Full-Potential Screened KKR Calculations for Magnetism of Co_2MnSi , Ni_2MnAl and Ru_2MnSi , Based on the Generalized Gradient Approximation

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We present systematic ab-initio calculations for nonmagnetic (NM), ferromagnetic (FM), and antiferromagnetic (AFM) states of full-Heusler alloys (X_2YZ) such as Co_2MnSi ($\text{X} = \text{Co}$, $\text{Y} = \text{Mn}$, $\text{Z} = \text{Si}$), Ni_2MnAl ($\text{X} = \text{Ni}$, $\text{Y} = \text{Mn}$, $\text{Z} = \text{Al}$), and Ru_2MnSi ($\text{X} = \text{Ru}$, $\text{Y} = \text{Mn}$, $\text{Z} = \text{Si}$). The calculations are based on the all-electron full-potential (FP) screened Korringa-Kohn-Rostoker (KKR) Green's-function method combined with the generalized-gradient approximation in the density-functional formalism. We show that the present calculations reproduce very well the experimental ground states of these alloys (FM of Co_2MnSi and Ni_2MnAl , AFM of Ru_2MnSi) and the available measured values for lattice parameters and magnetic moments. It is also shown that the fundamental features of the magnetism of Co_2MnSi (strong FM) and Ni_2MnAl (weak FM) are understood by using the Mn spin-flip energies and the Mn-Mn exchange interaction energies in X ($= \text{Co}$, Ni), both of which are obtained by the present FP-KKR calculations for the impurity systems. We can show that the magnetism of Ni_2MnAl may be changed from FM to AFM by atomic disorder (B2-structure) occurring at elevated temperatures.

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1. Introduction

Intermetallic full-Heusler alloys of L_{21} structure have attracted a great deal of interest during the last century because of high possibilities as materials of various high qualities.^{1,2)}

For examples, Co_2MnSi is expected as half-metallic (100% spin polarization at the Fermi level) ferromagnetic (FM) alloys with high Curie temperatures. The band-structure calculations without the spin-orbit interaction predicted 100% spin polarization for this material.^{3,4)} Therefore the Co-based full-Heusler alloys such as Co_2MnSi were considered as the ideal materials for spin electronics. However, the spin polarizations of only 50–60% were experimentally obtained for Co_2MnSi .^{5–7)} The decrease may be attributed to defects in the materials, such as antisites and swaps.⁸⁾

On the other hand, Ni_2MnAl is expected as FM shape-memory alloys.^{9,10)} However, it is also known experimentally that the magnetism of Ni_2MnAl changes easily from the FM state to antiferromagnetic (AFM) state at elevated temperatures.^{11,12)} This change of magnetism may be caused by the change of the atomic structure, from the L_{21} structure to the B2-disordered structure, which occurs at elevated temperatures.^{11,12)} The fabrication of Ni_2MnAl at the L_{21} structure seems to be very difficult. The electronic structures and magnetism of these full-Heusler alloys may be unstable for the defects and the substitutional disordering. The stability of Ni_2YAl ($\text{Y} = \text{V}$, Cr , Mn) were investigated experimentally and also by using the thermodynamic calculations on the basis of the Bragg-Williams-Gorsky approximation.¹³⁾ The magnetism of a new Heusler alloy Ru_2MnSi was also investigated both experimentally^{14–16)} and theoretically.¹⁷⁾ The experimental results showed that the ground state of Ru_2MnSi is AFM and that the atomic structure is in partially disordered form (Ru-Si disorder).

Thus, the development of the electronic devices of high qualities needs the study of the magnetism of the full-Heusler alloys with and without defects. The simple band calculations such as the linear muffin-tin orbital method combined with the atomic sphere approximation (LMTO-ASA) have already been performed in order to study the host magnetism of many full-Heusler alloys.^{4,17)} The calculations are based on the local spin density approximation (LSDA) in the density functional formalism (DFT) and the spherical potentials, and the ratios of Muffin-tin radii were determined empirically. Although these calculations are useful for the preliminary discussions, they sometimes fail to reproduce the experimental ground states.¹⁸⁾ It was recently discussed that the ab-initio calculations based on the full-potential (FP) and the generalized-gradient approximation (GGA) in the DFT are needed to reproduce correctly the experimental results for the ground states for the full-Heusler alloys together with the equilibrium lattice parameters,^{18,19)} although the gap widths of the half-metallic alloys may be underestimated.

Developing the ab-initio calculations based on the FP-Korringa-Kohn-Rostoker (KKR) Green's function method combined with the GGA, we have also shown that, for most of fcc and bcc metals ($\text{Li} \sim \text{Au}$), the GGA corrects very well the deficiencies of the LSDA, such as the underestimation of the equilibrium lattice parameters and the overestimation of the bulk moduli and monovacancy formation energies²⁰⁾ and that the atomic structures of the ground states of 3sp-, 3d-, and 4d-elemental metals are reproduced very well by the FP screened (S) KKR calculations (FPSKKR) combined with the GGA.^{21,22)} Thus, the GGA-FPKKR calculation methods, which can treat both the properties of bulk and defect systems in the same accuracy, may be most useful for the study of the magnetism of the full-Heusler alloys. Under these circumstances, using the GGA-FPKKR calculations, we plan to study the electronic structures and magnetism of the full-Heusler alloys with and without defects.

Fig. 1 (a) Crystal structure of full-Heusler alloys (L_{21}). The arrangements of Mn-moment for (b) FM, (c) AFM-I, and (d) AFM-II are also shown.

Using the LSDA-FPSKKR calculations, Galanakis *et al.* have already succeeded in elucidating the fundamental features of many half-metallic full-Heusler alloys, such as the relation for magnetic moments (MMs) with valence-electron numbers per unit cell, called “the Slater-Pauling rule”.^{1,23)} They used the experimental values for the lattice parameters and restricted to the FM states. The Slater-Pauling rule is very useful for the prediction of MMs of a variety of half-metallic full-Heusler alloys (X_2YZ) and also for the quaternary half-metallic full-Heusler alloys such as $\text{Co}_2(\text{Cr}_{1-x}\text{Fe}_x)\text{Al}$.

In the present paper, as the first result of our project, we show the calculated results for NM, FM, and AFM states of Co_2MnSi , Ni_2MnAl , and Ru_2MnSi . The reason for choosing these alloys is a variety of the magnetism of these alloys, being known experimentally, such as strong FM of Co_2MnSi ,⁵⁾ weak FM of Ni_2MnAl ,^{11,12)} and (presumably weak) AFM of Ru_2MnSi .¹⁶⁾ We show: (1) the present calculations reproduce the experimental ground states of magnetism, the measured values for the lattice parameters and the available values for the MMs of these alloys, and elucidate the fundamental features of magnetism; (2) the change from the FM to the AFM state of Ni_2MnAl at elevated temperatures, being known experimentally, is understood by the Mn spin-flip energies and the Mn-Mn exchange interaction energies in X ($\text{X} = \text{Co}, \text{Ni}$), both of which are also calculated in the present work; (3) the Co_2MnZ ($\text{Z} = \text{sp-element}$) at the L_{21} structure shows the half-metallicity if the valence-electron number of Z is between 3 and 5. The calculated results for the defect energies in these alloys, such as swap and antisite energies, will be published in the following paper.²⁴⁾

2. Method of Calculations

The calculations for the total energies of full-Heusler alloys are based on the density functional formalism in the generalized gradient approximation (GGA) and the scalar-relativistic approximation.^{20,25)} In order to solve the Kohn-Sham equations we use a multiple scattering theory in the form of the KKR Green’s function method for full potentials (FP). We use the screened version of KKR calculations (SKKR) for ordered alloys, which simplifies very much the numerical calculations by introducing the short-range structural Green’s functions.²⁶⁾ The accuracy of FPSKKR calculations are discussed in Ref. 27).

In order to calculate the total energies in the GGA formalism, we use the electronic densities obtained self-consistently by the LSDA calculations for simplicity. The accuracy of the present GGA calculations is discussed in Refs. 20) and 25).

It is also noted that an imaginary part of the small energy (0.001 Ry) was added to the energy when calculating the density of states (DOS) by means of the Green function. As a result, the very small, non-vanishing density emerges in the half-metallic gap of minority states at the Fermi level. However, we must remember that the complete half-metallic gap is impossible because a coupling between majority (up) and minority (down) spin states is always expected in the full relativistic calculations.³⁾ It is also noted that the temperature effect above 0 K may destroy the half-metallic gap, due to the smearing of the DOS around the Fermi level. Therefore, the small error due to the present treatment for calculating the DOS may be neglected for the discussions of the possibility of half-metallicity of the realistic alloys, as discussed in Appendix.

3. Calculated Results for Co_2MnSi , Ni_2MnAl , and Ru_2MnSi

The crystal and magnetic structures of the full-Heusler alloys X_2MnZ are shown in Figs. 1. In the present calculations we treat the four kinds of states for magnetism; (a) NM, (b) FM, (c) AFM type I (AFM-I), and (d) AFM type II (AFM-II). AFM-I and AFM-II are characterized by alternating ferromagnetic planes of up- and down-Mn-moments, being perpendicular to the [001] and [111] directions, respectively. There are differences in numbers of parallel and antiparallel Mn-Mn coupling pairs. In AFM-I, one up-Mn-moment interacts with the 1st-neighboring four up-Mn-moments and eight down-Mn-moments, while in AFM-II with the 1st-neighboring six up-Mn-moments and six down-Mn-moments.

3.1 Lattice parameter dependence of total energies and magnetic moments

Figures 2 show the theoretical results for the lattice parameter dependence of total energies of Co_2MnSi , Ni_2MnAl , and Ru_2MnSi , obtained by the GGA-SFPKKR and LSDA-FPSKKR calculations. The four kinds of magnetic (NM, FM, AFM-I, AFM-II) states are treated in the present paper. The measured lattice parameters are shown by

Fig. 2 Lattice parameter dependence of total energies per molecular unit for the different magnetic states of Co_2MnSi , Ni_2MnAl , and Ru_2MnSi , obtained by the present GGA-FPSKKR (a)–(c) and LSDA-FPSKKR (d)–(f) calculations.

Table 1 Equilibrium lattice parameters of the ground states of Co_2MnSi , Ni_2MnAl , and Ru_2MnSi , obtained by the GGA-FPSKKR and LSDA-FPSKKR calculations, together with the available experimental results (Refs. 2), 7), 16)).

	Equilibrium lattice parameter, a/nm		
	Experiment	GGA	LSDA
Co_2MnSi	0.565	0.565	0.553
Ni_2MnAl	0.582	0.580	0.566
Ru_2MnSi	0.589	0.592	0.582

the vertical lines in Figs. 2.^{2,5,16)} The calculated results are listed in Table 1. It is obvious that the present calculations (both of the LSDA and GGA) reproduce the ground states of these full-Heusler alloys: FM for Co_2MnSi ⁵⁾ and Ni_2MnAl ,¹¹⁾ and AFM-II for Ru_2MnSi .^{16,17)} It is also obvious that the GGA calculations correct the deficiencies of the LSDA (the underestimation of lattice parameters): the errors for the lattice parameters in the GGA calculations are within 1%, as have been shown for most of elemental fcc and bcc metals (Li–Au).²⁰⁾

The lattice parameter dependence of total magnetic moments (MMs) of the ground states and their components are shown in Figs. 3. The local Mn MMs in the FM, AFM-I, AFM-II states are compared in Figs. 4. It is noted that for Ru_2MnSi (AFM-II, Fig. 3(c)) only the MMs of one kind of molecular unit (Ru_2MnSi) are shown. Since the MMs for another kind of molecular unit in the AFM-II unit cell are opposite sign, the total MM is zero. As seen in Fig. 3(a), the calculated results for total MMs per unit cell of Co_2MnSi do not depend on the lattice parameter and are kept to be $4.95 \mu_B$ (almost an integer as a character of half-metallicity), corresponding to the measured value $5.10 \pm 0.04 \mu_B$.⁵⁾

Fig. 3 Total magnetic moments per molecular unit cell for (a) Co_2MnSi , (b) Ni_2MnAl , (c) Ru_2MnSi (AFM-II). For (d) Ru_2MnSi (FM), the magnetic moments for one unit of Ru_2MnSi are shown.

It is also noted that the calculated value (or the measured value) is predicted very well by the Slater-Pauling rule.^{1,23)} Although the local Mn MM increases with the lattice parameters, its increase is cancelled out by the decreases of Co and Si moments. For Ni_2MnAl (FM, Fig. 3(b)), the total and local Mn MM increase very much with the lattice parameter. It may be a signal that Ni_2MnAl is not an alloy of half-metallicity, as discussed in 3.3 and shown in Fig. 7(b). For Ru_2MnSi (AFM-II, Fig. 3(c)), the total and local Mn

Fig. 4 Magnitude of local magnetic moments of Mn for (a) Co_2MnSi , (b) Ni_2MnAl , (c) Ru_2MnSi .

MMs for the sublattice increase with the lattice parameter and the MM of Ru is almost zero. The effective total MM obtained from the temperature dependence of magnetization is $2.8\mu_B$,¹⁶⁾ corresponding to the calculated result $2.96\mu_B$. It is also noted that the total MM ($2.99\mu_B$) in the FM state of Ru_2MnSi (Fig. 3(d)) do not depend on the lattice parameter. We will show in 3.3 that the Ru_2MnSi in the FM state is an alloy of half-metallicity.

Now we examine the fundamental features of magnetism of these alloys, using the calculated results. First we summarize the calculated results for the characteristic features of magnetism.

- (1) The FM of Co_2MnSi is the ground state and very stable. The energy difference between FM and AFM is as large as 0.453 eV per unit cell. The local MMs of Co and Mn at the FM state are 1.02 and $2.99\mu_B$, respectively.
- (2) The FM of Ni_2MnAl is the ground state, but not so stable. The energy difference between AFM and FM states is as small as 0.070 eV per molecular unit (Ni_2MnAl). The local magnetic moments of Ni and Mn at the FM state are 0.37 and $3.4\mu_B$, respectively.
- (3) The AFM-II of Ru_2MnSi is the ground state, but not so stable. The energy difference between AFM-II and FM is as small as 0.035 eV per molecular unit. The local MM of Mn in the AFM-II is the largest among the FM, AFM-I, and AFM-II, as seen in Fig. 4(c): $2.961\mu_B$ for AFM-II, $2.926\mu_B$ for AFM-I, and $2.915\mu_B$ for FM.

These fundamental features are qualitatively understood by considering the magnetism of the constituent elements, such as strong FM of Co (large MM), weak FM of Ni (small MM), NM of Ru, and AFM of Mn.²⁸⁾ The difference between the FM and AFM states of 3d-transition-metals is fundamentally understood by the 3d-electron numbers. The stable magnetism becomes AFM around the half-filled 3d bands because the energy gain due to the band shift overcomes the energy gain due to the band broadening.²⁹⁾ The strong FM state of Co_2MnSi is mainly due to the strong FM of Co. The weak FM state of Ni_2MnAl is due to the weak FM of Ni, which is further weakened by the AFM of Mn. The difference on the stability of FM between Co_2MnSi and Ni_2MnAl is understood by using the Mn spin-flip energies and the Mn-Mn exchange interaction energies in X (= Co, Ni), as discussed in 3.2. The stability of AFM-II of Ru_2MnSi may be due to the AFM of Mn. The difference on AFM-I and

AFM-II may be due to the numbers of AFM-coupling and FM-coupling Mn-Mn pairs: the pair numbers of AFM-coupling and FM-coupling are (6, 6) for AFM-II configuration, while (8, 4) for AFM-I configuration. The AFM state of Mn in Ru_2MnSi may be the strongest in the magnetic configuration of Mn in the AFM-II state, because the Mn MM is the largest in the AFM-II state, as shown in Fig. 4(c).

3.2 Spin-flip energies of Mn and distance-dependence of Mn-Mn exchange interaction energies in X (= Co, Ni)

We try to understand qualitatively the difference on the FM between Co_2MnSi and Ni_2MnAl by using the calculated results for the Mn spin-flip energies and the Mn-Mn exchange interaction energies in X (= Co, Ni). They are the 1st- and 2nd-lowest order (one-body and two-body of Mn impurities) terms in the cluster expansion (from a dilute limit) of the internal energies of alloys³⁰⁾ and may be important to study the characteristic features of magnetism of alloys. The definition and accuracy of the cluster expansion from a dilute limit are discussed in Ref. 30). By using these impurity interaction energies, we have already succeeded in understanding the physical mechanism of the NMR experimental results of Mn impurities in NiMn and NiFe alloys.^{31,32)}

3.2.1 Spin-flip energy (one-body interaction of Mn)

First we show the calculated results for the spin-flip energies of 3d impurities in X (= Co, Ni). There exist three magnetic solutions for 3d impurities in Co and Ni, as shown in Figs. 5(a) and 5(b). The calculations were performed for 3d impurities of non-integer nuclear charge. For 3d impurities in a NM host such as Cu, it is well known that there are three solutions; one is NM (unstable) and two are doubly degenerated magnetic (MMs of equal magnitude in the opposite direction). On the other hand, for 3d impurities in FM metals such as Co and Ni, a NM solution shifts to a solution of a very small (S)-MMs and the degeneracy of the magnetic solutions is lifted, as seen in Figs. 5(a) and 5(b), resulting in two solutions of parallel (P, corresponding to the FM) and anti-parallel (AP, corresponding to the AFM) MMs to the bulk magnetization. The three solutions exist around $Z = 23.9\text{--}27.2$ (Z is a nuclear charge of X) for Ni-host,³¹⁾ while around $Z = 24.3\text{--}26.1$ for Co-host.

The change of the MMs of Co and Ni atoms at nearest-neighboring sites of 3d impurities is shown in Figs. 5(c) and 5(d). The change depends strongly on the magnetic states

Fig. 5 Local magnetic moments (MMs) for 3d impurities in (a) Co and (b) Ni, MMs of 1st-neighboring Co (c) and Ni (d), total energy differences between the parallel and anti-parallel states, and those between the parallel and small states in (e) Co and (f) Ni.

of 3d impurities. It is noted that for the solutions of AP and S states of 3d impurities the decrease of MM's of nearest-neighboring Co and Ni becomes very large and leads to the large magnetic energy loss. The total-energy differences between the P and AP states, and those between the P and S states are shown in Figs. 5(e) and 5(f). The total-energy change is very large for 3d impurities in Co. For example, it costs 0.729 eV to excite one Mn-MM from P to AP. This spin-flip energy, being defined by the different sign of the total energy difference between the P and AP states, may be an important part of the energy difference (0.453 eV, see Fig. 3(a)) between the AFM and FM states of Co_2MnSi . The difference (0.266 eV) between two values (0.729 and 0.453 eV) should be understood by the pair (Mn-Mn) and many-body (of Mn and Si) interaction energies which are the higher-order terms in the cluster expansion of the total energy difference obtained by the (AFM-I, FM) band calculations of Co_2MnSi , as discussed in the following paragraphs. However, it may be obvious that the large value of the spin-flip energy corresponds to the strong stability of the P state of 3d impurities in Co.

On the other hand, for 3d impurities in Ni the spin-flip energy is small. For example, the spin-flip energy of Mn impurity in Ni is 0.220 eV. This energy may be an important part of the energy difference (0.070 eV) between the AFM and FM states of Ni_2MnAl . The difference between two values (0.220, 0.070 eV) is not small and may be understood by the Mn-Mn exchange interaction energies (two-body of Mn) and many-body interaction energies of Mn and Al. However, by comparing the Mn spin-flip (one-body) energies in Ni and Co, we can at least qualitatively understand that the FM of Ni_2MnAl is very weak compared with that of Co_2MnSi .

3.2.2 Mn-Mn exchange interaction energy (two body interaction of Mn)

Now we discuss the Mn-Mn exchange interaction energies $E_{\text{exc}}(\text{Mn-Mn})$, which may be the next important term in the

Fig. 6 Distance dependence of exchange interaction energies of Mn-Mn in (a) Co and (b) Ni.

cluster expansion of the total energy differences obtained by the band calculations. By considering the distance dependence of $E_{\text{exc}}(\text{Mn-Mn})$, we can show that the FM state of Ni_2MnAl may be easily changed to the AFM state by the atomic disorder (of Mn and Al) occurring at elevated temperatures.

First we give the definition of $E_{\text{exc}}(\text{Mn-Mn})$. It is written as follows,

$$E_{\text{exc}}(\text{Mn-Mn}) = E_{\text{up-down}} - E_{\text{up-up}} - (\text{spin-flip energy of Mn}) \quad (1)$$

where $E_{\text{up-down}}$ ($E_{\text{up-up}}$) represents the total energy of the impurity system with the Mn pair of up-down(up-up) configurations. The spin-flip energy is subtracted in the eq. (1). Thus, $E_{\text{exc}}(\text{Mn-Mn})$ becomes zero at the infinite interatomic distance of a Mn-Mn pair. Figures 6 show the distance dependence of the $E_{\text{exc}}(\text{Mn-Mn})$ in X (= Co, Ni).

Fig. 7 DOS of (a) Co_2MnSi (FM), (b) Ni_2MnAl (FM), and (c) Ru_2MnSi (FM).

It is noted that the distance dependences of $E_{\text{exc}}(\text{Mn-Mn})$ in Co and Ni are very similar to each other.

The important feature of $E_{\text{exc}}(\text{Mn-Mn})$ is that the AFM-coupling of Mn-Mn is stable up to the 4th neighbor and very strong at the 1st and 2nd-neighbors. If one Mn atom at the $L2_1$ structure is spin-flipped, the twelve Mn-Mn AFM-coupling pairs at the 3rd neighbor are created (see Fig. 1(b)). Thus, the energy gain of $E_{\text{exc}}(\text{Mn-Mn})$ due to this spin-flip is $-0.01 \times 12 = -0.12$ eV and $-0.005 \times 12 = -0.06$ eV for Co and Ni hosts. Thus, the total energy differences obtained by considering the spin-flip and $E_{\text{exc}}(\text{Mn-Mn})$ energies are 0.609 eV ($= 0.729 - 0.120$) and 0.160 eV ($= 0.220 - 0.06$), which become a little bit close to the values 0.453 and 0.070 eV for Co_2MnSi and Ni_2MnAl , obtained by the band calculations. The remaining differences should be due to the pair interactions at the long interatomic distance of Mn-Mn and the many-body interactions of Mn and sp-elements (Si for Co_2MnSi or Al for Ni_2MnAl). The effect of sp-elements may be qualitatively important. We will examine the sp-element effect by calculating the Mn spin-flip energies and the Mn-Mn exchange interaction energies in Co_3Si ($X = \text{Co}$, $Y = \text{Co}$, $Z = \text{Si}$) and Ni_3Al ($X = \text{Ni}$, $Y = \text{Ni}$, $Z = \text{Al}$).

Now we can show how the AFM of Ni_2MnAl becomes stable at elevated temperatures. According to the experiment, the $L2_1$ structure of Ni_2MnAl is changed to the B2 (the disordering of Mn and Al). It is important that the 2nd-neighboring Mn-Mn pairs are created at the B2 structure. The AFM-coupling at the 2nd-neighbor is stable by -0.05 eV, compared with the FM-coupling. Thus, the energy change due to the atomic rearrangement of one Mn with one Al and the spin-flip of one Mn atom is $-0.3 (= -0.05 \times 6) + 0.22 = -0.08$ eV. The negative value means that the AFM state is more stable than the FM state. Thus, the magnetism of Ni_2MnAl may change from FM to AFM at elevated temperatures because the AFM is stable at the B2 structure (the disordering of Mn and Al) which occurs at elevated temperatures. On the other hand, for Co_2MnSi , the total energy change, due to the disordering of Mn and Si and the spin-flip of Mn, is $-0.3 + 0.729 = 0.429$ eV. This large positive value means that the FM state is still stable for the B2 structure of Co_2MnSi .

We may conclude that the fundamental features of the magnetism, such as the strong FM of Co_2MnSi compared with the FM of Ni_2MnSi , and the change from FM to AFM of Ni_2MnAl at elevated temperatures are understood by considering the Mn spin-flip energies (one-body of Mn) and the Mn-Mn exchange interaction energies (two-body of Mn)

in X ($= \text{Co}$, Ni), which are the 1st- and 2nd-lowest order terms in the cluster expansion (from a dilute limit) for the total energy differences between the FM and AFM-I states of Co_2MnSi and Ni_2MnAl .

3.3 Half-metallicity

Figures 7 show the DOSs of the FM states of (a) Co_2MnSi , (b) Ni_2MnAl , and (c) Ru_2MnSi . The FM is the ground state of Co_2MnSi and Ni_2MnAl , but the excited state for Ru_2MnSi . It is obvious that Co_2MnSi shows half-metallicity (Fig. 7(a)), while Ni_2MnAl does not (Fig. 7(b)). These results were successfully understood by analyzing the partial DOSs obtained by the LSDA-FPSKKR calculation results.²³⁾ The gap in the down-spin (minority-spin) band of Co_2MnSi is located at the middle of the antibonding states between Co-Co d-orbitals, and the electrons are occupied up to the states just below the gap, the energy of which corresponds to the Fermi level. For the Ni_2MnAl , the states above the gap are also occupied by electrons. As a result, the Ni_2MnAl alloy does not show the half-metallicity. The DOS of Ru_2MnSi (FM) shows half-metallicity (Fig. 7(c)). This result may be easily understood because Ru is almost isoelectronic to Co. It is obvious that the DOS of the Ru_2MnSi (AFM) does not show the half-metallicity because the DOSs of up and down spin states per unit cell of the AFM are the same to each other and may be approximated by the superposition of DOSs of up and down spin states of the FM of Ru_2MnSi (Fig. 7(c)).

4. Half-Metallicity and Slater-Pauling Behavior in Co_2MnZ ($Z = \text{Na} \sim \text{P}$)

The Co_2MnZ ($Z = \text{sp-element}$) alloys are expected as the ideal materials for spin electronics. Thus, we study the half-metallicity of Co_2MnZ ($Z = \text{Na} \sim \text{S}$). We also examine the Slater-Pauling rule for these alloys.^{1,23)} We determined the lattice parameters by the present GGA-FPSKKR calculations. The calculated results and the available experimental values are listed in Table 2. The calculated DOSs are shown in Figs. 8. We can expect the half-metallicity for Co_2MnZ ($Z = \text{Al}$, Si , P). It is noted that the valence-electron numbers are 3, 4 and 5 for Al, Si and P. Thus, the MMs increase from 4 to 6 for $Z = \text{Al}$, Si and P . The relations of MMs with valence-electron number per unit cell are shown in Fig. 9. We can see very well the Slater-Pauling behavior (the linear relation of MMs with valence-electron numbers per unit cell) around Al, Si, P: from $Z = \text{Al}$ to $Z = \text{P}$, the added electrons are occupied by the up-spin (majority) band, because there is

Table 2 Calculated and experimental equilibrium lattice parameters of Co_2MnZ ($Z = \text{Na}\sim\text{P}$) (Refs. 2), 7)).

	Equilibrium lattice parameter, a/nm		
	Experiment	GGA	LSDA
Co_2MnNa	—	0.588	0.570
Co_2MnMg	—	0.580	0.569
Co_2MnAl	0.576	0.570	0.559
Co_2MnSi	0.565	0.565	0.553
Co_2MnP	—	0.566	0.552
Co_2MnS	—	0.576	0.559

Fig. 8 DOS for Co_2MnZ ($Z = \text{Na}\sim\text{S}$). The number of valence electrons changes from 26 ($Z = \text{Na}$) to 31 ($Z = \text{S}$).

Fig. 9 Valence-electron number dependence of local magnetic moments per unit cell for Co_2MnZ ($Z = \text{Na}\sim\text{S}$).

a gap in the down-spin (minority) band. It is noted that the calculated results for Z of non-integer nuclear charge are also shown in Fig. 9. For $Z = \text{Na}$, Mg , S , we can not expect the Slater-Pauling behavior because the Fermi level is located outside of the gap, as shown in Figs. 8(a), (b) and (f). As a

result, the Co_2MnZ ($Z = \text{Al}$, Si , P) alloys without defects may be expected as the materials of the spintronics. It is also expected that the quaternary alloys of Co_2Mn ($\text{Z}_{1-x}\text{Z}_2_x$) show the half-metallicity if the valence-electron numbers of ($\text{Z}_{1-x}\text{Z}_2_x$) are between 3 and 5, corresponding to the valence electron numbers of Al and P . However, for Co_2MnSi , being most expected as the half-metallic alloy,⁴⁾ only the 50–60% of spin-polarization was obtained experimentally. This decrease may be due to the defects such as antisites and swaps. The study of the defect effect to the bulk properties of these alloys is strongly requested.

5. Conclusions

We have shown that the present GGA-FPSKKR calculations reproduce the experimental ground states of Co_2MnSi , Ni_2MnAl , Ru_2MnSi and the equilibrium lattice parameters within the error of 1% of the experimental values. The fundamental features of Co_2MnSi (strong FM) and Ni_2MnAl (weak FM) may be understood by the Mn spin-flip and the Mn-Mn exchange interaction energies in X ($= \text{Co}$, Ni). We have also shown that for Ni_2MnAl , the magnetism changes from FM to AFM at elevated temperatures because the energy gain due to the 2nd neighboring Mn-Mn exchange interaction, which is induced by the atomic disordering of Mn and Al (B2-structure) at elevated temperatures, overcomes the energy loss due to the spin-flip energy of Mn impurity in Ni. This result explains the experimental results^{11,12)} very well. The possibility of half-metallicity of Co_2MnZ ($Z = \text{Na}\sim\text{S}$) was examined qualitatively. The Co_2MnZ ($Z = \text{Al}$, Si , P) without defects show the half-metallicity. The quaternary alloys Co_2Mn ($\text{Z}_{1-x}\text{Z}_2_x$) may also show the half-metallicity if the number of valence electrons of sp-elements ($\text{Z}_{1-x}\text{Z}_2_x$) is between 3 and 5. However, the decrease of the spin-polarization at the Fermi level may occur by the existence of the defects. We are now calculating the defect energies of Co_2MnZ ($Z = \text{Na}\sim\text{S}$), such as antisites and swaps, by using the impurity GGA-FPKKR calculations. The results will be published in the following paper.²⁴⁾

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- 3) As the spin-orbit interaction induce the mixing of up-spin and down-spin electrons, it is impossible to obtain the spintronics devise of

complete (100%) spin-polarization. However, it was shown by Marvropoulos *et al.* (Phys. Rev. B **69** (2004), 054424) that the effect due to the spin-orbit interaction is very small for the materials such as 3d element-based alloys. For example, the 100% spin-polarization for the NiMnSb , obtained by the calculations without the spin-orbit interaction, decreases only by $\sim 1\%$ by taking into account the spin-orbit interaction.

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Appendix: Dependence on an Imaginary Part of Energy and on a Number of k -points for DOS

We calculate the DOS as a function of the complex energy with an imaginary part of the small energy (δ_{imag}). It is

Fig. A-1 Dependence on a imaginary part of energy for calculating DOS. The k -number dependence is also shown.

obvious that the large imaginary part of energy induces the large densities in the gap region. For example, the DOS at the complex energies with $\delta_{\text{imag}} = 0.016 \text{ Ry}$ and a number of k -points in the irreducible Brillouin zone (N_k) = 3107 is shown in Fig. A-1(a). We can see the densities in the gap region. It is noted that, for the smaller δ_{imag} , the larger number of N_k is needed to get the converged DOS.

Thus, we examine the dependence of the DOSs on δ_{imag} with the convergence of k -point number. Figures A-1 show the dependences on the imaginary energy ($\delta_{\text{imag}} = 0.016, 0.008, 0.004, 0.002, 0.0005 \text{ Ry}$). We used the k -point numbers ($N_k = 1140-22776$) on the basis of $n \times n \times n$ ($n = 35-100$; n is a number of k_x, k_y , and k_z) mesh. We may conclude from the comparison of the calculation results with different k -point numbers that for $\delta_{\text{imag}} \geq 0.0005 \text{ Ry}$, $N_k = 3107$ is enough to get the converged result for DOS: for example, compare Figs. A-1(e) and (f) for $\delta_{\text{imag}} = 0.001 \text{ Ry}$, and Figs. A-1(g) and (h) for $\delta_{\text{imag}} = 0.0005 \text{ Ry}$.

Now we discuss the δ_{imag} -dependence for DOS. As shown in Fig. A-1, the densities in the gap decrease with the decreasing value of δ_{imag} , and the DOS obtained with $\delta_{\text{imag}} = 0.001 \text{ Ry}$ and $N_k = 3107$ is almost converged and shows the half-metallicity very well. The spin-polarizations at the Fermi level are 71, 82, 90, 95, 97, 99% for $\delta_{\text{imag}} = 0.0016, 0.008, 0.004, 0.002, 0.001, 0.0005 \text{ Ry}$. The error for the spin-polarization is as small as 3% for $\delta_{\text{imag}} = 0.001 \text{ Ry}$.