First-principles study for electronic structure and physical property of Co-based Heusler alloys

Yohei Kota and Akimasa Sakuma
Department of Applied Physics, Tohoku University, Sendai, Japan
E-mail: kota@solid.apph.tohoku.ac.jp

Abstract.
The statistical investigation of the physical property of Co-based Heusler alloys with the atomic composition or configuration dependence are carried out in first-principles approach. In particular, the electronic structure, magnetic moment and electrical resistivity due to disorder alloy effects of Co$_2$Mn$_{1-z}$Si$_z$ (0.0 < z < 1.0) and Co$_2$Mn$_{1-y}$Fe$_y$Si (0.0 < y < 1.0) with the L2$_1$, B2 and A2 structure are calculated by using the tight-binding linear muffin-tin orbital method combined with the coherent potential approximation based on the local spin-density functional approximation and by using the Kubo-Greenwood formula, respectively. The obtained results indicate that these properties of the Co-based Heusler alloys significantly depend on the atomic configuration and composition, especially, they are sensitive to the existence of the half-metallic property.

1. Introduction
Co-based Heusler alloys are one of the strong candidates for a high spin-polarized material after the predictions of their half-metallic property from the results of some electronic structure calculations. Thus they have attracted much attention because of their potential in the application to Spintronics. In these years, there are a lot of experimental reports that large magnetoresistance ratios have been obtained from the tunnel magnet resistance (TMR) [1, 2] and current perpendicular to plane giant magnetoresistance (CPP-GMR) [3, 4] devices by using Heusler alloys as a ferromagnetic electrode. These experimental results show an evidence of the high degree of the spin-polarization of Heusler alloys due to half-metallic property which had been previously expected in the theoretical viewpoints.

The half-metallic property of Heusler alloys, however, is considered to be quite sensitive to their atomic configuration and composition [5, 6]. It is pointed out that if there is some lattice defects in crystal, the half-metallic property is possibly broken. Recently, artificial Fermi level controlling of half-metallic Heusler compounds Co$_2$MnSi is attempted by Al doping, and the observed data is good agreement with the results obtained by the first-principles calculation [7]. These facts indicate that the electronic structure of Heusler alloys are strongly influenced by both atomic configuration and composition, therefore, their physical properties based on the electronic structure are also influenced.

Furthermore, it is a serious problem that the fundamental properties, in particular transport property, of Heusler alloys are not investigated enough experimentally and theoretically. Motivated by these background, we calculate some fundamental properties of Co-based Heusler...
alloys such as the electronic structure, magnetic moment and electrical resistivity by first-principles approach in the present study. The statistical investigation of these properties depending on the atomic configuration and composition is carried out to clarify the effect of the atomic defection and substitution in crystal.

2. Methodology
For the present calculation, we adopt the three types of the typical crystal structure of Co$_2$YZ full-Heusler alloys, which is so called L$_2^1$ (full-ordered), B$_2$ (disordered between Y and Z atom) and A$_2$ (full-disordered) structure as shown in Fig. 1. The compounds of Co$_2$MnAl$_{1-z}$Si$_z$ (Y=Mn, Z=Al-Si, 0.0 $\leq$ z $\leq$ 1.0) and Co$_2$Mn$_{1-y}$Fe$_y$Si (Y=Mn-Fe, Z=Si, 0.0 $\leq$ y $\leq$ 1.0) alloys are dealt in the bulk crystals with L$_2^1$, B$_2$ and A$_2$ structure. At first, we carry out the electronic structure calculation in disordered alloys system by using the tight-binding linear muffin-tin orbital (TB-LMTO) method in conjunction with the coherent potential approximation (CPA) to deal with the substitution-type alloy effects [8]. The local spin-density functional approximation (LSDA) is adopted for the self-consistent electronic structure calculation. Next, the electrical conductivity based on the obtained electronic structure is calculated by using the Kubo-Greenwood formula assuming zero temperature, which is formulated by Turek et.al. in the TB-LMTO-CPA scheme [9]

$$\sigma_\mu = \lim_{\delta \to +0} \frac{e^2}{4\pi \hbar V} \mathrm{Tr} \langle (g^\beta (\epsilon_F^+)) - (g^\beta (\epsilon_F^-)) \rangle [X_\mu, S^\beta] [g^\beta (\epsilon_F^+)) - (g^\beta (\epsilon_F^-)) \rangle [X_\mu, S^\beta] \rangle_{\text{conf.}}$$

where $X_\mu$, $V$, $\epsilon_F$ are the Cartesian coordinate operator ($\mu = x, y, z$), the volume of the unit cell, the Fermi level ($\epsilon_F^\pm = \epsilon_F \pm i\delta$), respectively, and $\langle \cdots \rangle_{\text{conf.}}$ means the configuration average of random system. $S^\beta$, $g^\beta (\epsilon_F^\pm)$ are the structure constant and the retarded and advanced anxiously Green’s function in the most localized $\beta$ representation of the TB-LMTO-CPA method [8]. Note that the vertex correction is evaluated by means of the ladder approximation to satisfy the charge conservation law [10]. The lattice constants are set to a experimental data, $a = 5.755$ Å for Co$_2$MnAl, $a = 5.655$ Å for Co$_2$MnSi [11] and $a = 5.640$ Å for Co$_2$FeSi [12]. In the intermediate region of these compounds, the lattice constants are estimated by the Vegard’s law, i.e. $a = 5.755 \times (1 - z) + 5.655 \times z$ Å for Co$_2$MnAl$_{1-z}$Si$_z$ and $a = 5.655 \times (1 - y) + 5.640 \times y$ Å for Co$_2$Mn$_{1-y}$Fe$_y$Si.

3. Results and Discussions
First, we show the density of the states (DOS) of Co$_2$MnSi with the L$_2^1$, B$_2$ and A$_2$ structure divided into the majority and minority spin states in Fig. 2. In the L$_2^1$ and B$_2$ structure, it is confirmed that their DOS of the minority spin states have an energy gap at the Fermi level and become a half-metal. The energy gap around the Fermi level of Co-based full-Heusler alloys
in the ordered L2₁ structure is mainly constructed by the states based on the second nearest Co-Co hybridization [13]. So the half-metallic property of the B2 structure is still preserved due to the ordering of the Co-sub-lattice as well as Co2CrAl [6]. The magnetic moment in the L2₁ and B2 structure become close to 5.0 μB, which reflects the feature of half-metals having integer magnetic moment. On the other hand, in the A2 structure, the energy gap around the Fermi level in the minority spin states is completely disappeared, therefore, the magnetic moment deviates from integer to 4.7 μB.

Next, we investigate the physical property such as the magnetic moment and residual resistivity due to substitution type alloy effect in Co₂MnAl₁₋ₓSiₓ (0.0 < x < 1.0) and Co₂Mn₁₋ₓFeₓSi (0.0 < y < 1.0) with the L2₁, B2 and A2 structure, respectively. The atomic composition dependence of the magnetic moment is shown in Fig. 3 as a function of the number of the valence electron (Nᵥ). Note that the number of the valence electron is corresponding to Nᵥ = 28 for Co₂MnAl, Nᵥ = 29 for Co₂MnSi and Nᵥ = 30 for Co₂FeSi. The left half (28 < Nᵥ < 29) of Fig. 3 belongs to the Co₂MnAl₁₋ₓSiₓ region, while the right half (29 < Nᵥ < 30) to the Co₂Mn₁₋ₓFeₓSi region.

When we focus on the Co₂MnAl₁₋ₓSiₓ region in Fig. 3, there is a linear increase of the magnetic moments in L2₁ and B2 structure, which is proportional to the valence electrons number. This tendency is one of the features of half-metals that is so called the Slater-Pauling behavior, and the magnetic moment of half-metallic full-Heusler alloys is expressed in Nᵥ − 24 μB [13]. In the region of Co₂Mn₁₋ₓFeₓSi, however, the Slater-Pauling behavior is not obtained, and the magnetic moments have a peak about 5.2 μB around y = 0.4. These results are corresponding to the result of a similar calculation in Refs. [14] for Co₂Mn₁₋ₓFeₓSi (y = 0.05, 0.10, 0.20) with the L2₁ structure. If Fe concentration is increased, there is two significant changes in the electronic structure. One is that the partial DOS of Fe lie in overall lower energy side than that of Mn, so in the minority spin states the edge of states of Fe laps over the energy gap constructed by Co-Co hyblidization. The other is the increase of the valence electrons number, therefore, the Fermi level shifts to higher energy side. Consequently, the position of the Fermi level of Co₂Mn₁₋ₓFeₓSi goes into the conduction band in the minority spin states, so the behavior of the magnetic moment is deviated from Nᵥ − 24 μB. In the A2 structure, since the half-metallic property is broken in the whole region, the composition dependence of the magnetic moment is different behavior from those of the L2₁ and B2 structure.

The calculated resistivities in the bulk system as a function of the valence electrons number are shown in Fig. 4. Some of the experimental measurements of the electrical resistivity of Co-based Heusler alloys are reported by several workers, 7 μΩcm [15] for the single crystal, 106
Figure 3. Magnetic moments as a function of valence electrons number. The red, blue and orange line indicates the results in L2\textsubscript{1}, B2 and A2 structure, respectively.

Figure 4. Electrical resistivities as a function of valence electrons number.

$\mu\Omega\text{cm}$ [16] for the thin film of Co\textsubscript{2}MnSi, and $0.2\ \mu\Omega\text{cm}$ [17] for the single crystal, $41\ \mu\Omega\text{cm}$ [18] for the thin film of Co\textsubscript{2}FeSi, respectively. These data seem to be good agreement with the calculated results, although there is no guarantee that the degree of the order, i.e. order parameter, of these samples is corresponding to the situation of the present calculation. Thus we have to be more careful to compare them.

When we pay attention to the calculation results, the electrical resistivities are originated only in the alloy effects, therefore, the electrical resistivity of Co\textsubscript{2}MnAl, Co\textsubscript{2}MnSi and Co\textsubscript{2}FeSi with the full-ordered L2\textsubscript{1} structure vanish. The measured resistivities of them are, of course, finite due to the scattering by impurities and lattice defects in samples. In the intermediate region between these compositions in the L2\textsubscript{1} structure, the electrical resistivities become finite values about $20\ \mu\Omega\text{cm}$ for Co\textsubscript{2}MnAl\textsubscript{1-z}Si\textsubscript{z} and $10\ \mu\Omega\text{cm}$ for Co\textsubscript{2}Mn\textsubscript{1-y}Fe\textsubscript{y}Si, which are close to most 3\textit{d} transition metal alloys. They are strictly smaller than those of the B2 and A2 structure in the whole region, because the scattering probability due to random alloys effects, i.e. the inverse of electrons relaxation-time, in the ordered structure is clearly decreased comparing with other disordered structures. In the Co\textsubscript{2}MnAl\textsubscript{1-z}Si\textsubscript{z} region, the electrical resistivities in the B2 and A2 structure are more than $100\ \mu\Omega\text{cm}$. Worth mentioning is that the resistivities of the A2 structure are smaller than those of the B2 structure in spite of the small relaxation-time. Within the phenomenological theory the electrical conductivity of metals is proportional to the electrons velocity, relaxation-time and DOS around the Fermi level, respectively. Total DOS at
the Fermi level in the A2 structure is larger than that of the B2 structure due to the breakdown of the half-metallic property. This may lead to the small resistivities in the A2 structure. By the similar reason, the electrical resistivities in Co$_2$Mn$_{1-y}$Fe$_y$Si with the L2$_1$ and B2 structure are relatively smaller than Co$_2$MnAl$_{1-z}$Si$_z$, since their Fermi level goes into the conduction band of the minority-spin states with increasing the valence electrons number.

Lastly, these results imply that it is possibly to cause the abrupt change of the electrical resistivities in a series of half-metallic Heusler compounds. In other word, the transport property of Heusler alloys is quite sensitive to whether it is half-metal or not. More detailed theoretical analysis of the transport property in Heusler alloys would be performed soon.

4. Summary
In the present study, we carried out the statistical investigation of the several properties such as the magnetic moment and electrical resistivity in Heusler compounds Co$_2$MnAl$_{1-z}$Si$_z$ (0 < z < 1.0) and Co$_2$Mn$_{1-y}$Fe$_y$Si (0 < y < 1.0) with the L2$_1$, B2 and A2 structures by using first-principles calculations. As a theoretical result, these properties strongly depend on the atomic configuration and composition that change the electronic structure of these alloys. In particular Co-based Heusler alloys, the existence of the half-metallic property significantly influences their physical properties.

Acknowledgments
This work is supported by Grant-in-Aids from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. Y. K. is also supported by the Grant-in-Aid for Japan Society for the Promotion of Science (JSPS) Fellows.

References
[1] Sakuraba Y, Hattori M, Oogane M, Ando Y, Kato H, Sakuma A, Miyazaki T and Kubota H 2006 Appl. Phys. Lett. 88 192508
[2] Tsunegi S, Sakuraba Y, Oogane M, Takanashi K and Ando Y 2008 Appl. Phys. Lett. 93 112506
[3] Sakuraba Y, Iwase T, Saito K, Mitani S and Takanashi K 2009 Appl. Phys. Lett. 94 012511
[4] Iwase T, Sakuraba Y, Bosu S, Saito K, Mitani S and Takanashi K 2009 Appl. Phys. Exp. 2 063003
[5] Picozzi S, Continenza A and Freeman A J 2004 Phys. Rev. B 69 094423
[6] Miura Y, Nagao K and Shirai M 2004 Phys. Rev. B 69 144413
[7] Sakuraba Y, Kota Y, Kubota T, Oogane M, Sakuma A, Ando Y and Takanashi K 2010 Phys. Rev. B 81 144422
[8] Turek I, Drchal V, Kudrnovský J, Söb M and Weinberger P 1997 Electronic structure of disordered alloys, surface and interfaces (Kluwer, Boston, 1997)
[9] Turek I, Kudrnovský J, Drchal V, Szunyogh L and Weinberger P 2002 Phys. Rev. B 65 125101
[10] Carva K, Turek I, Kudrnovský J and Bongone 2006 Phys. Rev. B 73 144421
[11] Webster P J 1971 J. Phys. Chem. Solids 32 1221
[12] Wurmehl A, Fecher G H, Kandpal H C, Ksenofontov V, Felser C and Lin H-J 2006 Appl. Phys. Lett. 88 032503
[13] Galanakis I, Dederichs P H and Papanikolaou N 2002 Phys. Rev. B 66 174429
[14] Galanakis I, Özdoğan K, Aktaş B and Şaşıoğlu E 2006 Appl. Phys. Lett. 89 042502
[15] Geiersbach U, Bergmann A and Westerholt K 2002 J. Magn. Magn. Mater. 240 546
[16] Raphae M P, Ravel B, Huang Q, Willard M A, Cheng S F, Das B N, Stroud R M, Bussmann K M, Claassen J H and Harris V G 2002 Phys. Rev. B 66 104429
[17] Schneider H, Jakob G, Kallmayer M, Elmers H J, Cinchetti M, Balke B, Wurmehl S, Felser C, Aeschlimann M and Adrian M 2006 Phys. Rev. B 74 174426
[18] Bulm C G F, Jenkins C A, Barth J, Felser C, Wurmehl W, Friemel G, Hess C, Behr G, Büchner B, Reller A, Rieggl S, Ebbinghaus S G, Ellis T, Jacobs P J, Kohlhepp J T and Swagten H J M 2009 Appl. Phys. Lett. 95 161903