relative to those of the atoms in the positions ‘1’. The atoms at the positions ‘3’ (marked in Fig. 1) become deeper beneath the surface, and are separated with vacuum by five atomic layers, which is deep enough to be regarded as in the bulk environment. The total DOS of Al, Fe, and Co atoms in the positions ‘3’ all show metallic character in the majority states. However, in the minority states of each atom, there opens an energy gap at the Fermi level, indicating an insulating character. According to the evolution of total DOS, it is found that in the ordered Co2FeAl(001) surface, the spin polarization increases with the atom depth beneath the surface. When the atom depth is close to 0.8 nm which is deeper than the positions ‘3’, the spin polarization equals to that of the bulk phase.

![Figure 3. PDOS of atoms at different depth in 3 layers surface.](image)

The change of spin polarization with the atom depth beneath the Co2FeAl(001) surface comes from the distribution of PDOS, which is sensitive to the coordinate environment. According to the geometry optimization results, the bond length at the Co2FeAl(001) surface will shrink to minimize the total energy. In the optimized surface, the distance between the first layer and the second one at the FeAl termination is 1.278 Å, from which the lattice parameter in z direction at the surface is calculated to be 5.112 Å. While in the middle of the surface, the optimized lattice parameter is close to that of the bulk phase. Similar trend can also be observed in the Co termination. Accordingly, the bond length increases with the depth beneath the surface and finally reaches the value of the bulk phase, which is accompanied by the evolution of electronic orbits. As shown in Fig. 3 column (a), the s and p states...
are main contribution to the total DOS of Al. When Al depth changes from the positions of ‘1’ to ‘3’, the minority states of s and p decrease to zero at the Fermi level, so that there opens an energy gap. The PDOS patterns of Fe atoms are presented in Fig. 3 column (b). The minority states at the Fermi level mainly come from 3d states which decide the spin polarization. It is obvious that the 3d minority states at the Fermi level decreases dramatically with the Fe atom depth, and the 3d minority spin band at the Fermi level shifts to the high energy region. As shown in Fig. 3 column (c), the evolution of Co PDOS is similar with that of Fe, except that the Co 3d minority spin band at the Fermi level shifts to the low energy region with the Co atom depth increasing. The bond length at the surface is shorter than that beneath the surface, hence the electronic orbits largely overlap, and the energy levels are much degenerated. As a result, the 3d states disperse around the Fermi level due to the surface-localized state at the surface. However, beneath the surface, a longer bond length results in localized electronic states. The full occupied 3d majority states are not sensitive to the bond length increase, while in the partially occupied minority states, the band-gap opens up due to the decay of the surface-localized state beneath the surface. The minority charge density slices for (010) and (110) planes of the CoFeAl surface are shown in Figures 4(a) - (d), associated to the states with in the energy region from -0.1 eV to 0.7 eV. Comparing the charge density of atoms at different depth, we can see that the minority state is metallic at the surface and insu lated beneath the surface, which shows the space-localization states in the Co2FeAl(001) surface.

![Figure 4. Minority charge density of Co2FeAl surface.](image)

The magnetic moments of Co and Fe atoms mainly come from the 3d states. The s and p states only have very small induced magnetic moments. It is found that the atomic magnetic moments of both Fe and Co atoms decrease with the depth beneath the surface. In the bulk CoFeAl \(L2_1\) phase, the calculated magnetic moments of Fe and Co atoms are 3.0 and 1.2 \(\mu_B\), which are close to those in the positions ‘3’ in Fig. 1. Therefore, the variation of the atomic magnetic moments also demonstrates that the magnetic properties become close to those of the bulk CoFeAl with the depth increasing. The saturation magnetization of the CoFeAl(001) surface is higher than that of the bulk phase based on the simulation results.

According to the analysis above, the CoFeAl(001) surface can be regarded as a composite tri-layer structure which has low spin polarization at the surface and high spin polarization beneath the surface. When CoFeAl is fabricated into thin films, the half-metallic property will fade due to the low spin polarization at the surface.

**4. Conclusion**

In summary, the first-principles calculations on the CoFeAl surface reveal that the minority states are metallic at the surface due to the crystal lattice distortion. However, the DOS of individual atoms show
a trend of minority gap opening at the Fermi level beneath the surface, which indicates that the electronic structures become close to those of the bulk Co$_2$FeAl. Accordingly, the Co$_2$FeAl(001) surface has a composite tri-layer structure, which can illustrate the half-metallic property fading in thin films against ideal character of bulk materials.

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