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## The effect of addition of Ru to Fe on the electronic structure and magnetic properties

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**Abstract.** Band structure calculations based on the Korringa–Kohn–Rostoker coherent-potential approximation method are used to study the electronic structure and magnetic properties of BCC FeRu alloys within a Ru concentration of 20 at.%, although it is experimentally known that FeRu alloys include the FCC and HCP structures beyond a 5 at.% Ru concentration. The results show that the ruthenium is ferromagnetic in  $\alpha$ -Fe with a moment of about  $0.5\mu_B$  and that the ruthenium addition to  $\alpha$ -Fe enhances the magnetic moment at Fe sites by about  $0.02\mu_B/\text{Ru at.}\%$  because of the magnetovolume effect and large spin splitting by Ru addition. The density of states calculated in the paramagnetic state shows that the strong d–d hybridization between Fe and Ru causes the spin splitting of Ru. The BCC structure is important in the process of Ru becoming ferromagnetic. We have clarified the reason why the average magnetic moment of the FeRu BCC alloy scarcely decreases with the Ru addition.

### 1. Introduction

It is well known that the addition of paramagnetic elements to Fe generally reduces the average magnetic moment in proportion to the amount added [1, 2]. Ru is one of the elements which scarcely decreases the average magnetic moment [3]. While the Ru concentration is below 5 at.%, the magnetic moment of the FeRu alloy is almost the same as that of pure Fe, though the magnetic moment of the FeRu alloy decreases drastically when the Ru concentration exceeds 5 at.%. Collins and Low [4] observed, using neutron scattering techniques that Ru impurity in Fe has a magnetic moment of  $0.9 \pm 0.5\mu_B$ .

The effect of impurities of 3d and 4d transition metals in Fe has been studied [5] by band calculations and it has been shown that the results were in good agreement with the experimental results. Calculations for Fe alloys diluted by the 3d transition metals are made systematically [6] and the Slater–Pauling curve obtained experimentally is confirmed by the band calculations based on the local-spin-density approximation. However, the electronic structure and magnetic properties of FeRu alloys have not yet been theoretically studied in detail because FeRu alloys have not been considered with investigation.

Recent experiments show that the addition of Ru to Fe based alloys causes the enhancement of anti-corrosion, wear resistance and thermal stability without reduction of the average magnetic moment [7, 8]. It is known that the corrosion resistance of Fe based alloys can be improved by the addition of small amounts of platinum group metals (PGMs),

e.g. Pt, Pd and Ru [9, 10]. Ru is occasionally more effective than Pt and Pd [11]. Ru has been thought to be an effective alloying element for Fe based alloys.

We have calculated the band structure of the Ru for an assumed BCC structure [12] and found the possibility of ferromagnetic Ru. In this paper, we study the electronic structure and magnetic properties of the  $\text{Fe}_{1-x}\text{Ru}_x$  BCC alloy ( $0 < x < 0.2$ ) by using the first-principle Korringa–Kohn–Rostoker coherent-potential approximation method based on the local-spin-density approximation. The effect of Ru addition to Fe on electronic structure and magnetic moment is studied.

## 2. Calculation methods

The electronic structure and magnetic properties of the BCC FeRu alloy are calculated using the Korringa–Kohn–Rostoker [13, 14] coherent-potential approximation [15, 16] (KKR–CPA) Green’s function method, based on the local-spin-density approximation. In this method the electron density  $\rho(r)$  is given by

$$\rho(r) = \rho^\uparrow(r) + \rho^\downarrow(r) \quad (1)$$

$$\rho^{\uparrow(\downarrow)}(r) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_f} dE G^{\uparrow(\downarrow)}(r, r, E) \quad (2)$$

where  $G(r, r, E)$  is a Green function, and  $\uparrow$  and  $\downarrow$  refer to the electron spin. The formulation of the total energy calculation using the configuration-averaged interstitial electron density is discussed in detail by Johnson *et al* [17]. The basic idea in the KKR CPA is the calculation of the local electronic structures for one pure site A, which is surrounded by an effective medium that is a configuration average over all sites. According to density functional theory, the charge density is varied to obtain the minimum energy for a given potential. The potential of the  $i$ th site is given by the variation of the energy with respect to the electron density of  $i$ th site as follows.

$$V_i(r) = \frac{\delta U}{\delta \rho_i(r)} + \frac{\delta E_{XC}}{\delta \rho_i(r)} = -2 \sum_i Z_i \frac{1}{|r - R_i|} + 2 \int d^3r' \frac{\rho_i(r)}{|r - r'|} + \mu_{XC}[\rho_i^\uparrow(r), \rho_i^\downarrow(r)] \quad (3)$$

The Perdew–Zunger formula [18] for the exchange and correlation potential  $\mu_{XC}$  is adopted. The potential is obtained as follows

$$V_i(r) = \begin{cases} 0 & (r > R_m) \\ -\frac{2Z_i}{r} + 8\pi \int_0^r dr' \left( \frac{r'^2}{r} - r' \right) \rho_i(r') + 8\pi \int_0^{R_m} dr' r' \rho_i(r') & \\ + C \frac{\rho_0 \sqrt{2} \sigma_0}{a} + \mu_{XC}[\rho_i^\uparrow(r), \rho_i^\downarrow(r)] - \mu_{XC}[\rho_0^\uparrow(r), \rho_0^\downarrow(r)] & (r < R_m) \end{cases} \quad (4)$$

the value of  $C$  is obtained by Janak [19]. The basis set contains s, p, and d orbitals. The energy integral is performed by the complex energy method [20]. The integral path on the complex energy plane is shown in figure 1. The lowest energy of  $E_s$  of the real axis can be chosen arbitrarily between the core and valence states, so  $-0.2$  Ryd is used in the present work. The imaginary part  $\gamma$  of the path is chosen to be 0.5 Ryd because  $G(r, r, E)$  can be a smooth function of  $E$  in the complex plane. The upper real part of the path is the Fermi energy that is determined every iteration. On that path, 63 energy points are used. It is sufficient to estimate the energy integral. The  $k$ -integral for the effective scattering amplitude used to solve the KKR CPA equation within the  $1/48$  irreducible wedge of the Brillouin zone, is calculated with 8 points using the special point method far away from

real axis, and 1920 points using the prism method [21,22] near the real axis. The total energy converges to less than  $10^{-2}$  mRyd/atom. The lattice constant is chosen by the total energy minimum. On the above condition, the band structure of the BCC  $\text{Fe}_{1-x}\text{Ru}_x$  alloy ( $0 < x < 0.2$ ) is calculated in the ferromagnetic and paramagnetic states.

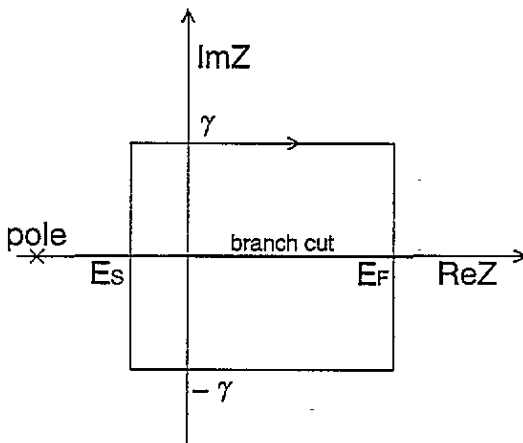


Figure 1. An integral path on the complex energy plane.

### 3. Results and discussion

Figure 2 shows the magnetic moment as a function of the Ru concentration. The solid and open squares show the average magnetic moment obtained by experiment and calculation, respectively. The solid and open circles show the magnetic moments obtained by the calculation at Fe and Ru sites, respectively. The average moment of our calculation is in good agreement with the experimental results [3] at less than 5 at.% Ru concentration. However, our calculation does not change drastically beyond an Ru concentration of 5 at.%, though the experimental results show a rapid decrease of the average magnetic moment. This discrepancy is thought to be due to a change in the crystal structure. Raub and Plate [23] experimentally showed that the FeRu alloy has a BCC structure while the Ru concentration is less than 5 at.%, but, when the Ru concentration exceeds 5 at.%, the FeRu alloy includes FCC and HCP structures. Moreover, Pearson and Williams [24] observed, using Mössbauer absorption spectroscopy, that the HCP FeRu alloy is antiferromagnetic. Our work [12] showed that the energy of pure FCC Ru is smaller than that of BCC Ru, and that of pure BCC Fe is smaller than that of FCC Fe. Considering the continuity of KKR and KKR CPA methods at the ultimate Ru concentration, we can expect that BCC FeRu changes its structure at some Ru concentration.

Our calculation suggests that if a FeRu alloy of high Ru concentration could be prepared in BCC structure by some thermal treatment or epitaxial technique, the average magnetic moment of FeRu would not decrease even if the Ru concentration is beyond 5 at.%.

Ru is ferromagnetic in an Fe matrix with a moment of about  $0.5\mu_B$ . Ru addition enhances the magnetic moment at Fe about  $0.02\mu_B/\text{Ru at.}\%$ . The magnetic moments both at Fe and Ru sites increase as the Ru concentration increases.

Figures 3 and 4 show the calculated density of states (DOS) of FeRu with a Ru concentration of 0.5 and 2 at.%, respectively. The majority and minority spins at the

Ru site are split in spite of the fact that the Ru is normally a paramagnetic element. The spin splitting locates the Fermi energy on the valley of the DOS and makes the state stable. The DOS at the Ru site in FeRu is similar to that of ferromagnetic BCC Ru [12].

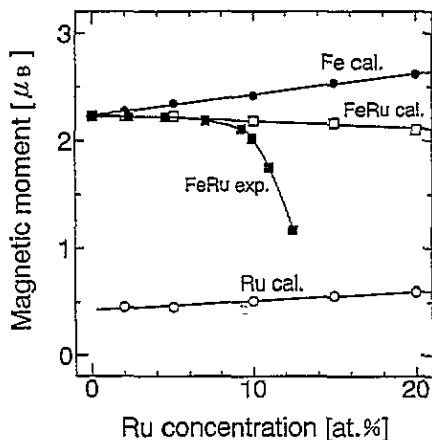


Figure 2. The magnetic moments at various Ru concentrations. The solid and open squares show the average magnetic moment obtained by experiment and calculation, respectively. The solid and open circles show the magnetic moments obtained by calculation at Fe and Ru sites, respectively.

Figures 5 and 6 show the DOS calculated in a paramagnetic state of  $\text{Fe}_{98}\text{Ru}_2$  and  $\text{Fe}_{90}\text{Ru}_{10}$ , respectively. It is well known that if the Fermi energy is on the peak of the paramagnetic DOS, the elements have a tendency of becoming ferromagnetic [25]. Not only Fe but also Ru have the peak of the DOS at around the Fermi energy. It has been shown [12] that BCC Ru has the peak of the DOS at the Fermi energy and that a BCC-like structure is effective for Ru becoming ferromagnetic. Actually the DOS at the Ru site in FeRu calculated in a paramagnetic state is very similar to that of BCC Ru [12]. The DOS at Ru site at the Fermi energy is 20.71 states  $\text{Ryd}^{-1}$  when the Ru concentration is 2.0 at.% and 21.20 states  $\text{Ryd}^{-1}$  when the concentration is 10 at.%. Supposing that the effective exchange integration  $J_{eff}$  of Ru is 0.022 Ryd [26], the product of the DOS at the Fermi energy ( $n(E_F)$ ) and  $J_{eff}$  is 0.456 for  $\text{Fe}_{98}\text{Ru}_2$ , and 0.466 for  $\text{Fe}_{90}\text{Ru}_{10}$ , respectively. The electron of the Ru site does not locally satisfy the Stoner criterion [27] for the ferromagnetic transition ( $n(E_F) J_{eff} > 1$ ).

Figures 7 and 8 show the DOS of the d-electron. The solid and dotted lines show the DOS at the Ru and Fe sites, respectively. Comparing with figures 6 and 7, we can see that the DOS of the d-electron characterizes the DOS of the s, p and d electrons. The d-band-width of Ru is larger than that of Fe but the peak of the DOS near the Fermi energy of Ru overlaps with that of Fe. Ru becomes ferromagnetic by this strong d-d hybridization [28] near the Fermi energy between Fe and Ru.

Figure 9 shows the lattice constant as a function of the Ru concentration. The solid and open circles show the lattice constant obtained by calculation and experiment [29], respectively. The lattice constant is increased in proportion to the Ru concentration. The difference between the calculation and experiment is about 0.07 au. It is well known that the LDA underestimates the lattice constant. Another reason is thought to be the thermal expansion. The experiment was performed at 310 K, but our calculation indicates that it is in the ground state so the thermal expansion is ignored.

Figure 10 shows the magnetic moment at the Fe site as a function of the lattice constant.

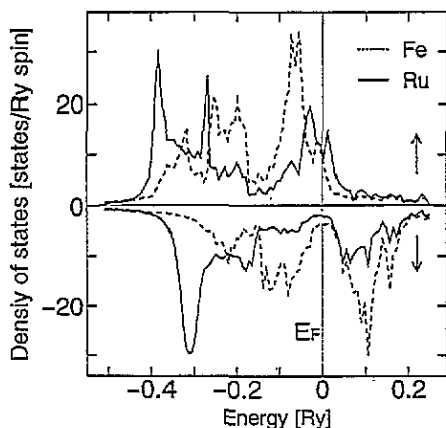


Figure 3. The density of states of FeRu with a Ru concentration of 0.5 at.%. The solid line shows the DOS at the Ru site and the dotted line shows the DOS at the Fe site.

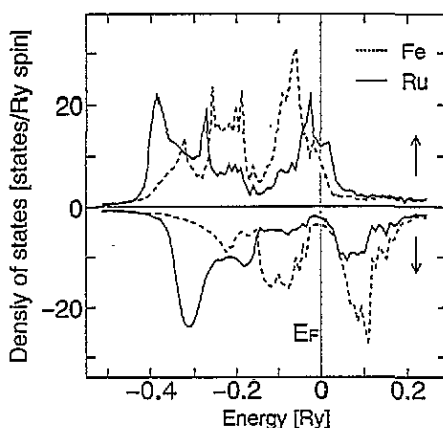


Figure 4. The density of states of FeRu with a Ru concentration of 2.0 at.%. The solid line shows the DOS at the Ru site and the dotted line shows the DOS at the Fe site.

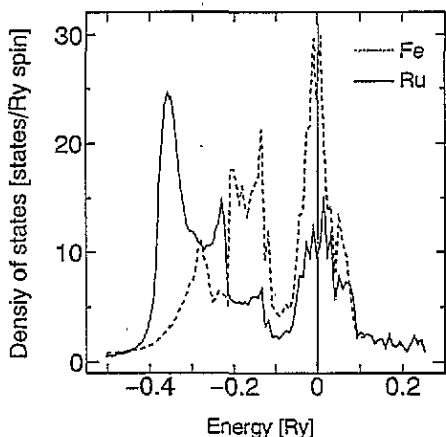


Figure 5. The density of states calculated in a paramagnetic state of  $\text{Fe}_{99}\text{Ru}_2$ . The solid line shows the DOS at the Ru site and the dotted line shows the DOS at the Fe site.

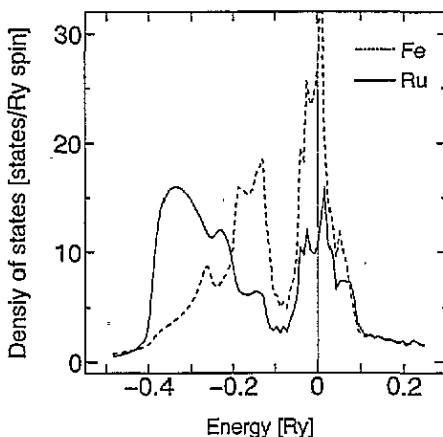


Figure 6. The density of states calculated in a paramagnetic state of  $\text{Fe}_{90}\text{Ru}_{10}$ . The solid line shows the DOS at the Ru site and the dotted line shows the DOS at the Fe site.

The full circles show the magnetic moment at the Fe site calculated for FeRu. The open circles show the magnetic moment calculated for pure Fe using the KKR Green function method with the same accuracy as the calculation of FeRu. The dotted line shows the value of pure Fe calculated by Moruzzi *et al* [30] using the augmented-spherical-wave method. The open circles and the dotted line show the general magnetovolume effect of Fe. The increase in the magnetic moment at the Fe site in FeRu is large compared with the general magnetovolume effect.

Table 1 shows the local charges of  $\text{Fe}_{98}\text{Ru}_2$  for both spin directions separated with respect to their s, p, d<sub>e</sub> and d<sub>γ</sub> character. The magnetic moment at the Fe site in  $\text{Fe}_{98}\text{Ru}_2$

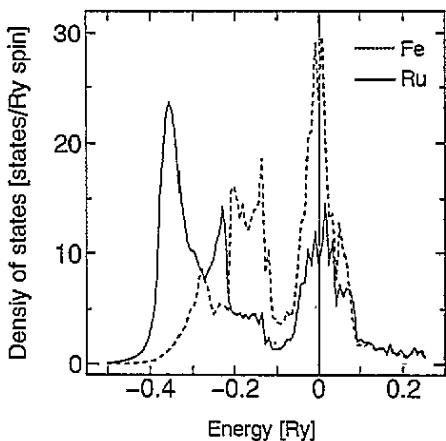


Figure 7. The density of states of d-electrons calculated in a paramagnetic state of  $\text{Fe}_{98}\text{Ru}_2$ . The solid line shows the DOS at the Ru site and the dotted line shows the DOS at the Fe site.

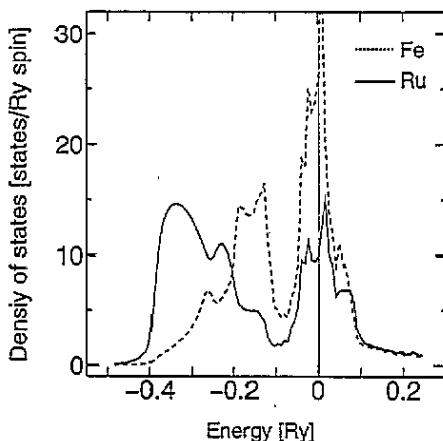


Figure 8. The density of states of d-electrons calculated in a paramagnetic state of  $\text{Fe}_{90}\text{Ru}_{10}$ . The solid line shows the DOS at the Ru site and the dotted line shows the DOS at the Fe site.

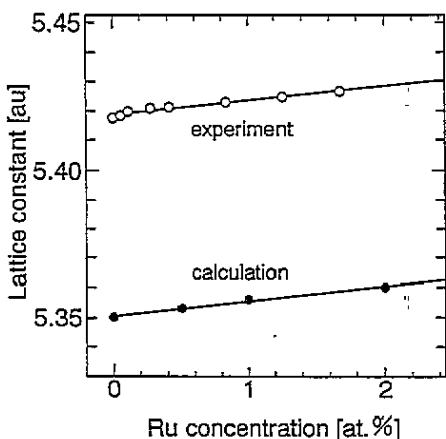


Figure 9. The lattice constants at various Ru concentrations. The solid and open circles show the lattice constant obtained by calculation and experiment, respectively.

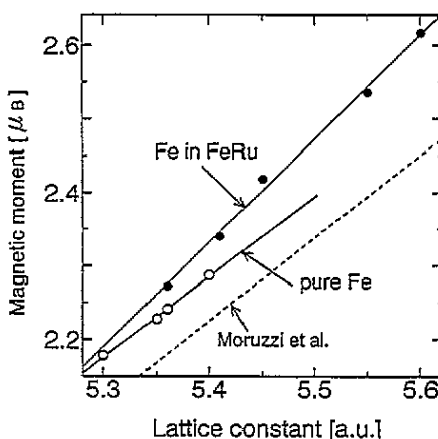


Figure 10. The magnetic moments at the Fe site at various lattice constants. The full circles show the magnetic moment at the Fe site calculated in FeRu. The open circles show the magnetic moment calculated for pure Fe. The dotted line shows the value calculated by Moruzzi *et al* [30].

is larger than that in pure Fe by  $0.031\mu_B$ . The addition of Ru to Fe decreases the minority spin at the Fe site of 0.014, therefore the increase of the magnetic moment at the Fe site is  $0.028\mu_B$  by the splitting of itself. The rest of  $0.003\mu_B$  is brought by the charge transfer from Ru site.

The addition of Ru to Fe shows two effects: (1) the Ru itself becomes ferromagnetic, (2) the magnetic moment at the Fe site is much enhanced because of the magnetovolume effect and large spin splitting. Therefore the addition of Ru to Fe scarcely decreases the

**Table 1.** The calculated local moments and partial local charges for both spin directions of Fe in Fe<sub>98</sub>Ru<sub>2</sub> and Fe in pure Fe.

	Spin (+)				Spin (-)				moment
	s	p	d <sub>ε</sub>	d <sub>γ</sub>	s	p	d <sub>ε</sub>	d <sub>γ</sub>	
Fe in Fe <sub>98</sub> Ru <sub>2</sub>	0.308	0.371	2.625	1.833	0.317	0.416	1.460	0.673	2.272
Fe in pure Fe	0.307	0.361	2.618	1.834	0.316	0.404	1.478	0.681	2.241

average magnetic moment.

#### 4. Conclusion

The first-principle KKR CPA calculation clarifies the reason why the Ru addition to Fe scarcely decreases the average magnetic moment. One reason is that Ru in  $\alpha$ -Fe becomes ferromagnetic by the strong d-d hybridization between Fe and Ru, due to the BCC structure. Another reason is that Ru addition to Fe enhances the magnetic moment at the Fe site because of the magnetovolume effect and large spin splitting. Our calculations showed that BCC structure is important for the Ru alloy to become ferromagnetic. If we could prepare the BCC FeRu at high Ru concentrations, the average magnetic moment would not decrease. It is concluded that Ru can be regarded as an effective alloying element to magnetic materials of Fe base.

#### Acknowledgments

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