Half-Metallic Properties and Stability of Ferromagnetic State in the Full-Heusler Alloys (Fe$_x$Ru$_{1-x}$)$_2$CrSi (0 ≤ x ≤ 1)

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We investigate the half-metallic properties and the stability of the ferromagnetic state in the alloys (Fe$_x$Ru$_{1-x}$)$_2$CrSi (0 ≤ x ≤ 1) with orderly and disorderly atomic arrangement based on the Heusler structure. It is predicted from the electronic structures that the ordered alloys are half-metals in the range of 1/3 < x < 3/4 and ferromagnets with high spin polarization in the range of 3/4 ≤ x ≤ 1. However, in the ferromagnetic state, the atomic arrangement with the Fe–Cr disorder tends to be energetically more favorable than the orderly arrangement, and the Fe–Cr disorder decreases the spin polarization of the ordered alloys. This is attributed to the fact that occupation of Cr sites by Fe destroys the gap near the Fermi energy in the minority spin state. But, because the Fe–Cr disorder shows a tendency to keep the spin polarization high as x increases, it is deduced that (Fe$_x$Ru$_{1-x}$)$_2$CrSi are materials with high spin polarization if x is high.

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1. Introduction

A half-metal (HM) is metallic in one spin band, while is semiconducting in the other spin band, that is, it makes the spin polarization (P) complete (100%). This character is considered to be very useful in spintronics, such as a tunneling magnetoresistance (TMR) device because it has been expected to get huge magnetoresistive effect in TMR devices. For example, in the film with three layers where a non-magnetic layer is sandwiched between two magnetic layers, the TMR is represented as

\[ \text{TMR} = \frac{2P_1P_2}{1 - P_1P_2}, \]

where $P_n$ is the spin polarization of the n-th magnetic layer.\(^1\) If the magnetic layers are HMs, the TMR becomes infinite.

HMs have been studied more than 20 years since De Groot \textit{et al.} predicted those materials in the half-Heusler alloys NiMnSb and PtMnSb.\(^2\) Ishida \textit{et al.} have searched various HMs in not only the half-Heusler alloys but also the full-Heusler alloys (X$_2$YZ) and the results have been summarized in Ref. 3). They have predicted that Co$_2$MnZ (Z = Si, Ge) alloys are HMs as one example of those,\(^3\) but the presence of the disorder between Co and Mn in those alloys has been proved experimentally by Raphael \textit{et al.} and band calculations by Piccozzi \textit{et al.} have proposed that Co anti-sites destroy the half-metallicity.\(^5\) Inomata \textit{et al.} have demonstrated that a spin valve type tunneling junction with a layer of Co$_2$(Cr$_{0.6}$Fe$_{0.4}$)Al has large TMR of 16% at room temperature and 26.5% at 5 K.\(^9\) However, they have also shown the existence of the disorder between Al and Y (Y = Cr, Fe), that is, that the Co$_2$(Cr$_{0.6}$Fe$_{0.4}$)Al film has the B2 structure, and Miura \textit{et al.} have predicted from band calculations that the spin polarization of Co$_2$(Cr$_{1-x}$Fe$_x$)Al with the disordered B2 structure is a little smaller than that of the L2$_1$ structure.\(^10\) Using a full-potential \textit{ab initio} technique, Galanakis has suggested that the (001) surfaces of Co$_2$MnGe and Co$_2$MnSi lose the half-metallic character, while the CrAl-terminated (001) surface of Co$_2$CrAl does not lose it very much, showing the spin polarization of about 84%.\(^11\) He has explained that the high spin polarization for the surface of Co$_2$CrAl is attributed to not only maintenance of the pseudogap at the Fermi energy ($E_F$) in the minority spin state but also the very high density of states (DOS) of Cr and Co at the $E_F$ in the majority spin state.

Thus, the high spin polarization expected from the theoretically predicted HMs has not been obtained experimentally. The fact may be considered to be due to the various problems, such as atomic disorder and effect of surface. However, acquisition of the materials with high spin polarization or HMs may be possible if we can find the materials, like Co$_2$CrAl, which possess very high DOS at the $E_F$ in the majority spin state and a pseudogap or gap at the $E_F$ in the minority spin state.\(^12\) In other words, the full-Heusler alloys X$_2$CrZ in which Cr occupy the Y sites in X$_2$YZ may be the candidates as those materials.

In this study, we pay attention to the full-Heusler alloys (Fe$_x$Ru$_{1-x}$)$_2$CrSi (0 ≤ x ≤ 1), and investigate the effect of the atomic disorder on the half-metallic properties of the alloy system. However, Ru$_2$CrSi may be antiferromagnetic because it has been reported experimentally and theoretically that Ru$_2$MnSi is antiferromagnetic.\(^13\) Therefore, the stability of the ferromagnetic state is also examined in (Fe$_x$Ru$_{1-x}$)$_2$CrSi where Fe are partially or totally substituted for Ru.

2. Methods of Calculations

Band calculations are carried out self consistently by the linear muffin tin orbital (LMTO) method and the atomic sphere approximation (ASA).\(^15\) The exchange correlation...
potential is treated within the framework of the local-spin-density (LSD) approximation.\(^{16}\)

The unit cell of the L2\(_1\) structure is treated as a trigonal structure because of consideration for atomic disorder with the various levels and a small amount of substitution of Fe for Ru in (Fe\(_x\)Ru\(_{1-x}\))\(_2\)CrSi. The crystal structure is shown in Fig. 1. The theoretical values of the lattice constant for the ordered alloys (Fe\(_x\)Ru\(_{1-x}\))\(_2\)CrSi are shown in Table 1. The lattice constant \(a\) of the trigonal structure adopted in the band calculations is \(\sqrt{2}\) times as large as that of the cubic structure.

About the disorder type of (Fe\(_x\)Ru\(_{1-x}\))\(_2\)CrSi, we consider three types of disorder, Cr–Si, X–Cr and X–Si (X = Fe, Ru). The molecular formulae of the Cr–Si, X–Cr and X–Si types are described as (Fe\(_x\)Ru\(_{1-x}\))(Cr\(_{1-x}\)Si\(_x\)), \(((\text{Fe}_{x-\gamma/2} \text{Ru}_{\gamma/2}))(\text{Cr}_{1-x} \text{Si}_{x})\))\(_2\), \(((\text{Fe}_{x-\gamma/2} \text{Si}_{\gamma/2}))(\text{Ru}_{1-x} \text{Cr}_{x})\))\(_2\) and \(((\text{Fe}_{x-\gamma/2} \text{Si}_{\gamma/2}))(\text{Ru}_{1-x} \text{Cr}_{x})\))\(_2\), respectively, where \(y\) (\(=y' + y''\)) is the ratio of Cr (Si) occupying anti-sites to the total number of Cr (Si). In this paper, \(y\) is defined as the disorder level in each type of disorder, and \(y'\) and \(y''\) are done as the disorder levels between Fe and Cr (Si) and between Ru and Cr (Si), respectively.

To study the stability of the ferromagnetic state in the ordered alloys (Fe\(_x\)Ru\(_{1-x}\))\(_2\)CrSi, the calculations for the antiferromagnetic state are also performed. We assume two models, AF1 and AF2, as the magnetic arrangement of the antiferromagnetic state. As shown in Fig. 2, in AF1 the X (Cr, Si) magnetic moments are ferromagnetically coupled on the (001) plane and are antiferromagnetically coupled along the [001] direction. On the other hand, in AF2 the X (Cr, Si) magnetic moments are ferromagnetically coupled on the (111) plane and are antiferromagnetically coupled along the [111] direction as seen in Fig. 1.

### 3. Results of Calculations

#### 3.1 Ordered (Fe\(_x\)Ru\(_{1-x}\))\(_2\)CrSi

First, we examine the electronic structures of the ordered alloys (Fe\(_x\)Ru\(_{1-x}\))\(_2\)CrSi in the ferromagnetic state. The total DOS of (Fe\(_x\)Ru\(_{1-x}\))\(_2\)CrSi in the cases of \(x = 0, 1/4, 1/2, 3/4, 1\) and the ordered ferromagnet Co\(_2\)MnSi is shown in Figs. 3(a)–(f). The total spin magnetic moment per unit cell and the spin polarization are written in each figure. Converting the moment per unit cell into that per formula unit, the total moment of (Fe\(_x\)Ru\(_{1-x}\))\(_2\)CrSi is about 2 \(\mu_B\) in any range of \(x\) and follows the rule \(M_t = Z_t - 24\), where \(M_t\) is the total spin magnetic moment per formula unit and \(Z_t\) is the total number of valence electrons.\(^{17}\) The spin polarization \(P\) is defined as \(P = (D_1 - D_2)/(D_1 + D_2)\), where \(D_1\) and \(D_2\) are DOS at the \(E_F\) in the majority spin state and in the minority spin state, respectively. From the expression, it is remarked that very high \(D_1\) approaches \(P \approx 1\) even if \(D_1\) somewhat appears. Seeing Figs. 3(a)–(f), it is found that the \(D_1\) of (Fe\(_x\)Ru\(_{1-x}\))\(_2\)CrSi is much higher than the \(D_1\) of Co\(_2\)MnSi. In addition, the \(D_1\) of those alloys shows a tendency to increase as the Fe concentration \(x\) becomes higher.
of the high $D_\uparrow$, we investigate the local DOS of (Fe,Ru$_{1-x}$)$_2$CrSi. The local DOS in the cases of $x = 0$, 1/2, 1 is shown in Figs. 4(a)–(g). From these figures, it is noticed that although the Cr magnetic moment decreases as $x$ increases, the local $D_\uparrow$ of Cr greatly contributes to the high $D_\uparrow$ as we have expected. Also, the local $D_\uparrow$ of Fe shows the pretty contribution to it. That is, the high $D_\uparrow$ of (Fe,Ru$_{1-x}$)$_2$CrSi is based on that of Cr and its increase with $x$ is mainly due to that of Fe. As for the half-metallicity in (Fe,Ru$_{1-x}$)$_2$CrSi, the $E_F$ is in a gap in the range of $0 \leq x \leq 11/16$, but a small amount of $D_\uparrow$ exists in $3/4 \leq x \leq 1$. Therefore, it is inferred in the ferromagnetic state that the ordered alloys (Fe,Ru$_{1-x}$)$_2$CrSi are HMs in $0 \leq x < 3/4$ and materials near a HM in 3/4 $\leq x \leq 1$.

Next, we consider the antiferromagnetic state (AFi; $i = 1$, 2) in order to study the stability of the ferromagnetic state in the orderly arrangement because it is essential that a HM is ferromagnetic. The relationship between the Fe concentration $x$ and $\Delta E_i$ is shown in Fig. 5. Here, $\Delta E_i$ is the total energy difference per formula unit between the antiferromagnetic state and the ferromagnetic state. From this figure, it is found that although $\Delta E_i$ is negative for the case of $x = 0$, $\Delta E_1$ and $\Delta E_2$ are positive from $x = 1/4$ and from $x = 3/8$, respectively, that is, the ferromagnetic state is more favorable than the antiferromagnetic state in $1/3 < x \leq 1$. Organizing the above, it is predicted that the ordered alloys (Fe,Ru$_{1-x}$)$_2$CrSi are HMs in $1/3 < x < 3/4$ and are ferromagnets with high $P$ in $3/4 \leq x \leq 1$. However, the range in which the ferromagnetic state is more stable may change a little because the magnetic arrangement assumed in this study is not necessarily the most stable one in the antiferromagnetic state.

### 3.2 Disordered (Fe,Ru$_{1-x}$)$_2$CrSi

As mentioned above, it is supposed that very high $D_\uparrow$ keeps $P$ high even if a small amount of $D_\uparrow$ appears for some effect, so we investigate the effect of the atomic disorder on the half-metallic properties of (Fe,Ru$_{1-x}$)$_2$CrSi. After this, we assume these alloys ferromagnetic, even in the range of $x$ where the antiferromagnetic state is more favorable.

In (Fe,Ru$_{1-x}$)$_2$CrSi ($x = 0, 1/4, 1/2, 3/4, 1$), the relationship between $P$ and the disorder level $y$ is shown in Figs. 6(a)–(e). Seeing these figures, it is found that $P$ holds high even though the Cr–Si disorder occurs very much, while the X–Cr and X–Si disorder decreases $P$ as $y$ increases. However, the X–Cr disorder does not degrade $P$ as rapidly as the X–Si disorder, and the Fe–Cr disorder tends to keep $P$ as $x$ becomes higher.

Next, we show $\Delta E$, which is the total energy difference per unit cell between each type disordered structure and the
ordered one, as a function of $y$ for $(\text{Fe}_{1/2}\text{Ru}_{1/2})\text{CrSi}$ in Fig. 7. In this figure, we can see that the atomic arrangement with the Fe–Cr disorder is more stable than the orderly arrangement to a certain $y$ (in this case, $y = 1/4$). The arrangement with the other types of disorder is, on the contrary, more unstable than the orderly one and tends to become more unstable on the whole as $y$ increases.

Tendencies like these are also shown in the other cases of $x$, and the orderly arrangement is more favorable than any type disorder for Ru$_2$CrSi where the Fe–Cr disorder is impossible. From these, it is predicted that $(\text{Fe}_x\text{Ru}_{1-x})_2\text{CrSi}$ have the Fe–Cr disorder if $x$ is not 0. Hereafter, we focus on the disorder except the X–Si one in this paper because the atomic arrangement with the X–Si one is very unstable and the probability of the occurrence may be low.

In order to understand the cause of the decrease in $P$, we examine the DOS of those alloys with the disordered structure. The total DOS of $(\text{Fe}_{1/2}\text{Ru}_{1/2})_2\text{CrSi}$ with each type disorder in the case of $y = 3/8$ is shown in Figs. 8(a)–(c). Comparing these figures with Fig. 3(c) corresponding to the orderly arrangement, it is found that the Cr–Si disorder does not destroy the gap near $E_F$ in the minority spin state very much, but the X–Cr disorder destroys it completely, which leads to the decrease in $P$. In addition, all types of disorder lowers the $D_1$ of the orderly arrangement’s case and this is also the cause of the decrease in $P$. We study the local DOS in the above cases to research further on the destruction of the gap and the decrease in $D_1$. Figures 9(a)–(e) show the DOS of the atoms occupying anti-sites in the above cases. Comparing these figures with Figs. 4(c)–(e) corresponding to the orderly arrangement, it is remarked that the Cr–Si disorder does not bring about great change in the electronic structures of the atoms occupying anti-sites, while the X–Cr disorder greatly affects them. The DOS of the atoms occupying ordinary sites (not shown in this paper) is not affected in shape very much by the Cr–Si and X–Cr disorder. The destruction of the gap is attributed mainly to X occupying Cr sites, and the causes of the decrease in $D_1$ are chiefly due to the atoms occupying anti-sites, especially Fe occupying Cr sites and Cr occupying X sites. In addition,
the absolute values of the spin moments of X occupying Cr sites increase and the moments of Cr occupying X sites get to have the opposite direction of those of Cr occupying ordinary sites. Such tendencies on atomic disorder are also obtained in the other cases of x.

As mentioned above, the spin moments of X and Cr occupying anti-sites dramatically change in the atomic arrangement with the X–Cr disorder, so we investigate the change caused by atomic disorder in the total spin moment. The relationship between the total spin magnetic moment and y for (Fe1/2Ru1/2)2CrSi is shown in Fig. 10. From this figure, one can find that although the Fe–Cr disorder decreases gradually the total moment as y becomes higher, the Cr–Si and Fe–Cr disorder almost keeps it. However, the Ru–Cr disorder reduces it considerably. This is due to that Ru at Cr sites do not compensate for the decrement in the moment of Cr at Ru sites (but Fe at Cr sites almost does that of Cr at Fe sites). Regardless of x, all types of disorder shows similar tendencies on the whole, but the Ru–Cr disorder decreases further the total spin moment in high y when x is low.

By the way, it is noticed from Figs. 6(c) and 10 that although (Fe1/2Ru1/2)2CrSi does not show half-metallicity, the total spin moment per formula unit is 1.50 \( \mu_B \), that is, (Fe1/2Ru1/2)2CrSi does not show the Slater-Pauling behavior. This indicates that the total spin magnetic moment of a HM does not necessarily follow the Slater-Pauling rule. In this case, the peak near the Fermi level is attributed to the effect of Fe occupying Cr sites in the case x = 0 or 1. Considering the stability of the ferromagnetic state in the ordered alloys (Fe, Ru)2CrSi, Fe2CrSi is regarded as the best candidate of materials with high P. However, the partial substitution of Ru for Fe in Fe2CrSi shows the following merit. Figure 11 shows the DOS of Fe 3d at Cr sites in (Fe, Ru)2CrSi with the Fe–Cr type disorder for the case of y = 3/8. x = (a) 1/4, (b) 1/2, (c) 3/4, (d) 1. The solid and the broken lines indicate the majority and the minority spin state, respectively, and the vertical line shows the \( E_F \).

Fig. 10 The relationship between total spin magnetic moment and y for (Fe1/2Ru1/2)2CrSi with the Cr–Si (triangle), Fe–Cr (closed square) or Ru–Cr (open square) type disorder.

Fig. 11 The DOS of Fe 3d at Cr sites in (Fe, Ru)2CrSi with the Fe–Cr type disorder for the case of y = 3/8, x = (a) 1/4, (b) 1/2, (c) 3/4, (d) 1. The solid and the broken lines indicate the majority and the minority spin state, respectively, and the vertical line shows the \( E_F \).
4. Summary

We have investigated the half-metallic properties and the stability of the ferromagnetic state, by means of first-principle calculations, in the alloys \((\text{Fe}_{x}\text{Ru}_{1-x})_{2}\text{CrSi}\) with the orderly and disorderly arrangement based on the \(L_2^1\) structure. From the results, it has been found that the ordered alloys are HMs in \(0 < x < 3\) and materials near a HM in \(3/4 < x < 4\), if those are ferromagnetic. And the results have shown that the ferromagnetic state is energetically more stable than the antiferromagnetic state in \(1 < x < 3\). That is, it has been predicted that the ordered alloys are HMs in \(1 < x < 3\) and ferromagnets with high \(P\) in \(3/4 < x < 1\). However, in the ferromagnetic state, the atomic arrangement with the Fe–Cr disorder tends to be energetically more favorable than the orderly arrangement, but the other type disorder to be not. In addition, the Fe–Cr disorder decreases \(P\) of the ordered alloys and this is attributed to that Fe occupying Cr sites destroy the gap near the \(E_F\) in the minority spin state. But, the Fe–Cr disorder tends to keep \(P\) high as \(x\) increases and to be restrained as \(x\) decreases. Therefore, we conclude that \((\text{Fe}_{x}\text{Ru}_{1-x})_{2}\text{CrSi}\) will be promising materials in spintronics if \(x\) is high.

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REFERENCES