Electronic Structures, Magnetism and Half-metallicity of Quaternary Heusler Compounds FeMnCrZ (Z = Ga, In): A First-principles Study

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Abstract. Electronic structures, magnetism and half-metallicity of quaternary Heusler compounds FeMnCrZ (Z = Ga, In) are investigated by the all-electron full-potential linearized augmented plane wave method within the generalized gradient approximation (GGA) and GGA+U schemes to the exchange-correlation potential. All three types of phases with different atomic orderings in the unit cell were considered for FeMnCrZ compounds, namely, type-I, II, and III phases. The equilibrium lattice constants of FeMnCrZ in the three types of phases are calculated. It is found that FeMnCrGa has a ground state in the type-I phase, whereas the ground state of FeMnCrIn is in the type-II phase. The ground states of FeMnCrGa and FeMnCrIn compounds are paramagnetic and ferrimagnetic, respectively. Both FeMnCrGa and FeMnCrIn compounds with the type-II phase are found to be nearly half-metals and the total magnetic moments follow the Slater-Pauling rule, $M_t = Z_t - 24$ (μ_B). In the type-II phase, the minority-spin band gap of FeMnCrGa is larger than that of FeMnCrIn, suggesting that FeMnCrGa is more suitable than FeMnCrIn as a spin-injection electrode. It is shown that the GGA+U calculation increases the magnetic moments and the spin-splitting of the transition metal atoms for the compounds.

1. Introduction

Half-metals have 100% spin-polarization, thus, which regarded as promising electrodes for tunneling magnetoresistance (TMR) based devices [1]. So far, many materials have predicted to be half-metal and some of them confirmed by experiments. Full-Heusler compounds with half-metallic character give growing attention because of their high Curie temperatures and similar lattice structures with zinc-blende semiconductors [2].

Full-Heusler compounds have a composition of X_2YZ, where X and Y are transition metal elements and Z is a main-group element from III to V. The compounds crystallize in the face-centered cubic structure and the X, Y, and Z atoms can be placed at the 4a (0,0,0), 4b (0.5,0.5,0.5), 4c (0.25,0.25,0.25), and 4d (0.75,0.75,0.75) sites in Wyckoff positions [3,4], respectively. Recently, scientists found that a few quaternary Heusler compounds, which also belong to the group of full-Heusler compounds, have half-metallic character [5-9]. Quaternary Heusler compounds have chemical formula of XX′YZ, where X, X′,Y are transition metal atoms and Z is a main-group element. For quaternary Heusler compounds, there are three possible types of atomic orderings in the

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unit cell, as demonstrated in Figure 1. In the type-I phase, the X, X′,Y, and Z atoms occupy the 4a, 4b, 4d, and 4c sites, respectively. The type-II (III) phase can be obtained from the type-I phase by interchanging the X′and Y (X′and Z) atoms. All three phases of quaternary Heusler compounds have space group $F\bar{4}3m$ (space group No. 216). By first-principles calculations, Gao *et al* found that CoFeCrZ (Z = Al, Si, Ga, Ge) is most stable with type-I structure and all of them possess the half-metallic character [8]. Özdoğan *et al* calculated a series of quaternary Heusler compounds and predicted that 41 compounds such as FeMnCrAs, CoFeMnAl, CoFeMnSi, etc are found to be half-metals, whereas FeMnCrAl is a semiconductor [9].

The CoFeMnZ (Z = Al, Si, Ga, Ge) compounds were synthesized successfully by Alijani *et al* and have high Curie temperatures (above room temperature) [10]. The high spin-polarizations of CoFeMnZ compounds were confirmed by measured magnetic moments. Quaternary full-Huesler $Co_2FeAl_{0.5}Si_{0.5}$ as an electrode of magnetic tunneling junctions (MTJs), Shan *et al* observed a large TMR ratio of 162% at 26 K [11]. Recently, Bainsla *et al* reported that the CoFeMnSi/MgO/CoFe MTJs can have maximum TMR ratios of 101% and 521% at room temperature and 10 K [12].

To our knowledge, there are no experimental and theoretical studies reported on quaternary Heusler compounds FeMnCrZ (Z = Ga and In). In this paper, I investigated the electronic structures, magnetism and half-metallicity of quaternary Heusler compounds FeMnCrZ (Z = Ga and In) by using a first-principles calculation.

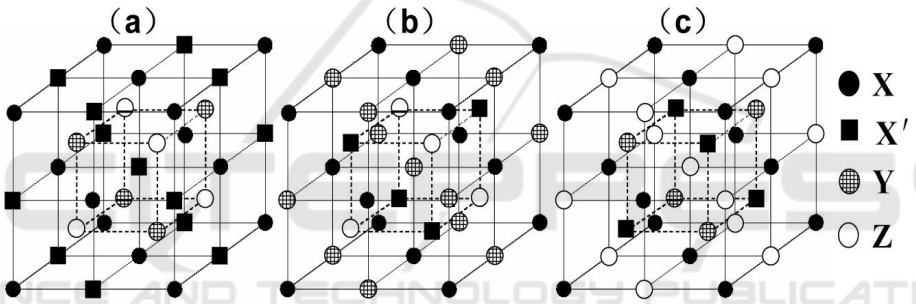

Figure 1. Schematic demonstrations of the three types of phases for quaternary Heusler compound XX′YZ.Where (a), (b), and (c) represent the type-I, type-II, and type-III, respectively.

2. Calculation method

The calculations were performed by using the all-electron full-potential linearized augmented plane wave (FLAPW) method [13] as implemented in the FLEUR code [14] within the generalized gradient approximation (GGA) [15] and GGA+U [16, 17] schemes to the exchange-correlation potential.

In the GGA+U scheme, the effective Coulomb-exchange interaction (U_{eff} = U-J) was used to account the on-site correlation at the transition metal atoms. The U_{eff} values of Fe, Mn and Cr atoms were chosen to be 1.80, 1.69 and 1.59 eV, respectively [8, 18].

Lattice harmonics with $l \leq 8$ were employed to expand the charge density, potential, and wave functions inside the muffin-tin (MT) radius of 1.164 Å for Fe, Mn, and Cr atoms, 1.217 Å for Ga and In atoms. A plane wave cutoff of 16 Ry was employed for the LAPW basis set, and a 210 Ry star-function cutoff was used to depict the charge density as well as the potential in the interstitial region. Integrations inside the Brillouin zone (BZ) were performed by summation over a 21×21×21 ***k***-space grid in the full BZ. All core electrons were treated fully relativistically, whereas valence states were treated scalar relativistically, i.e., without spin-orbit coupling. Self-consistency was assumed when the difference between the input and the output charge (spin) densities is less than 10^{-5} electrons/(a.u.)^3.

3. Results and discussion

3.1. Equilibrium lattice constants

Since there are no available experimental lattice constants for quaternary Heusler compounds FeMnCrZ (Z = Ga, In). I calculated equilibrium lattice constants of the compounds by minimizing the total energy with respect to the lattice constant variation.

Figure 2 shows the relative total energy *vs*. lattice constant curves for FeMnCrZ (Z = Ga, In) compounds in the three types of phases, where the energy value of the type-I phase is set as the zero reference point. The fitted equations of ground states are as follows: $\Delta E = E - E_0 = B_0 + B_1 x + B_2 x^2 + B_3 x^3$, where ΔE, E_0, x are relative total energy, the energies of FeMnCrZ with type-I phase at their equilibrium lattice constants, the lattice constant, respectively. The equilibrium lattice constants of FeMnCrGa (In) in the type-I, II, and III phases are 5.699 (6.191), 5.847 (6.164), 5.869 (6.191) Å, respectively, as listed in Table 1. The equilibrium lattice constants are close to that of several semiconductors, such as Ge (5.66 Å), InP (5.87 Å), AlSb (6.14 Å) etc. It is found that FeMnCrGa has a ground state in the type-I phase, whereas the ground state of FeMnCrIn is the type-II phase. The results are consistent with the previous first-principles findings for quaternary Heusler compounds. The Co based quaternary Heusler compounds with Z = Al, Ga, Si, Ge, As and Sb have the lowest energy in the type-I phase [8, 9, 10, 19, 20], whereas the most stable phase of FeMnCrSn and FeMnCrSb is the type-II phase [21, 22]. From the figure 2, it can be seen that three different phases of FeMnCrZ (Z = Ga, In) compounds are well separated energetically, except between the type-I and II phases of FeMnCrGa. The difference in total energy between the type-I and II phases of FeMnCrGa is about 0.024 eV, which is close to the energy (0.026 eV) of temperature fluctuation (k_BT) at room temperature (300 K). Therefore, a competition between the type-I and II phases is probable during the synthesis of FeMnCrGa compound.

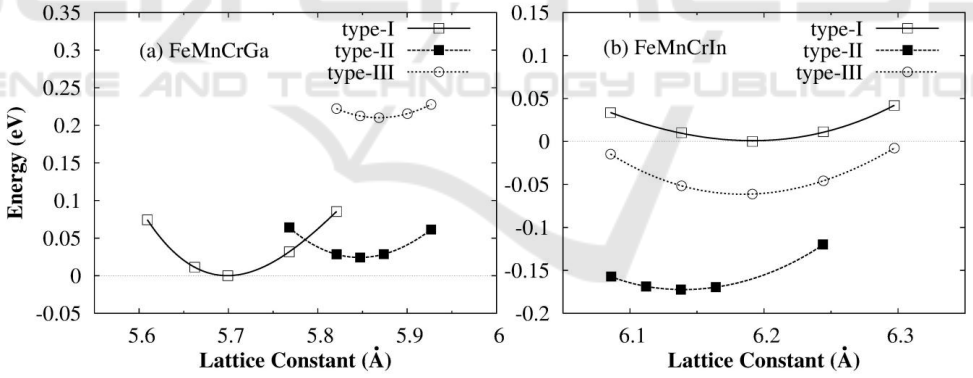

Figure 2. Relative total energy *vs*. lattice constant curves for FeMnCrZ (Z = Ga, In) compounds in the three types of phases.

3.2. Total and atom resolved magnetic moments

Table 1 presents the total and atom resolved magnetic moments of FeMnCrZ (Z = Ga, In) compounds in the three types of phases. For FeMnCrZ (Z = Ga, In) compounds, the type-I phase of FeMnCrGa is paramagnetic, whereas the other phases are ferrimagnetic. A quaternary FeMnCrAl compound is also reported as a semiconductor [9]. It is found that for FeMnCrZ (Z = Ga, In) compounds with same phase the magnetic moments of transition metal atoms in FeMnCrIn is larger than that in FeMnCrGa except for the Fe atom in the type-II phase. This can be ascribed to the larger lattice constants of FeMnCrIn with respect to FeMnCrGa. The magnetic moments of Fe/Mn/Cr atoms

in the FeMnCrIn with type-II phase are -0.073/3.146/-2.746, while those are 0.863/2.941/-2.782 in the FeMnCrSn [21].

A similar strong variation of magnetic moment of Fe atom, which even changes the sign, is found for quaternary Heusler CoFeMnGa and CoFeMnGe compounds [10]. Comparing the atomic magnetic moments of FeMnCrZ (Z = Ga, In) compounds between the GGA and GGA+U calculations, it is clear that the Coulomb interactions increase the magnetic moments of the transition metal atoms. This implies that the GGA+U scheme increases the spin-splitting of transition metal atoms. For magnetic quaternary Heusler compounds, there is a simple way to test the half-metallicity, i.e., by using the Slater-Pauling rule [6]. For Co and Fe based quaternary Heusler compounds the Slater-Pauling rule can be described as $M_t = Z_t - 24$ (μ_B), where the M_t and Z_t denote the total magnetic moment and the total number of valence electrons in the unit cell, respectively. The Z_t is 24 for both FeMnCrGa and FeMnCrZIn compounds. The total magnetic moments of FeMnCrZ (Z = Ga, In) compounds in the type-II phase are 0.074 and 0.105 μ_B following the Slater-Pauling rule, which implies that the compounds in the type-II phase are nearly half-metals. A true half-metal has an integer number of M_t.

Table 1. Relative total energies ΔE (eV), equilibrium lattice constant a (Å), total magnetic moments per unit cell (M_t) and atomic magnetic moments (μ_B), and spin-polarizations (P) for FeMnCrZ (Z = Ga, In) compounds in the three types of phases. The values within GGA+U presented in the parentheses.

FeMnCrGa	ΔE	a	M_t	M_{Fe}	M_{Mn}	M_{Cr}	M_{Ga}	P
type-I	0.000	5.699	0.000	0.000	0.000	0.000	0.000	0
type-II	0.024	5.847	0.074 (0.035)	-0.305 (-0.284)	2.797 (3.415)	-2.280 (-2.912)	0.003 (0.021)	84 (91)
type-III	0.210	5.869	3.195 (3.163)	2.265 (2.639)	2.593 (3.268)	-1.605 (-2.620)	-0.011 (-0.010)	33 (53)
FeMnCrIn	ΔE	a	M_t	M_{Fe}	M_{Mn}	M_{Cr}	M_{In}	SP
type-I	0.000	6.191	2.454 (2.950)	2.236 (2.822)	3.079 (3.651)	-2.665 (-3.236)	-0.013 (-0.017)	71 (79)
type-II	-0.172	6.138	0.105 (0.186)	-0.073 (0.257)	3.14 (3.599)	-2.746 (-3.307)	-0.008 (-0.017)	80 (64)
type-III	-0.061	6.191	3.018 (3.111)	2.542 (2.809)	3.028 (3.556)	-2.439 (-3.067)	-0.007 (-0.008)	47 (63)

3.3. Electronic structures and half-metallicity

Figure 3 and Figure 4 present the atom resolved density of states (DOS) for FeMnCrZ (Z = Ga, In) compounds at their equilibrium lattice constants of three phases. The solid and dashed lines denote the DOSs within GGA and GGA+U, respectively. Positive and negative values correspond to majority-spin and minority-spin states. The Fermi levels were set to zero and the DOS value of Ga atom was multiplied by 10 for clarity. For FeMnCrZ (Z = Ga, In) compounds within GGA+U calculation, the exchange splitting between majority-spin and minority-spin states of transition metal atoms becomes larger than that of GGA calculation, which is consistent with the previous discussion. Comparing the DOSs of FeMnCrIn and FeMnCrSn [21] for their ground phases, it is found that the spin-up 3d states of Fe atom in FeMnCrIn shift toward higher energy region, and the Fermi level locate at the shoulder of a DOS peaks, indicating a decrease of the magnetic moment of the Fe atom.

In the type-I phase, the DOS of FeMnCrGa shows a paramagnetic character, whereas that of FeMnCrIn exhibits magnetic behavior. It is well known that the phase stability of systems is closely related to the DOS near the Fermi level [23, 24]. A system with a sharp peak at the Fermi level will be unstable. As shown in Figure 3, the Fermi level of FeMnCrIn in the type-I phase locate just at

large peaks, thus the phase is most unstable among the three phases for FeMnCrIn. The result is consistent with the total energy calculation.

For the case of type-II phase, the DOSs of FeMnCrGa and FeMnCrIn compounds have similar properties, i.e., there are band-gaps in the minority-spin bands and the Fermi levels locate just at the edges of them. Therefore, FeMnCrZ (Z = Ga, In) compounds with the type-II phase can be classified to be nearly half-metals. The minority-spin band gaps increase from 0.272 (0.094) eV within GGA to 0.352 (0.115) eV within GGA+U for FeMnCrGa (FeMnCrIn) compound. For spintronics applications, the spin-polarization of magnetic materials is one of the important features. The spin-polarization is defined as $P=\left|(N_{E_F}^{\uparrow}-N_{E_F}^{\downarrow})/(N_{E_F}^{\uparrow}+N_{E_F}^{\downarrow})\right|$, where the $N_{E_F}^{\uparrow}$ and $N_{E_F}^{\downarrow}$ are values of the majority-spin and minority-spin DOS at the Fermi level. The calculated spin-polarization of FeMnCrGa (FeMnCrIn) in the type-II phase is 84 (80)% and 91 (61)% with and without the on-site Coulomb correlations, respectively. These results suggest that FeMnCrGa is more suitable than FeMnCrIn as a spin-injection electrode.

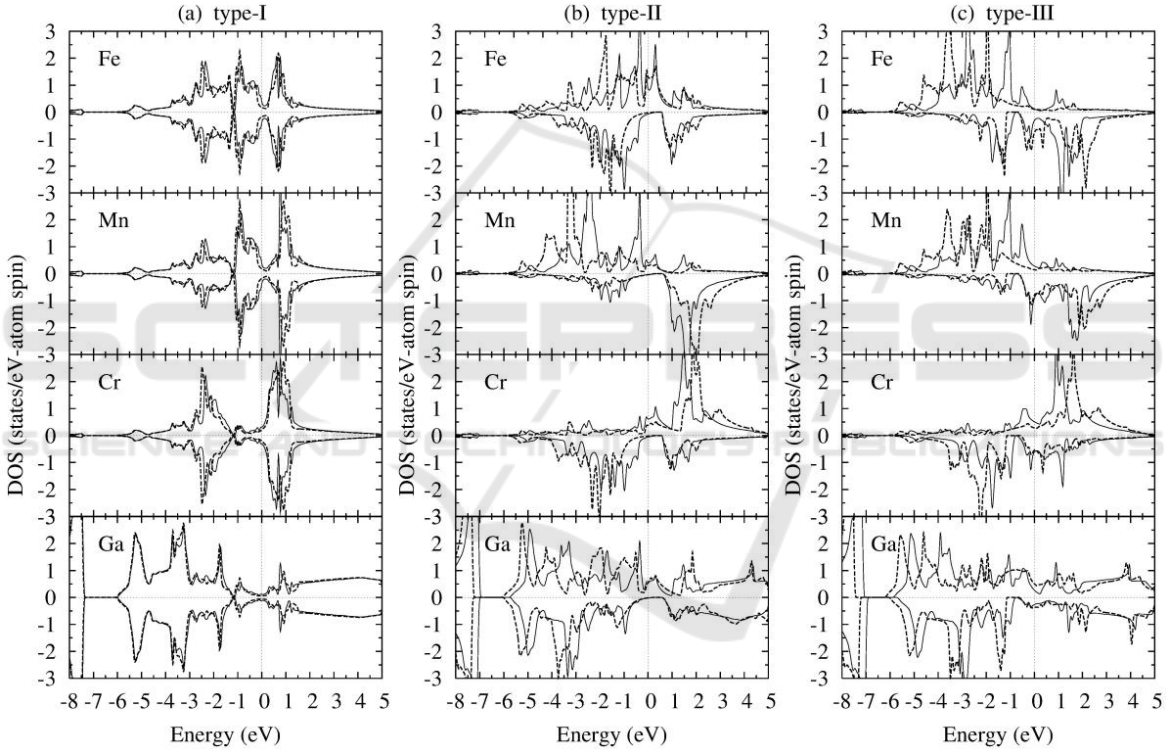

Figure 3. Spin-polarized density of states for FeMnCrGa at their equilibrium lattice constants of three phases. The solid and dashed lines denote the DOSs within GGA and GGA+U, respectively. The Fermi levels were set to zero and the DOS value of Ga atom was multiplied by 10 for clarity.

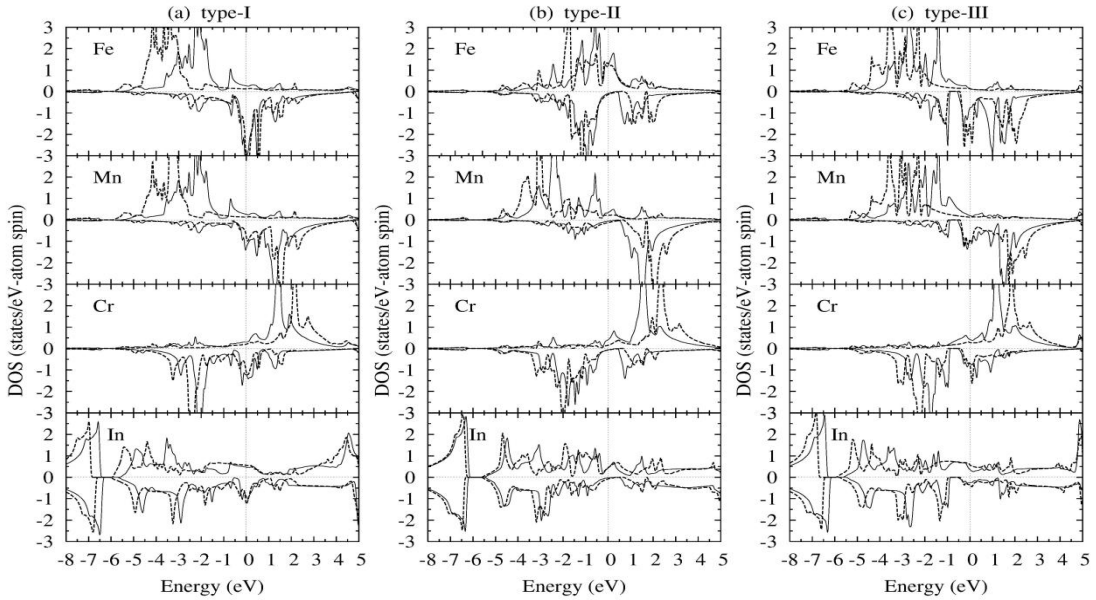

Figure 4. Spin-polarized density of states for FeMnCrIn at their equilibrium lattice constants of three phases. The solid and dashed lines denote the DOSs within GGA and GGA+U, respectively. The Fermi levels were set to zero and the DOS value of Ga atom was multiplied by 10 for clarity.

In the type-III phase, FeMnCrGa and FeMnCrIn compounds have finite values of DOSs in the majority-spin and minority-spin bands, therefore, the compounds are conventional ferrimagnets. The spin-polarization of FeMnCrGa (FeMnCrIn) in type-III phase is 33 (47)% and 53 (63)% for GGA and GGA+U calculations, respectively.

The half-metallic character of material is closely related to lattice constants. In order to explore the electronic properties with lattice constants, I present the minority-spin band structures (with GGA calculation) of FeMnCrGa with type-II phase at lattice constants of 5.503, 5.847, and 6.615 Å, corresponding to the compression (-6%), equilibrium (0%), and extension (+13%), respectively (see Figure 5). It is found that the minority-spin band shows semi-metallic behavior with compression, while the the minority-spin band gap disappear when expanding the lattice constant by +13%. The creation of true half-metallicity is possible by an intentional substitution of elements, which is widely used in the first-principles calculations and experiments [25, 26, 27].

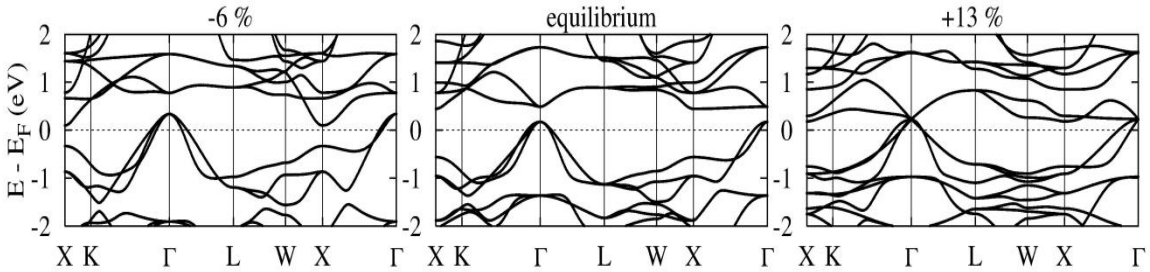

Figure 5. Minority-spin band structures of FeMnCrGa with the type-II phase at the -6% compression, equilibrium, and the +13% extension.

4. Conclusions

Using the all-electron FLAPW method within the GGA and GGA+U schemes, the electronic structures, magnetism and half-metallicity of quaternary Heusler compounds FeMnCrZ (Z = Ga and In) were investigated. For the compounds, the type-I, II, and III phases with different atomic orderings in the unit cell were considered. The equilibrium lattice constants of FeMnCrGa (In) in the type-I, II, and III phases are 5.699 (6.191), 5.847 (6.164), 5.869 (6.191) Å, respectively. FeMnCrGa has a ground state in the type-I phase, whereas the ground state of FeMnCrIn is in the type-II phase. The ground states of FeMnCrGa and FeMnCrIn are paramagnetic and ferrimagnetic, respectively. For FeMnCrGa and FeMnCrIn compounds with the type-II phase, the Fermi levels are located at the edges of minority-spin band gaps, and the compounds are nearly half-metals. The minority-spin band gap (0.272 eV within GGA and 0.352 eV within GGA+U) of FeMnCrGa with the type-II phase is larger than that (0.094 eV within GGA and 0.115 eV within GGA+U) of FeMnCrIn with the type-II phase, suggesting that FeMnCrGa is more suitable than FeMnCrIn as a spin-injection electrode. The total magnetic moments follow the Slater-Pauling rule of Mt = Zt – 24 (μB). FeMnCrGa in the type-III phase and FeMnCrIn in the type-I, III phases are conventional ferrimagnets. It is shown that the GGA+U calculation increases the magnetic moments and the spin-splitting of the transition metal atoms for the compounds.

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