Ab-initio search for half-metallic Co-based full Heusler alloys: Linear-response-based DFT+U study

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I. INTRODUCTION

A key property in emerging field of spintronics is the so-called half metallicity (HM): majority and minority states are completely spin polarized due to an imbalance in the number of electrons at Fermi level, where a finite density of states (DOS) exists for majority spin and an energy band gap is opened for minority spin. For example, a use of the HM materials as ferromagnetic electrodes in magnetic tunnel junctions (MTJs) is a straightforward way to enhance a tunneling magnetoresistance (TMR) ratio, leading to high-performance spintronics applications such as non-volatile magnetic random access memories and read-head of ultrahigh-density hard-disk drives. Family of Co-based full Heusler alloy has been paid particular much attention since some of them have a potential to possess a high spin polarization ($P$) or ultimately HM ($P = 100\%$) in addition to a high Curie temperature, e.g., 985 K for Co$_2$MnSi and 1100 K for Co$_2$FeSi. From the viewpoint of experiment, a large amount of works on measuring the $P$ value has been made for various Heusler alloys. However, existence of the HM electronic structure is still the subject of much controversy.

The spin polarization of the electrodes in MTJ device might be evaluated by the Jullièr model with a simple formula $\text{TMR} = \frac{2P_1P_2}{1-P_1P_2} \times 100\%$, where $P_1$ and $P_2$ are the tunneling spin polarizations of two ferromagnetic electrodes in MTJ. For Co$_2$MnSi MTJ with aluminium oxide (Al-O) barrier, Sakuraba et al. observed over the 80\% as the spin polarization. Then extremely high value 95.4\%, which may be close to fully spin-polarized electronic structure, was reported in MgO barrier MTJ instead of Al-O barrier one. However, an important note to be taken into account is that the $P_1(2)$ in the Jullièr formula is not the spin polarization in bulk system but the polarization of tunneling electrons in the MTJ. The electronic structure of the MTJ electrode differs from that of bulk material because the band structure is drastically changed due to the interfacial effect coming from insulating barrier. The tunneling electrons are also influenced by spin-filtering effect. These facts imply that there is a difficulty in accurate estimation of bulk spin polarization from the TMR of MTJ. This discrepancy may raise a fact that the spin polarization of Co$_2$FeSi estimated by Jullièr formula reaches only 50\% although several theoretical studies have predicted the HM ferromagnetism.

Point contact Andreev reflection (PCAR) technique has also been performed for the spin polarization in a lot of Heusler alloys. Conductance of metallic electron is measured at cryogenic temperature to evaluate the spin polarization in PCAR instead of tunneling electrons in
MTJ approach where the Julièr model is applied; hence, the \( P_{\text{PCAR}} \) referred as PCAR-measured spin polarization is expressed as \( P_{\text{PCAR}} = \frac{\langle N^{\uparrow}(E_F)v_{\uparrow}^2 \rangle - \langle N^{\downarrow}(E_F)v_{\downarrow}^2 \rangle}{\langle N^{\uparrow}(E_F)v_{\uparrow}^2 \rangle + \langle N^{\downarrow}(E_F)v_{\downarrow}^2 \rangle} \times 100 \% \). Here \( N^{\sigma}(E_F) \) and \( v_{\sigma}^2 \) are the DOS at Fermi energy and Fermi velocity with spin index \( \sigma (=\uparrow \text{ or } \downarrow) \) in diffusive regime\(^{17,19}\) where the current electrons are not assumed to be ballistic because of mean-free path shorter than point contact size in actual experiments. The \( v_{\sigma}^2 \) is the conductance of electrons, but the \( d \) orbital localized around Fermi energy is not dominant in current electron. This means the spin polarization arising from the \( d \) electron may be lost in the measured \( P_{\text{PCAR}} \). Previous works reported that the current spin polarization deduced by the PCAR is only 59 \% for Co\(_2\)MnSi\(^{10}\) and around 50 \% for Co\(_2\)FeSi\(^{9,11,12}\). The \( P_{\text{PCAR}} = 64 \% \) was also observed in Co\(_2\)(Fe,Mn)Si\(^1\).

Another critical subject to overcome is weak temperature resistivity in \( P \)\(^{9,11,14,17}\). Although extremely high value of TMR ratio (\~{}1000 \%) was obtained in Co\(_2\)MnSi/MgO/Co\(_2\)MnSi MTJ at low temperature, significant reduction of TMR leading to 335 \% at 290 K was reported\(^9\). Similar situation is also occurred in current-perpendicular-to-plane giant MR (CPP-GMR) device consisting of Co\(_2\)(Fe,Mn)Si electrodes and nonmagnetic Ag spacer\(^{11,16}\). For reasons of strong thermal-dependence of TMR and GMR performances, it is known that spin-flip inelastic tunneling process induced by magnon excitation affects adversely on the \( P \) in addition to spin-conserving elastic tunneling at increased temperature\(^{21,15}\). In this sense, a width of energy band gap in minority state is also of importance in searching HM material to improve the weak resistivity on the temperature.

Because of these augment from the experiment, the \textit{ab-initio} calculations based on the density functional theory (DFT)\(^{21,22}\) are expected to play a leading role for understanding fundamental electronic and magnetic structures in the search for HM Heusler materials. In the framework of the DFT calculation within local spin density approximation (LSDA), Galanakis \textit{et al.}\(^{23}\) presented an energy diagram of atomic orbital hybridization of Co\(_2\)MnGe system to clarify a mechanism of the HM; the minority energy band gap at Fermi level is originated by the \( t_{1u} \) and \( e_u \) orbitals that are arose from the \( d \) orbital hybridizations of two Co atoms sitting at different sublattices in the unit cell. Numerous other studies have also been done by the DFT calculations\(^{24,25}\).

However, dealing with correlation effects is a critical issue in the DFT study for Heusler compound. The standard DFT calculations based on the mean-field approximation such as LSDA and generalized gradient approximation (GGA) sometimes fail to predict the \textit{true} ground-state electronic structures due to a presence of \( d \) orbital localization in vicinity of transition metal atoms, meaning that many-body effect is problematic. Various approaches introducing the many-body effect into the DFT scheme have been proposed to recover the correlation problem that is missed in the LSDA and GGA; e.g., dynamical mean field theory (DMFT)\(^{26,27}\), GW approximation\(^{28,29}\), and DFT+U method\(^{30,31}\), but depending on which of method is employed to calculate, obtained electronic structures differ from each other even for same compound. For Co\(_2\)MnSi as an example, within the LSDA+DMFT framework, where dynamical correlation effect such as the spin-flip term is taken into account quantitatively, the Fermi energy locates at conduction edge of minority state by linear muffin-tin orbital (LMTO) method\(^{32}\) but at valence edge by Korringa-Kohn-Rostoker (KKR) method\(^{33}\). The GW calculation\(^{34}\), in which the electronic self-energy correction is included by many-body perturbation theory, predicts the Fermi energy is between the valence and conduction bands. For these approaches, a huge computational cost is also serious problem; applying to the MTJ model for properties including interfacial magnetocrystalline anisotropy and spin-dependent transport may be difficult. On the other hand, the DFT+U method\(^{35,36}\), in which parametrized on-site Coulomb (\( U \)) and exchange (\( J \)) interactions for \( d \)-orbital are introduced in the manner of the Hubbard model\(^{31,32}\), is a suitable approach on a practical level. Because of the efficient calculation cost, the DFT+U method can be applied to not only simple bulk materials but also large and realistic systems.

Generally, a property of electronic localization emerges significantly at interfaces and surfaces due to a broken symmetry. In this context, even in the bulk Heusler alloy consisting of two kinds of transition metals in its unit cell, one can expect that a strength of the electronic localization is not equivalent at different metal sites. This means the correlation parameters, \( U \) and \( J \) in the DFT+U method, are necessary to be treated \textit{independently} for non-equivalent atoms. Nonetheless, most of DFT+U studies have dealt the correlation effects in a perfunctory manner. One of typical attempts is assuming the \(+U\) value as an adjustable parameter to reproduce the experimental results including magnetic moment and band structure. When the unit cell has more than two of transition metal atoms like Heusler alloy, cursory handling of correlation term may increase a concern about misunderstanding of physical property. For instance, employing same \( U \) (and \( J \)) values for all metal sites is the situation where the nature of correlation interaction correction is equivalent at every vicinity of metal site. Even for a case where non-equivalent \(+U\) values are introduced to different sites, detailed analysis in terms of the electronic structure is completely lacking, thus this approach has not been verified so far.

The suitable values of the \( U \) and \( J \) for the DFT+U method are unknown; they depend on the atomic species and surroundings of the atom. A linear response (LR) approach\(^{37,38}\) is one of the advanced way to determine the correlation terms theoretically and to exclude \textit{ad hoc} treatment of the parameters. This method, in which the \(+U\) values at respective localized atom sites can be evaluated by response function of charge density obtained from the standard LSDA or GGA potential, has been applied.
for various correlated systems and succeeded to describe the ground state accurately. Recent study also reported that the +U values are not transferable among different calculation methods due to non-negligible dependence on computational setups even in theoretically determined parameters. This implies that the optimal correlation correction for the system of interest is to be estimated by each method used for the calculation, but unfortunately application of this LR-based DFT+U method to Heusler compounds has been limited only to structural phase transition.

In present paper, we address these issues in the Co-based full Heusler alloy. At the beginning, focusing on the Co$_2$MnSi, energy diagram of atomic-orbital hybridization is reconsidered. Our calculations reveal important atomic-orbital hybridizations in minority state, which are newly discovered and mainly dominate the energy gap at the Fermi energy. This unified energy diagram gives us a guideline for tuning the HM gap. By using the DFT+U method where the varying +U parameter is applied to the Mn and Co atoms independently, we investigate how the correlation parameter affects the property at high temperature.

**FIG. 1.** (Color online) Geometric crystal structures in $L_2_1$ symmetry for (a) Co$_2$MnSi, (b) Co$_2$(Y$_{0.25}$Mn$_{0.75}$)Si, (c) Co$_2$(Y$_{0.50}$Mn$_{0.50}$)Si, and (d) Co$_2$(Y$_{0.75}$Mn$_{0.25}$)Si. Red, blue, white, and green circles indicate Co, Mn, Si, and Y atoms, respectively, where Y is 3d transition metal atoms as Ti, V, Cr, or Fe.

is a promising candidate in terms of the Fermi level that locates at a center of gap between valence and conduction states, leading to a great advantage in stable HM property at high temperature.

**II. MODEL AND METHOD**

To model the full Heusler Co$_2$MnSi compound in $L_2_1$ structure, fcc-primitive cell that contains two Co atoms sitting at (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4) in Wyckoff positions, one Mn atom at (1/2, 1/2, 1/2), and one sp-element Si at (0, 0, 0) was prepared (a conventional unit cell is shown in Fig. 1 (a)). The lattice constant is set to experimental value of 5.645 Å. The detailed crystal structures for ternary system Co$_2$YSi, where the Mn is replaced to Y of Ti, V, Cr, or Fe, and quaternary Co$_2$(Y,Mn)Si, where a part of Mn is substituted with Y, are described in Sec. II D.

The self-consistent DFT calculations were performed by means of the *ab-initio* package of Quantum-ESPRESSO implementing the ultrasoft pseudopotentials which are parametrized by the scheme of Rappe, Rabe, Kaxiras, and Joannopoulos. The plane wave basis set for the wave function and charge density has a energy cutoff of 40 and 400 Ry, respectively. The self-consistent procedures had been achieved until iterative total energy difference becomes less than convergence criterion of 10$^{-8}$ Ry by using Monkhorst-Pack special k-point mesh of $16 \times 16 \times 16$ in the first Brillouin zone by Methfessel-Paxton smearing method with a broadening parameter, 0.02 Ry.

The GGA is used for exchange-correlation term and the correlation correction of the +U in the atomic limit approximation is incorporated in the simplified rotational-invariant formulation. In order to exclude any experimental and/or empirical knowledges from selection of the absolute parameter value, the effective onsite Coulomb interaction, $U_{eff}$, is computed within the LR theory for all transition metal atoms. Here, the $U_{eff}$ is defined as $U_{eff} = U - J$ (or approximately, $J \approx 0$), hence, we assume that the Coulomb interaction is more
dominant than the exchange one at localized electron sites.

In the framework of the LR theory\cite{23} the on-site parameter for an atom $\alpha$, $U_{\text{eff}}^{LR(\alpha)}$, is evaluated from the second derivatives of the total energy functional as

$$U_{\text{eff}}^{LR(\alpha)} = \frac{\partial^2 E_{\text{SCF}}^{\text{eff}}([q_\alpha])}{\partial q_\alpha^2} - \frac{\partial^2 E_{\text{KS}}^{\text{eff}}([q_\alpha])}{\partial q_\alpha^2}. \quad (1)$$

The total energies $E_{\text{SCF}}^{\text{eff}}$ and $E_{\text{KS}}^{\text{eff}}$ correspond to interacting (fully screened) and non-interacting systems. The second term in Eq. (1) is necessary to subtract unphysical contributions in the total energy\cite{24,25} that are caused by standard exchange-correlation functionals (LSDA and GGA), where the total energy has a curvatures for non-integer occupation $q_\alpha$ and often misleads to incorrect energy minima. The total energy derivatives are calculated by constrained DFT approach;

$$E^\alpha_i([q_\alpha]) = \min_{n(r),\mu_\alpha} \left\{ E_{\text{GGA}}^\alpha[n(r)] + \sum_\alpha \mu_\alpha (n_\alpha - q_\alpha) \right\}, \quad (2)$$

where

$$\frac{\partial}{\partial q_\alpha} E^\alpha_i([q_\alpha]) = -\mu_\alpha, \quad \frac{\partial^2}{\partial q_\alpha^2} E^\alpha_i([q_\alpha]) = -\frac{\partial \mu_\alpha}{\partial q_\alpha}. \quad (3)$$

Using nonlocal linear response matrices

$$(\chi_{\text{SCF}})_{\beta\alpha} = \frac{\partial n_\beta}{\partial \mu_\alpha}, \quad (\chi_{\text{KS}})_{\beta\alpha} = \frac{\partial n_\beta^{\text{KS}}}{\partial \mu_\alpha}, \quad (4)$$

the Eq. (1) is rewritten to obtain the $U_{\text{eff}}^{LR(\alpha)}$ as

$$U_{\text{eff}}^{LR(\alpha)} = (\chi_{\text{KS}}^{-1} - \chi_{\text{SCF}}^{-1})_{\alpha\alpha}. \quad (5)$$

The matrix elements of response matrices are numerically computed; the $\chi_{\text{SCF}}$ is obtained from the self-consistent (interacting) calculations under applied local potential $\mu_\alpha$ and the $\chi_{\text{KS}}$ is from the first iteration in self-consistent cycle after the end of GGA ground-state calculations – the latter is occupation changes that arise from the non-interacting hybridization due to the $\mu_\alpha$. The LR approach, in principle, requires a response of electron occupations with regard to the perturbed potentials at a single site in an infinite crystal environment for the $U_{\text{eff}}$ evaluation, in which any artifacts due to the periodic boundary conditions are excluded\cite{23,24} We checked a convergence behavior of $U_{\text{eff}}$ as a function of supercell size, and found a $3 \times 3 \times 3$ supercell is practically large enough to get converged parameters, thus the LR calculations were performed in this supercell size containing 108 atoms to obtain the reasonable $U_{\text{eff}}$ value.

### III. RESULTS AND DISCUSSIONS

#### A. Revisiting fundamental electronic structure of Co$_2$MnSi within GGA

We start the GGA calculations to reconsider a fundamental electronic structure in Co$_2$MnSi. Figure 2 (a) shows projected band structures in the minority spin states for Co $e_g(u)$ and $t_{2g}(1u)$, Mn $e_g$ and $t_{2g}$, and Si $t_{1u}$ orbitals. Since the two Co atoms in primitive cell are at tetrahedral $T_d$ site symmetry, corresponding to a subgroup of $O_h$ symmetry, the $d$ orbital of a Co split into doublet $e_g$ and $e_u$, and triplet $t_{2g}$ and $t_{1u}$ states due to hybridizations with the $d$ orbitals of second nearest another Co atom, as discussed in Ref. \cite{24}. The Mn $d$ simply split into $e_g$ and $t_{2g}$ states. Now, the eigenstates at $\Gamma$ point in the Brillouin zone is focused. The Co $e_u$ orbital locates at 0.4 eV above the Fermi energy and has no hybridization with the any orbitals because there are nothing having same symmetry character in other atoms. Anti-bonding Co $t_{2g}$ state that hybridizes with bonding Mn $t_{2g}$ can be seen at $-0.3$ eV. As a result, it is found that a minority band gap is formed by the anti-bonding $t_{2g}$ and non-bonding $e_u$ of Co atom, where the minority energy band gap, $E_{\text{gap}}^\alpha$, leads to about 0.5 eV. Another essential atomic hybridization is found at $t_{2g}^\alpha$ symmetry character; Co $t_{1u}$ orbital is appeared at higher energy, 3.8 eV, from Fermi level due to a hybridization with Si $p$ state that belongs to $t_{1u}$ site symmetry in the $T_d$ crystal field. We do not mention the $e_g$ hybridization between Co and Mn since it has been already discussed in previous work\cite{23}.

Figure 2 (b) presents an energy diagram of atomic-orbital hybridizations for minority spin state. The $a_{1g}$ character corresponds to the Si $s$ orbital that is at very low energy and is not appeared in the band structures of Fig. 2 (a). As mentioned above, the highest orbital state of valence band is dominated by Co $t_{2g}$ orbital that hybridizes with Mn $t_{2g}$ and that forms anti-bonding state just below the Fermi energy. The Co $t_{1u}$ is pushed up to quite higher energy through the hybridization with Si $p$ orbital, and Co $e_u$ is left at above the Fermi level. Thus, this diagram suggests that the main contributions to construct the minority band gap are come from $t_{2g}$ coupling of Co and Mn atoms, and the $t_{1u}$ orbital of Co no longer contributes to the gap; this conclusion is different from previous study\cite{24} where the band gap in minority state is mostly dominated by Co $e_u$ and $t_{1u}$ orbitals. More importantly, our diagram emphasizes that the HM property and electronic structure near the Fermi level are tunable by controlling the $t_{2g}$ coupling through a select of $Y$ atom in $L_2$ Heusler alloy.

Even though our diagram is at variance with previously reported one\cite{24}, the 12 valence electrons for Co$_2$MnSi occupy three Co $t_{2g}$, three Mn $t_{2g}$, two Co $e_g$, three Si $t_{1u}$, and one Si $a_{1g}$ orbitals in down-spin state. This means our diagram satisfies the well-known Slater-Pauling relationship\cite{24}. The magnetic moment of the system, $m_{\text{spin}}$, is
FIG. 2. (Color online) (a) Projected band structures in minority spin for Co$_2$MnSi; the color map shows the orbital-component spectral weights of $e_g$ and $t_{2g}$ symmetries for Co $d$, $e_g$ and $t_{2g}$ for Mn $d$, and $t_{1u}$ for Si $p$ orbitals by blue, red, skyblue, orange, and green, respectively. Total band structure of minority spin is also shown by white solid line. The Fermi energy is set to zero. (b) Minority-spin state atomic-orbital energy diagram that shows hybridizations among Co–Co $d$, Mn $d$, and Si $p$. The $a_{1g}$ is $s$ orbital of Si atom that is not appeared in projected band structures given in (a).

Note that the previous study was carried out for Co$_2$MnGe$^{24}$ Since the Ge atom belongs to the same group as Si in periodic table, the number of valence electrons of Co$_2$MnGe is equivalent to that of Co$_2$MnSi. Therefore, as expected, the Co$_2$MnGe is confirmed to be similar results to the Co$_2$MnSi. The energy diagram obtained from the band structure calculations corresponds to Fig. 2 (b) and the integer value of spin magnetic moment is calculated ($m_{\text{spin}} = 5.00 \mu_B$).

B. Role of correlation effects for Mn and Co in Co$_2$MnSi

As mentioned in the introduction, the behaviors of electron localizations are supposed to be different in Co and Mn sites. Therefore, we emphasize an importance of role of the correlations for different sites. In order to understand the influence of the +U upon the atomic energy diagram, modifications of band structures are investigated by performing the DFT+U calculations with varying $U_{\text{eff}}$ parameters for Co and Mn atoms independently. Here, we refer to the case where the $U_{\text{eff}}$ is applied to only Mn (Co) site as $+U_{\text{Mn}}$ ($+U_{\text{Co}}$) representation.

We firstly mention the $+U_{\text{Mn}}$ case. As the correlation parameter for Mn, $U_{\text{Mn}}^{\text{eff}}$, increases, as presented in Fig. 3 (a), the total $m_{\text{spin}}$ is constant but Mn (Co) $m_{\text{spin}}$ monotonically increases (decreases). Note that two of Co atoms exist in the primitive cell so the variation of Co $m_{\text{spin}}$ is to be twice. The increased $m_{\text{spin}}$ of Mn is arose from significant reduction of minority spin electron occupations, as shown in Fig. 3 (b). This reflects following behavior; the large +U value intensifies the Coulomb interaction aspect and allows electrons to occupy not same but different orbitals with parallel spins by Pauli exclusion principles and Hund’s rule, leading to a gain in kinetic energy.

Since the $t_{2g}$ orbitals of Co and Mn change the most noticeably by different $U_{\text{eff}}$ value, we traced modifications in the band structures of these orbitals. Figure 4 (a) presents the minority spin band structures around $\Gamma$ point calculated by standard GGA, and the GGA+$U_{\text{Mn}}$
TABLE I. Total and atom-resolved magnetic moments (in $\mu_B$) for Co$_2$MnSi with the comparison of present and previous theories as well as experiments. The $U_{\text{eff}}$ values determined by LR approach are employed in present work; the $U_{\text{eff}} = 3.535$ eV for Mn (GGA+$U_{\text{Mn}}$), 6.570 eV for Co (GGA+$U_{\text{Co}}$), and both values for Mn and Co (GGA+$U_{\text{Mn,Co}}$). The first column gives the calculation methods (and types of the exchange-correlation functionals in parentheses) for theory and measurement techniques for experiment.

| Method          | Total | Co    | Mn    | Si    | Ref. |
|-----------------|-------|-------|-------|-------|------|
| Present work    |       |       |       |       |      |
| GGA             | 5.01  | 1.05  | 2.95  | -0.05 |      |
| GGA+$U_{\text{Mn}}$ | 5.01  | 0.75  | 3.57  | -0.07 |      |
| GGA+$U_{\text{Co}}$ | 5.08  | 1.38  | 2.67  | -0.14 |      |
| GGA+$U_{\text{Mn,Co}}$ | 5.16  | 1.08  | 3.50  | -0.17 |      |
| Theory$^a$      |       |       |       |       |      |
| FS-KKR (LSDA)   | 4.94  | 1.02  | 2.97  | -0.07 | 24   |
| ASA-ASW (GGA)   | 5.00  | 0.93  | 3.21  | -0.06 | 31   |
| FLAPW (GGA)     | 5.00  | 1.06  | 2.92  | -0.04 | 29   |
| FP-LMTO (GGA+$U^b$) | 5.00  | 1.08  | 2.97  | -0.08 | 65   |
| MLWF-FLAPW (GGA+$U^d$) | 5.00  | 1.05  | 3.01  | -0.06 | 69   |
| KKR (LSDA+DMFT$^c$) | 4.97  |       |       |       | 39   |
| FLAPW-GW (GGA)  | 5.00  |       |       |       | 40   |
| Experiment$^e$  |       |       |       |       |      |
| Sucksmith       | 5.07  | 0.75  | 3.57  |       | 61   |
|                 | 5.01  |       |       |       | 62   |
| SQUID           | 4.97  |       |       |       | 63   |
| SQUID           | 5.00  | 0.72  | 3.34  |       | 64   |

$^a$ FS-KKR: Full-potential screened Korringa-Kohn-Rostoker Green’s function method; ASA: atomic sphere approximation; ASW: augmented spherical waves method; FLAPW: full-potential linearized augmented plane wave method; FP-LMTO: Full-potential liner muffin-tin orbital method; MLWF: maximally localized Wannier functions; GW: GW approximation.

$^b$ The values $U (J)$ of 3.5 (1.0) and 5.0 (0.9) eV for Co and Mn, respectively, are chosen to reproduce total magnetic moment observed experimentally.

$^c$ The $U$ and $J$ values of 3.0 and 0.9 eV, which have been reported as average values of determined parameters by theory for 3d transition metal pure bulk, are used.

$^d$ The respective $U_{\text{eff}}$ values of 3.28 and 3.07 eV for Co and Mn are determined by constrained random phase approximation (cRPA).

$^e$ Sucksmith: Sucksmith ring-balance measurement by Faraday method; SQUID: Superconducting quantum interface device magnetometry.

FIG. 3. (Color online) The dependences of (a) the total and atom-resolved spin magnetic moments, $m_{\text{spin}}$, and (b) the $d$-electron occupations of majority and minority states with respect to the varying $U_{\text{eff}}^{\text{Mn}}$ for the $+U_{\text{Mn}}$ case. Opened black, red, blue, and green circles are $m_{\text{spin}}$ of total, Co, Mn, and Si, and red (blue) closed up-pointing and opened down-pointing triangles are $d$-occupations for majority and minority states of Co (Mn), respectively. The $U_{\text{eff}} = 0$ means the GGA result. The vertical solid line indicate the determined values of $U_{\text{eff}}^{LR}$. Similar plots for the $+U_{\text{Co}}$ are in (c) and (d) by the same notations with (a) and (b).
DOS lies at the Fermi energy, is different situation from the insulators and semi-conductors. In principle, the total number of valence electrons at each atom site must be conserved even though the +U effect is introduced. Accordingly, the upward shifting in the valence state of minority Mn orbital can be understood as follow; the occupations in a spin channel, namely majority state, vary to increase by the applied +U effect, but simultaneously, the occupations in opposite spin, minority state, is also changed to reduce sensitively for the total occupations to be a constant at each atom. This arguments that are based on the energy diagrams in Figs. 4 (b) and (c) are consistent with the behaviors of spin magnetic moment and electron occupations at each atom site [Figs. 3 (a) and (b)], thus, this scenario can be concluded as a possible reason behind effects of the +U on the Mn d orbitals.

Secondly, the +U_{Co} result is considered. In the range of U_{eff} less than around 6.0 eV, an increase of the spin magnetic moment at Co site is not significant, but suddenly increased afterward [Fig. 3(c)]. In Fig. 5, the U_{Co} dependence of the electronic structures and hybridization behaviors of Co and Mn are summarized. In the valence states, it can be seen that the contribution to the anti-bonding t_{2g} is switched from Co to Mn [Fig. 5(a)], contrarily, the bonding e_{g} state is from Mn to Co [Fig. 5(b)]. The e_{u} state in Fig. 5(b) moves to higher energy by the +U_{Co}, but obviously it does not hybridize with any atoms.

To understand the behavior of changing m_{spin} in the +U_{Co} in Figs. 3 (c) and (d), the possible energy diagrams for majority and minority states are illustrated in Figs. 5(c) and (d). The majority Co t_{2g} simply goes to lower energy by the introduction of the +U_{Co}, so that the Co d occupation increases and is saturated at larger U_{Co} values. For minority state, the d electrons' behavior of Co and Mn is intricate, but it can be understood by going back to the principle view that first focus is paid to the hybridization between Co atoms at different sub-lattices, and the hybridization between Mn and Co–Co states afterward. The Co d_{xz,yz} orbital is pused up (down) due to the U_{Co} and then it hybridizes with Mn e_{g} (t_{2g}) state [Fig. 5(d)]. Increasing the U_{Co} affects the energy gap and most notably Co e_{g} orbital contributes as an anti-bonding state at large U_{Co} value while it does as bonding state in small U_{eff} (see blue band of energy diagram in Fig. 5(d)). This event induces the significant reduction of the minority Co occupations [red down-pointing triangle in Fig. 3(d)], resulting in an increase of the total m_{spin} at over ~ 6 eV of the U_{Co} [black plot in Fig. 3(c)].

From above discussions, the underlying physical mechanism of the correlation effects on the magnetic moment can be understood from the viewpoint of electronic structure for both +U_{Mn} and +U_{Co} cases. This implies that a consistency of our energy diagram proposed in Fig. 3(b) is demonstrated.

FIG. 4. (Color online) (a) Dependence of the band structures in minority state of varying +U_{Mn} parameter, i.e., GGA (U_{eff} = 0.0 eV for Mn site), small (3.0) and large (6.0) values, where projected spectral weights for Co and Mn t_{2g} states are shown by red and orange color maps in left and right panels, respectively. The Fermi energy is set to zero and total minority band structure is also plotted by white line. Schematic summary of changes in atomic orbital hybridizations for (b) majority and (c) minority states. Arrows in (b) and (c) indicate the energy shift induced by the effect of +U_{Mn}.
FIG. 5. (Color online) Dependence of the minority band structures of varying +U_{Co} parameter, i.e., small (U_{eff} = 1.5 eV for Co site), medium (4.5), and large (7.5) values, where projected spectral weights for (a) t_{2g} states for Co (left panel) and Mn (right) are shown by red and orange color maps, and (b) e_{g} ones by blue and sky-blue, respectively. Note that energy ranges in (a) and (b) are different. Schematic summary of changes in atomic orbital hybridizations for (c) majority and (d) minority states. Notation is the same in Fig. 4.

C. LR-based DFT+U analyses of Ground-state electronic and magnetic structures in Co$_2$MnSi

Now, the non-empirical values of the +U parameter are incorporated into the band calculations. The LR calculations were carried out to determine the U_{LR}^{eff} and found to be 3.535 and 6.570 eV for Mn and Co, respectively. These values are surprisingly greater than we expected and typically-used empirical values, for instance, the U_{eff} (= U − J) of 2.5 and 4.1 eV for Co and Mn in FP-LMTO calculations and the U_{eff} of 2.1 eV for both sites in KKR calculations. The cRPA approach determines the similar parameter values for Mn (3.07 eV) to our work, but for Co (3.28 eV) almost a half value of our LR result. It was reported that even if the U_{eff} is theoretically determined, the obtained value depends on the approaches to derive the parameter and/or computational setups so that comparing the absolute values of U_{eff} may be meaningless. Thus, we employed the calculated U_{LR} values for a comparison of our results and experiments. The m_{spin} calculated by the GGA+U_{Mn} and GGA+U_{Co} are listed in Table I as well as GGA+U_{Mn,Co} where the U_{eff} is introduced to both Mn and Co sites. The GGA+U_{Mn}, +U_{Co}, and +U_{Mn,Co} calculations obtained the total m_{spin} of 5.01, 5.08, and 5.16 \mu_B, respectively, and they are in agreement with previous reports except for +U_{Mn,Co} case. When the m_{spin} for each atom site is focused, the +U_{Mn} results match to the experimental observations, although our values do not agree with other theories.

In the Fig. 6, we show the total and local DOS calculated by GGA, GGA+U_{Mn}, +U_{Co}, and +U_{Mn,Co}
schemes. For the minority state near the Fermi level, the total DOS of \( +U_{\text{Mn}} \) does not change much from the GGA and the HM nature is still confirmed with the \( E_{\text{gap}} \) of \( \sim 0.5 \) eV. However, the valence and conduction edges are dominated by only Co \( d \) components because of the Mn \( d \) orbital pushed away from the Fermi energy by the \( +U_{\text{Mn}} \) effects. In Fig. 6(c), the total DOS shows no longer the HM with the spin-down state of Co \( d \) crossing the Fermi energy. We expect this is comes from the exchange splitting of the Co atom; because the spin polarization is induced in Co \( d \) orbital by the \( +U_{\text{Co}} \), much majority states are occupied, contrarily slight minority states become empty at the Fermi level. In the case of \( +U_{\text{Mn,Co}} \), the exchange splitting of both Mn and Co atoms produces a big energy band gap compared to other \( +U \) schemes, but a finite minority DOS is appeared at Fermi level as \( +U_{\text{Co}} \) case. Importantly, in the experiment, the hard x-ray photoelectron spectroscopy measurements\(^{67}\) have reported that the valence band structure ranging from the Fermi energy to \( \sim 1.2 \) eV below is mostly contributed by Co 3\( d \) electrons.

From the above comparisons of the electronic structure and atom-resolved magnetic moment with experimental observations, hence, it can be concluded that the static many-body correlation \( +U \) is more important at \( Y \) site (\( Y=\text{Mn for } Co_2\text{MnSi} \)) compared to \( X \) site (\( X=\text{Co} \)) for a ground state where in good agreement with experiments. Here we explicitly mention that the energy diagram for the \( +U_{\text{Mn}} \) calculation corresponds to the GGA result presented in Fig. 2(b).

The LR calculations obtained the rather larger \( +U \) value for \( X \) site where the drastic changes in magnetic moment and electronic band structure as discussed in Figs. 3(c) and 5 (from medium to large \( U_{\text{eff}} \)). We do not have a strict description to explain why the \( +U \) for \( X \) site becomes a trigger bringing rather misled electronic and magnetic structures, but we may make an observation from the DOS in Fig. 6. The Co \( d \) orbital is rather delocalized in whole energy region compared to Mn \( d \) state. We speculate the itinerant orbital Co \( d \) is out of applicability where the LR approach can work properly, or the delocalized Co \( d \) state does not need the correlation correction. Further study might be necessary to inspect an appropriateness of the LR method as our future work. Hereafter, however, all LR-based GGA+\( U \) band calculations were carried out with \( U_{\text{eff}} \) parameters only for \( Y \) site, i.e., exclusion of the correlation at \( X \) site.

**FIG. 6.** (Color online) Local DOS obtained from (a) GGA, (b) GGA+\( U_{\text{Mn}} \), (c) GGA+\( U_{\text{Co}} \), and (d) GGA+\( U_{\text{Mn,Co}} \) calculations. Red, blue, and green lines are for Co \( d \), Mn \( d \), and Si \( p \) orbitals, and total DOS is also shown by gray filled area. Note that the local DOS for Co is twice since two Co atoms are included in primitive cell. Upper (bottom) area in each panel show the spin-up (down) state. The Fermi energy is set to zero.

### D. HM electronic structures in other ternary and quaternary systems

The ferromagnetic ternary Co\(_2\)YSi compounds, where \( Y \) is replaced from Mn to Ti, V, Cr, or Fe atom with the respective lattice constants of 5.743, 5.657, and 5.640 Å for Co\(_2\)TiSi\(^2\), Co\(_2\)VSi\(^2\), and Co\(_2\)FeSi\(^2\) were prepared. To the best of our knowledge, there are no experimental data for Co\(_2\)CrSi, so the equilibrium lattice constant is derived using Murnaghan fitting\(^{21}\) by the GGA potential. The obtained lattice constant for Co\(_2\)CrSi is found to be 5.369 Å and agrees with previous GGA result\(^{69}\). The correlation parameters of the \( Y \) atom derived by the LR calculations, \( U_{\text{eff}}(Y) \), are summarized in Table II.

We discuss the Co\(_2\)TiSi, Co\(_2\)VSi, and Co\(_2\)CrSi compounds where the number of valence electrons is less than in Co\(_2\)MnSi. As presented in bottoms of Figs. 7(n) and (b) for Co\(_2\)TiSi and Co\(_2\)VSi, the Fermi energy is found to be on the conduction state in minority spin although a gap is opened below the Fermi energy. On the other hand, in the Co\(_2\)CrSi, a band gap is not appeared in whole energy region (see bottom of Fig. 7(c)). These DOS’ result in \( m_{\text{spin}} \) values of 1.86, 2.86, and 4.02 \( \mu_B \) for Co\(_2\)TiSi, Co\(_2\)VSi, and Co\(_2\)CrSi, respectively. For the Co\(_2\)FeSi where the number of valence electrons is greater than Co\(_2\)MnSi, the Fermi energy seems to move...
to higher energetically, then the conduction edge of minority state is partially occupied. The calculation obtained 5.33 $\mu_B$ as the $m_{\text{spin}}$. The value of $P$ is also estimated as $P = \frac{D^\uparrow(E_F)-D^\downarrow(E_F)}{D^\uparrow(E_F)+D^\downarrow(E_F)} \times 100$ (%), where $D^\sigma(E_F)$ is the DOS of majority ($\sigma=\uparrow$) or minority ($\sigma=\downarrow$) spin state at the Fermi energy. The calculated values are -82.6, 11.5, 65.6, and -66.8 % for Y elements of Ti, V, Cr, and Fe, respectively, where the negative values for $Y = \text{Ti}$ and Fe are caused by higher peak of minority DOS than that of majority one at the Fermi level. Consequently, our LR-based DFT+U calculations indicate for ternary bulk system only Co$_2$MnSi shows the HM but the others do not.

We finally investigate the quaternary Heusler compounds with a chemical formula of Co$_2$(Y$_x$Mn$_{1-x}$)Si, where the Mn atom is partially substituted for $Y$ of Ti, V, Cr, or Fe atom with composition $x$ ($x = 0.25, 0.50, 0.75$). To model these systems in $L2_1$ structure, as illustrated in Figs. 1 (b)-(d), cubic primitive cells consisting of 16 atoms are considered. The lattice constant for Co$_2$(Y$_x$Mn$_{1-x}$)Si at composition $x$ is given by the Vegard’s law using equilibrium lattice constants for Co$_2$YSi ($a_{\text{YSi}}$) and Co$_2$MnSi ($a_{\text{CMS}}$) as $a(x) = xa_{\text{YSi}} + (1-x)a_{\text{CMS}}$. The $a$ values used for each composition in present work are listed in Table III. The $U_{\text{eff}}^{\text{LR}(\text{Mn})}$ and $U_{\text{eff}}^{\text{LR}(\text{Y})}$ that are determined by the LR in ternary Co$_2$MnSi and Co$_2$YSi.

Calculated total DOS for the systems, in which the Mn atom is partially substituted for light elements, Ti, V, and Cr, are presented in Figs. 7 (a)-(c). We do not mention the changes in electronic structures for projected orbital components in detail because of the complexity. The results indicate that the HM property can be seen in Co$_2$(Ti$_{x}$Mn$_{1-x}$)Si at $x = 0.25$ and 0.50, Co$_2$(V$_{x}$Mn$_{1-x}$)Si at $x = 0.25, 0.50$, and 0.75 (the $E_{\text{gap}}^\uparrow$ is listed in Table III). The Co$_2$(Cr$_{x}$Mn$_{1-x}$)Si does not show the HM because of a widely broadened few minority-DOS on the Fermi energy, but relatively high $P$ value is confirmed for every composition. When a part of Mn is substituted for Fe atom, the HM electronic structure is obtained only at $x = 0.25$. However, a remarkable feature in this model is that the Fermi level locates at the center between valence and conduction bands with the largest $E_{\text{gap}}^\uparrow$ in our study, $\sim 0.5$ eV. Figure 8 plots the total $m_{\text{spin}}$ for ternary and quaternary Co-based full Heusler compounds under study as a function of $N_{\text{cal}}$ in the system. The Slater-Pauling relationship is satisfied in range of less than 29.5 in $N_{\text{cal}}$ while slightly underestimated for over $N_{\text{cal}} = 29.5$ that corresponds to Co$_2$(Fe$_{x}$Mn$_{1-x}$)Si of $x = 0.75$ and Co$_2$FeSi.

The Co$_2$FeSi compound is under debate to judge whether its electronic structure shows HM or not for past few decades from theories with and without the correla-

### Table II. The lattice constants $a$ (in Å) and the LR-calculated $U_{\text{eff}}^{\text{LR}(\text{Y})}$ (eV) for quaternary Co$_2$(Y$_x$Mn$_{1-x}$)Si where the composition $x$ is 0.25, 0.50, 0.75, or 1.00. The atom-resolved $m_{\text{spin}}$ ($\mu_B$) where $\alpha$ of Co, Y, and Mn, spin polarization $P$ (%), and minority-energy band gap $E_{\text{gap}}^\uparrow$ (eV), which are calculated by the GGA+U$_{\text{Y,Mn}}$, are also summarized. The number of valence electrons, $N_{\text{val}}$, is listed in second column.

| Compound | $N_{\text{val}}$ | $a$ (Å) | $U_{\text{eff}}^{\text{LR}(\text{Y})}$ (eV) | $m_{\text{spin}}^{\text{Co}}$ ($\mu_B$) | $m_{\text{spin}}^{\text{Mn}}$ ($\mu_B$) | $m_{\text{spin}}^{\text{Y}}$ ($\mu_B$) | $P$ (%) | $E_{\text{gap}}^\uparrow$ (eV) |
|----------|-----------------|--------|-----------------|-----------------|-----------------|-----------------|--------|-----------------|
| Co$_2$TiSi | 26 | 5.743 | 2.942 | 0.95 | -0.01 | -82.6 |
| Co$_2$(Ti$_{0.25}$Mn$_{0.75}$)Si | 26.75 | 5.670 | 0.85 | -0.33 | 3.63 | 100.0 | 0.4 |
| Co$_2$(Ti$_{0.50}$Mn$_{0.50}$)Si | 27.5 | 5.694 | 0.90 | -0.17 | 3.69 | 100.0 | 0.4 |
| Co$_2$(Ti$_{0.75}$Mn$_{0.25}$)Si | 28.25 | 5.718 | 0.93 | -0.07 | 3.75 | 85.6 |
| Co$_2$YSi | 27 | 5.657 | 3.979 | 0.77 | 1.31 | 11.5 |
| Co$_2$(V$_{0.25}$Mn$_{0.75}$)Si | 27.5 | 5.648 | 0.77 | 1.29 | 3.58 | 100.0 | 0.4 |
| Co$_2$(V$_{0.50}$Mn$_{0.50}$)Si | 28 | 5.651 | 0.75 | 1.44 | 3.60 | 100.0 | 0.4 |
| Co$_2$(V$_{0.75}$Mn$_{0.25}$)Si | 28.5 | 5.654 | 0.74 | 1.47 | 3.62 | 100.0 | 0.4 |
| Co$_2$CrSi | 28 | 5.639 | 3.169 | 0.57 | 2.80 | 65.5 |
| Co$_2$(Cr$_{0.25}$Mn$_{0.75}$)Si | 28.25 | 5.643 | 0.70 | 2.86 | 3.57 | 94.8 |
| Co$_2$(Cr$_{0.50}$Mn$_{0.50}$)Si | 28.5 | 5.642 | 0.66 | 2.82 | 3.56 | 94.8 |
| Co$_2$(Cr$_{0.75}$Mn$_{0.25}$)Si | 28.75 | 5.640 | 0.62 | 2.80 | 3.55 | 93.1 |
| Co$_2$(Fe$_{0.25}$Mn$_{0.75}$)Si | 29.25 | 5.644 | 0.96 | 2.93 | 3.58 | 100.0 | 0.5 |
| Co$_2$(Fe$_{0.50}$Mn$_{0.50}$)Si | 29.5 | 5.642 | 1.15 | 2.95 | 3.61 | 87.8 |
| Co$_2$(Fe$_{0.75}$Mn$_{0.25}$)Si | 29.75 | 5.641 | 1.23 | 2.92 | 3.62 | -26.1 |
| Co$_2$FeSi | 30 | 5.640 | 3.922 | 1.26 | 2.89 | -66.8 |

$^a$ The energy gap is estimated from the DOS shown in Fig. 7.
$^b$ Equilibrium lattice constant is determined by Murnaghan fitting.
FIG. 7. (Color online) Dependence of total DOS on the composition $x$ for (a) $\text{Co}_2(\text{Ti}_x\text{Mn}_{1-x})\text{Si}$, (b) $\text{Co}_2(\text{V}_x\text{Mn}_{1-x})\text{Si}$, (c) $\text{Co}_2(\text{Cr}_x\text{Mn}_{1-x})\text{Si}$, and (d) $\text{Co}_2(\text{Fe}_x\text{Mn}_{1-x})\text{Si}$, respectively, from the GGA+$U_{\text{Y,Mn}}$ calculations. In each panel, upper (bottom) region shows the DOS for up- (down-) spin state, and the Fermi energy is set to zero. Note that vertical axis range of DOS at $x=1.00$ is different from that at the other compositions since the number of atoms per primitive cell at $x=1.00$ is a quarter of the others (see Fig. 1).

FIG. 8. (Color online) Total $m_{\text{spin}}$ as a function of $N_{\text{val}}$ for $\text{Co}_2(Y_x\text{Mn}_{1-x})\text{Si}$, where composition $x$ varies as 0.25, 0.50, 0.75, and 1.00. Opened red squares, blue triangles, green down-pointing triangles, and pink diamonds are for quaternary systems with $Y$ of Ti, V, Cr, and Fe, respectively. Ternary systems ($x=1.0$) are also plotted by filled symbols as well as the $\text{Co}_2\text{MnSi}$ (black circle). The Slater-Pauling relationship, $m_{\text{spin}} = N_{\text{val}} - 24$, is shown by dotted line.

Our LR-based DFT+$U$ calculations indicate it is not a HM ferromagnet. However, we emphasize that tuning the composition in quaternary $\text{Co}_2(\text{Fe,Mn})\text{Si}$ demonstrates the electronic structure is possible to have the HM nature. This conclusion is supported by a consistent result with anisotropic magnetoresistance (AMR) measurement. According to an extended model for AMR formulated by Kokado et al., a negative sign of AMR effect arising from the empty DOS either spin-up or -down states at Fermi level is a signature of HM. Using this model analysis, the positive behavior of AMR is found in $\text{Co}_2\text{FeSi}$ that indicates ferromagnetic without the minority band gap but negative one is confirmed in $\text{Co}_2(\text{Fe,Mn})\text{Si}$ meaning the HM. Note that a range of composition of Fe and Mn for $\text{Co}_2(\text{Fe,Mn})\text{Si}$, in which the HM is appeared, is different between our study and AMR experiment, this may be because the present quaternary models [Figs. 1 (b)∼(d)] are assumed to be periodic structure missing a perfectly disordered property, and/or the ordering parameter of $L2_1$ structure in Ref. [73] is rather low at every composition. Nonetheless, we can propose that the quaternary $\text{Co}_2(\text{Fe}_{0.25}\text{Mn}_{0.75})\text{Si}$ is the most promising candidate as HM ferromagnet in the investigated Heusler compounds from the aspects of the sizable $E_{\text{gap}}$, and Fermi energy position for the use in spintronics devices. Finally, we believe that our present results encourage the experiments to improve a degree of crystallinity of bulk Heusler alloys and/or to fabricate the clean interface without any atomic inter-diffusion in the MTJ and CPP-GMR devices for the enhancement of the MR performances in near the future.
IV. SUMMARY

In summary, revisiting of the HM property for Co-based full Heusler Co$_2$YSi was given by means of the DFT+$U$ method, in which the correlation correction $U_{	ext{eff}}$ determined by LR theory was introduced. We found that the correlation effect at $Y$ site is a key factor to describe the ground-state electronic and magnetic structures and this fact is justified by the comparison with experimental results. From the detailed band structure analyses in Co$_2$MnSi, the important hybridization of the $t_{2g}$ state between Co and Mn that governs the HM gap in the minority state around the Fermi energy was revealed, and the hybridization energy diagram was newly proposed. This unified diagram provides a new insight for $L_2_1$ full Heusler compounds $X_2YZ$; tunable HM property by the $t_{2g}$ hybridization through a (partial) substitution of $Y$ site. Further investigations were carried out to explore the possibility of HM ferromagnets, and our LR-based DFT+$U$ calculations indicate that the quaternary Co$_2$(Ti,Mn)Si, Co$_2$(V,Mn)Si, and Co$_2$(Fe,Mn)Si compounds can be promising candidates for a use of spintronics applications when the composition of $Y$ site is appropriately selected. Particularly, for the Co$_2$(Fe$_{0.25}$,Mn$_{0.75}$)Si, in which the HM nature is consistent with experimental AMR study, the Fermi energy position being at the center of wide minority gap can be a great advantage in terms of thermal stability in addition to the high Curie temperature.

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Because even the theoretically derived $U_{\text{eff}}$ value depends on the computational details, as discussed in Ref. [43], we explicitly specify which pseudopotential is employed in present study. The used pseudopotential scheme given in Ref. [53] is known to be appropriate for 3d transition metal and non-magnetic $sp$ atoms.

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