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Ab initio study on stability of half-metallic Co-based full-Heusler alloys

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We perform the first-principles density functional calculations of Co-based full-Heusler alloys, exploring 25 possible combinations of Co_2YZ (Y=Ti, V, Cr, Mn, and Fe; Z=Al, Ga, Si, Ge, and Sn) in order to clarify the stability for the Co-related atomic disorder, because this type of disorder is considered to degrade the spin polarization of Co_2YZ. We found that the disorder between Co and Y atoms correlates with the total valence electron charges around Y atom, because a difference in valence electron charges between Co and Y atoms leads to a different shape of the local potential at each site. This means that Ti-based alloys are better than Cr-, Mn-, and Fe-based alloys in preventing the atomic disorder between Co and Y atoms. From our results, we propose stable Co-based full-Heusler alloys with excellent prospects for half-metallic ferromagnets. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2176907]

Half-metallic ferromagnets (HMFs), where the majority-spin band is metallic and the minority-spin band is semiconducting with an energy gap at the Fermi level, have been extensively studied in recent years. The HMFs act as spin filters which provide current with a high degree of spin polarization and are key materials for spin-dependent phenomena in spintronics, such as tunneling magnetoresistance[1] (TMR) and spin injection into semiconductors.[2,3] While there are a lot of theoretically predicted HMFs,[4–10] the Co-based full-Heusler alloys Co_2YZ (Y: transition metal; Z: *sp* atom) are the most prospective candidates for application in the spintronics devices. This is due to a high Curie temperature beyond room temperature (RT) and the simple fabrication process such as dc magnetron sputtering in Co_2YZ.

The electronic and magnetic properties of a series of Co-based full-Heusler alloys have been investigated by using the first-principles calculations,[9,11] and it is found that many of Co_2YZ are half metallic and follow a Slater-Pauling behavior where the total spin magnetic moment per unit cell in μ_B (M_t) scales with the total number of valence electrons (Z_t) following the rule: $M_t = Z_t - 24$.

In spite of the theoretical predictions, it is difficult to demonstrate their half metallicity in experiments. Co_2MnSi, Co_2MnGe, and Co_2MnSn fabricated on top of a MgO(001) substrate showed the rather low electrical conductivity, indicating structural disorder.[12] Neutron-diffraction experiments for polycrystalline Co_2MnSi bulk showed that the antisite disorder is zero for Mn–Si-type disorder, but between 10% and 14% for the Co–Mn- type disorder.[13] Recently, relatively large TMRs at RT have been reported for magnetic tunneling junctions (MTJs) based on Co-based full-Heusler alloys Co_2YZ, e.g., 19% in the $B2$-type $Co_2(Cr_{0.6}Fe_{0.4})Al$ with $Al_{1-x}O_x$ barrier,[14,15] 40% in the $B2$-type Co_2MnAl with $Al_{1-x}O_x$ barrier,[16] 47% in the $A2$-type Co_2FeAl with $Al_{1-x}O_x$ barrier,[17] and 42% in the $B2$-type $Co_2(Cr_{0.6}Fe_{0.4})Al$ with MgO barrier.[18] However, estimated spin polarization from Julliére's model[19] in the above experiments are still much smaller than the theoretical predictions, we have to verify a lot of possibilities which degrade the device performances, such as atomic disorder, nonstoichiometry, oxidation and phase separation in the bulk and interface.[20]

In our previous works,[21] we investigate the atomic disorder effects on the half metallicity of the full-Heusler alloy $Co_2(Cr_{1-x}Fe_x)Al$ by using first-principles calculations. We found that disorder between Cr and Al hardly reduces the spin polarization of Co_2CrAl, i.e., the $B2$-type disorder does not affect to the half metallicity of Co_2CrAl, while disorder between Co and Cr leads to a significant reduction of the spin polarization. We consider that these properties would be observed in other Co-based full-Heusler alloys, because the half-metallic gap in the minority-spin states of Co_2YZ is mainly determined by the second nearest neighbor Co–Co $3d$ interaction. The suppression of the atomic disorder in Co_2YZ is the most important tasks in fabrications of the Co_2YZ based MTJ, understanding what causes the Co-related disorder would provide useful information in choosing the half-metallic full-Heusler alloys with excellent prospects.

In this work, we investigate and discuss the stability of Co-based full-Heusler alloys Co_2YZ (Y=Ti, V, Cr, Mn, and Fe; Z=Al, Ga, Si, Ge, and Sn) for the Co-related atomic disorder, exploring possible 25 combinations of the alloys by using the density functional first-principles calculation on the basis of the pseudopotential plane-wave method and the generalized-gradient approximation[22] (GGA) for the exchange correlation term in Vienna *ab initio* simulation package.[23,24] For atomic potentials, the projector augmented plane-wave potential[25,26] was used. In the calculations, we adopt a bulk $a \times a \times a$ simple cubic cell including 16 atoms (8 Co atoms, 4 Y atoms, and 4 Z atoms), where a is the initial lattice constant of Co_2YZ with $L2_1$ structure optimized for each alloy. Atomic positions, cell volume, and cell shape are fully relaxed in our calculations. We use $7 \times 7 \times 7$ Monkhorst-Pack sampling in the Brillouin zone for self-consistent calculations and $20 \times 20 \times 20$ to obtain the density of states. In our calculations the spin-orbit interaction and

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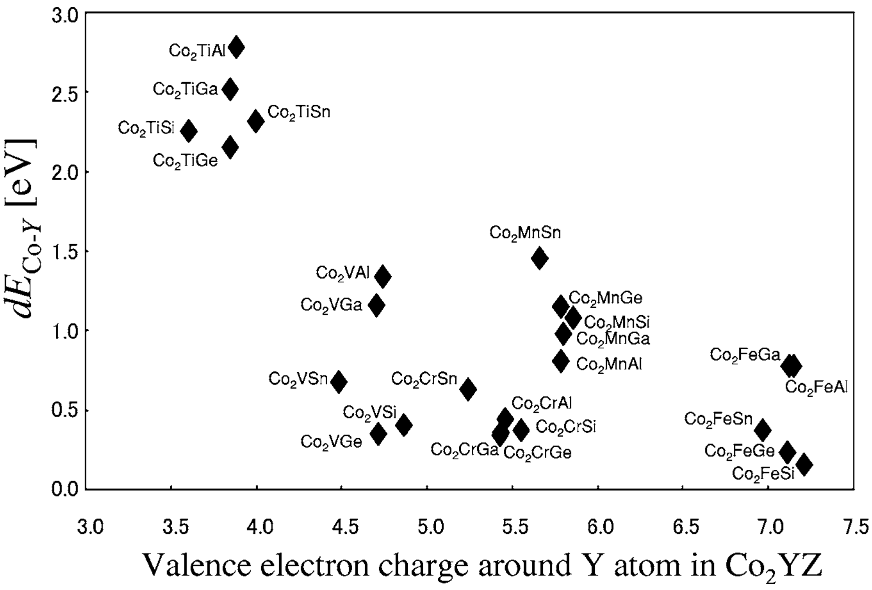

FIG. 1. Total energy difference between ordered $L2_1$ and the Co$-Y$-type disordered Co_2YZ ($dE_{\text{Co-}Y}$) as a function of the total valence electron charges around Y atom in ordered $L2_1$-type Co_2YZ.

noncollinear spin configuration are neglected. The atomic disorders are implemented by exchanging a position of Y atom with the nearest neighbor Co atom (Co$-Y$ type disorder), correspond to 12.5% of the disorder between Co and Y atom.

First, we calculate the electronic and magnetic properties of Co_2YZ (Y=Ti, V, Cr, Mn, and Fe; Z=Al, Ga, Si, Ge, and Sn) with ordered $L2_1$ structure. We have confirmed that the calculated total magnetic moments of Co_2YZ nearly obey the Slater-Pauling behavior of $M_t = Z_t - 24$, though there are small deviations from this rule in several compounds, which have been already mentioned in Ref. 9. Furthermore, many of these compounds show the high spin polarization which is defined by $(D_\uparrow - D_\downarrow)/(D_\uparrow + D_\downarrow)$, where D_σ denotes the majority ($\uparrow$)- and minority ($\downarrow$)-spin components in the density of states at the Fermi level. The Co-based full-Heusler alloys showing high spin polarizations more than 70% are Co_2TiAl(99.3%), Co_2TiSi(95.0%), Co_2TiGa(94.6%), Co_2TiGe(100%), Co_2TiSn(100%), Co_2VAl(97.3%), Co_2VGa(100%), Co_2VGe(80.6%), Co_2VSn(100%), Co_2CrAl(99.9%), Co_2CrSi(100%), Co_2CrGa(93.2%), Co_2CrGe(99.8%), Co_2CrSn(91.5%), Co_2MnSi(100%), Co_2MnGe(94.9%), Co_2MnSn(74.7%) and Co_2FeAl(86.5%), respectively. Note that the spin polarization of Co_2YZ is sensitive to calculation conditions. Furthermore, the density functional theory with the GGA usually underestimates minority band gaps of Co_2YZ around Fermi level. Thus, the theoretical spin polarization with in GGA shown here must be viewed with caution.

Next, we discuss the effects of Co$-Y$-type disorder in Co_2YZ. As mentioned in Ref. 20, the energy gap in the minority-spin state of Co_2YZ around Fermi level is mainly constructed by the bonding and antibonding features of the second nearest neighbor Co–Co 3*d* interaction. Thus the half-metallic electronic structure is broken by the Co$-Y$-type disorder due to the additional in-gap states originated from the nonbonding states of antisite Co. In the present results, we confirmed the reduction in spin polarization due to the Co$-Y$-type disorder. In Fig. 1, we show the total energy difference between ordered $L2_1$-type and the Co$-Y$-type disordered Co_2YZ ($dE_{\text{Co-}Y}$) which corresponds to a change in energy due to the Co$-Y$-type disorder from ordered $L2_1$ structure. A larger $dE_{\text{Co-}Y}$ indicates a lower possibility of the Co$-Y$-type disorder. We have tried to explain the chemical trend of $dE_{\text{Co-}Y}$ with several factors, and found that the $dE_{\text{Co-}Y}$ roughly correlates with the total valence electron charges around Y atom in the ordered $L2_1$-type Co_2YZ. Note that the valence electron charges are evaluated by projecting the wave functions onto spherical harmonics within spheres of a radius around each ion. As a sphere of the radius, we adopted covalent bond radius; i.e., 1.36 Å for Ti, 1.25 Å for V, 1.27 Å for Cr, 1.39 Å for Mn, and 1.25 Å for Fe, respectively. As shown in Fig. 1, the $dE_{\text{Co-}Y}$ decreases, in principle, with increasing the valence electron charges around Y atom. Since the shape of the local potential at each site is mainly determined by the charge distribution around each atom, the $dE_{\text{Co-}Y}$ increases as the valence electron charges around Y atom decrease as compared with those of Co. This chemical trend indicates that Ti-based alloys are better to prevent the Co$-Y$ (Y=Ti, V, Cr, Mn, and Fe)-type disorder, and Fe-based alloys cause the Co$-Y$-type disorder with high possibility.

While the main part of the $dE_{\text{Co-}Y}$ is characterized by the valence charge distribution of Y atom, there exists marked dependence of $dE_{\text{Co-}Y}$ on Z atom. In particular, the dependence is categorized as group III atoms (Al and Ga) and group IV atoms (Si, Ge, and Sn). We consider that there are mainly two effects which cause the Z atom dependence: one is the screening effect, and the other is the magnetic effect. The former effect is attributed to delocalized character of *sp* valence electrons which act to screen the charge transfer due to the defect formation. Since the group IV atoms have an additional *sp* electron compared with the group III atoms, the degree of the screening depends on Z atom. The latter effect also causes the Z atom dependence, because the magnetic moment of Co_2YZ varies according to Z atom. The total Z atom dependence in $dE_{\text{Co-}Y}$ is determined by the competition of these two effects. We have confirmed that the screening effect mainly contributes the Z atom dependence of $dE_{\mathrm{Co}-Y}$ in $\mathrm{Co_2Ti}Z$ and $\mathrm{Co_2}VZ$, while the magnetic effect is remarkable in $\mathrm{Co_2Cr}Z$, $\mathrm{Co_2Mn}Z$, and $\mathrm{Co_2Fe}Z$.

From our calculation results, we can propose stable Co-based full-Heusler alloys for the Co-related atomic disorder with excellent prospects for HMF. We consider that $\mathrm{Co_2TiSi}$, $\mathrm{Co_2TiGe}$, $\mathrm{Co_2TiSn}$, $\mathrm{Co_2VAl}$, and $\mathrm{Co_2VGa}$ are as promising as HMF, since these alloys exhibit high spin polarizations in the ordered $L2_1$ structure and high tolerances for the $\mathrm{Co}-Y$-type disorder. Although the Curie temperature of these alloys is not so high and expected to be around 300–400 K (Ref. 27) because of the small magnetic moment, the partial substitution of Ti or V by other transition metal having more valence electron charges such as Mn and Fe will provide higher Curie temperature. We also recommend $\mathrm{Co_2MnSn}$, because the $\mathrm{Co_2MnSn}$ also exhibits relatively high tolerance for the $\mathrm{Co}-Y$-type disorder and show high spin polarization of 89.3% for s and p states (74.7% for all states).

In conclusion, we investigate the stability of Co-based full-Heusler alloys $\mathrm{Co_2}YZ$ (Y=Ti, V, Cr, Mn, and Fe; Z=Al, Ga, Si, Ge, and Sn) for the Co-related atomic disorder, exploring possible 25 combinations of the alloys by using the density functional first-principles calculations. We found that the tolerance of $\mathrm{Co_2}YZ$ for the $\mathrm{Co}-Y$-type disorder correlates with the total valence electron charges around Y atom in the ordered $L2_1$-type $\mathrm{Co_2}YZ$, because a difference in valence electron charges between Co and Y atoms leads to a different shape of the local potential at each site. We propose that $\mathrm{Co_2TiSi}$, $\mathrm{Co_2TiGe}$, $\mathrm{Co_2TiSn}$, $\mathrm{Co_2VAl}$, $\mathrm{Co_2VGa}$, and $\mathrm{Co_2MnSn}$ are prospective candidates as stable HMF with Curie temperature higher than 300 K because of high spin polarizations in the ordered $L2_1$ structure and high tolerances for the Co-related atomic disorder and are worth further investigation.

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