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1996 J. Phys.: Condens. Matter 8 7863

(http://iopscience.iop.org/0953-8984/8/42/006)

J. Phys.: Condens. Matter **8** (1996) 7863–7868. Printed in the UK

Effect of Ru addition to Ni on the electronic structure and magnetic properties

Mitsuru Kobayashi†, Tadashi Kai†, Noriyuki Takano‡, Yoshiko Ohashi† and Kazuo Shiiki†

† Department of Instrumentation Engineering, Faculty of Science and Technology, Keio University, Yokohama 223, Japan

‡ Department of Mechanical Systems Engineering, Kanazawa Institute of Technology, Ishikawa 921, Japan

Received 22 April 1996

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 FCC Ni–Ru alloy with a Ru concentration of 20 at.%. The results show that the ruthenium is ferromagnetic in Ni with a moment of about 0.6 μ_B in the low-Ru-concentration region. The density of states calculated in the paramagnetic state shows that the strong d–d hybridization between Ni and Ru causes spin splitting of Ru, which is similar to the BCC Fe–Ru alloy. However, the local magnetic moment of Ru in the FCC Ni–Fu alloy drops abruptly as the Ru concentration increases. It is due to the non-magnetic character of FCC Ru, although BCC Ru is ferromagnetic. We clarified the reason why the average magnetic moment of the FCC Ni–Ru alloy drastically decreases on Ru addition.

1. Introduction

For the promotion of large-capacity magnetic recording, anticorrosive soft magnetic films with a high magnetic moment are necessary. It is known that the addition of Ru to Fe scarcely decreases the magnetic moment of the alloy and markedly improves the corrosion resistance [1]. The electronic structure of $Fe_{1-x}Ru_x$ has been studied [2] using band-structure calculations based on the local-spin-density approximation and the reason why the Ru addition to Fe does not cause the magnetic moment to be decreased is clarified. The improvement in the corrosion resistance of Ni-based alloys such as Permalloy with a highly soft magnetism, is useful for industrial purposes. However, the addition of Ru to Ni causes the magnetic moment of the alloy to decrease [3].

The magnetization of Ni–Ru alloy is calculated [4] by the tight-binding method but the band-structure calculation has not been done before in detail. The effect of Ru addition cannot be understood as yet. In this article, we studied the electronic structure of $Ni_{1-x}Ru_x$ ($0 < x < 0.2$) alloys using the Korringa–Kohn–Rostoker [5, 6] coherent-potential approximation (CPA) [7, 8] method based on the local-spin-density approximation.

2. Calculation method

The procedure and the accuracy of this calculation are the same as for the calculation for Fe–Ru alloy [2]. The electronic structure and magnetic properties of the FCC Ni–Ru alloy

0953-8984/96/427863+06$19.50

are calculated using the KKR CPA Green function method based on the local-spin-density approximation. In this method the electron density $\rho(r)$ is given by

$$\rho(r) = \rho^{\uparrow}(r) + \rho^{\downarrow}(r) \tag{1}$$

$$\rho^{\uparrow(\downarrow)}(r) = -\frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{E_f} \mathrm{d}E\; G^{\uparrow(\downarrow)}(r,\, r,\, E) \tag{2}$$

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 has been discussed in detail by Johnson *et al* [9]. The basic idea in the KKR CPA is to calculate 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 Perdew–Zunger [10] formula for the exchange and correlation potential is adopted. The basis set contains s, p and d orbitals.

The energy integral is obtained by the complex energy method [11]. The lowest energy of the real axis is -0.2 Ryd in the present work, which can be chosen arbitrarily between the core and valence states. The imaginary part of the path is chosen to be 0.5 Ryd because $G(r,\, r,\, E)$ is 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, which is sufficient to estimate the energy [11].

The k integral for the effective scattering amplitude to solve the KKR CPA equation within the one-fortyeighth irreducible wedge of the Brillouin zone is calculated with eight points using the special point method far away from real axis and 1920 points using the prism method [12, 13] near the real axis. The total energy converges to less than 10^{-2} mRyd atom^{-1}.

The lattice constants of pure Ni and Ru are chosen from the energy minimum and their lattice constants are 6.55 au and 7.40 au [14], respectively. The Vegard law is used to assume the lattice constant of Ni–Ru alloy. The deviation from the Vegard law in Ni–Ru alloy is estimated experimentally to be smaller than 1% [15], which can be ignored. With the above condition, the band structure of the FCC $Ni_{1-x}Ru_x$ alloy ($0 < x < 0.2$) is calculated in ferromagnetic and paramagnetic states.

3. Results and discussion

Figure 1 shows the average magnetic moment as a function of the Ru concentration. The full line and open squares show the value obtained by experiment [3] and calculation, respectively. The experimental value shows the drastic decrease in magnetic moment on Ru addition. Our calculation shows the agreement with this experiment qualitatively.

Figure 2 shows the local magnetic moment as a function of the Ru concentration obtained by this calculation. The full and open circles are the magnetic moments of the Ni and Ru sites, respectively. In the low-Ru-concentration region, Ru has a local magnetic moment as large as the magnetic moment of pure Ni. By neutron scattering techniques it is experimentally shown that the Ru impurity in Ni has a magnetic moment of 0.6 μ_B [16]. The value is in good agreement with our calculation.

Figure 3 shows the calculated density of states (DOS) of $Ni_{98}Ru_2$. The majority and minority spins at the Ru site are split even though 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.

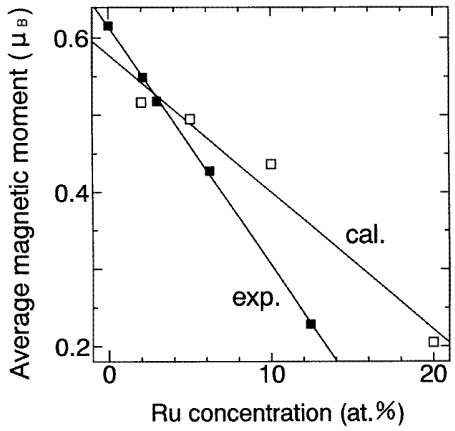

Figure 1. The average magnetic moment at various Ru concentrations. The full and open squares show the value obtained by experiment and calculation, respectively.

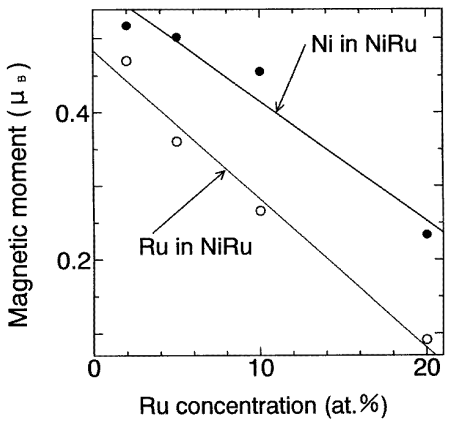

Figure 2. The local magnetic moment at various Ru concentrations obtained by this calculation. The full and open circles are the magnetic moments of the Ni and Ru sites, respectively.

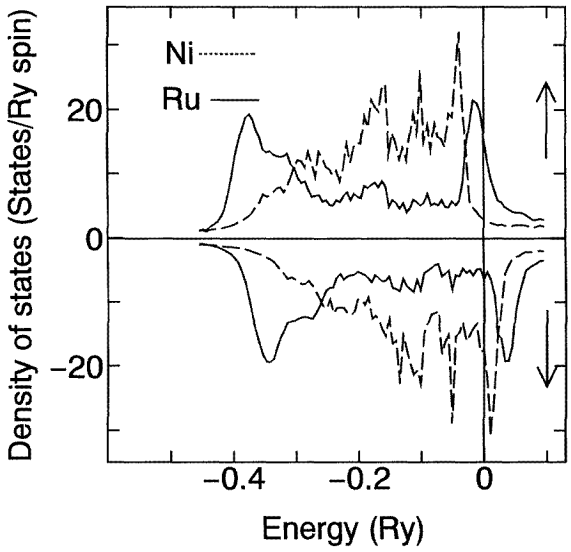

Figure 3. DOS of Ni–Ru with a Ru concentration of 2 at.%. The solid curve shows the DOS at the Ru site and the broken curve shows the DOS at the Ni site.

Figures 4 and 5 shows the DOS calculated in the paramagnetic state of $Ni_{98}Ru_2$ and $Ni_{90}Ru_{10}$, respectively. It is well known that the elements have the tendency to become ferromagnetic [17], if the Fermi energy is on the peak of the paramagnetic DOS. Ni and Ru have Fermi energies at the edge of the DOS, and the DOS at the Fermi energy is very large. The value of the DOS at the Fermi energy is as large as that of Ru in $Fe_{98}Fu_2$ [2]. It seems that the spin splitting of the Ru site is caused by the d–d hybridization [18] between Ni and Ru.

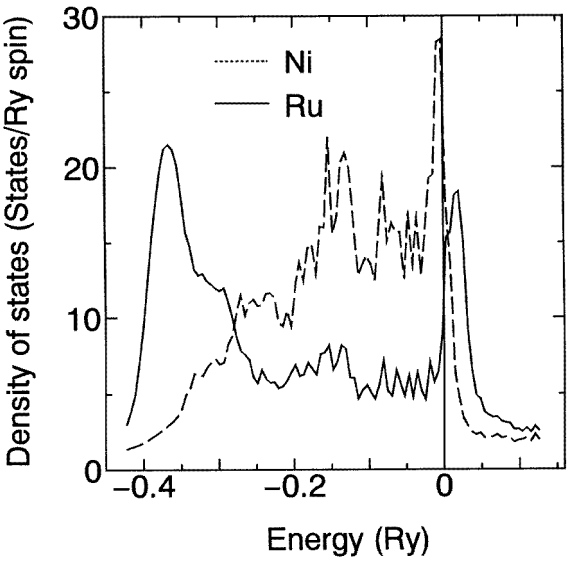

Figure 4. DOS calculated in a paramagnetic state of $Ni_{98}Ru_2$. The solid curve shows the DOS at the Ru site and the broken curve shows the DOS at the Ni site.

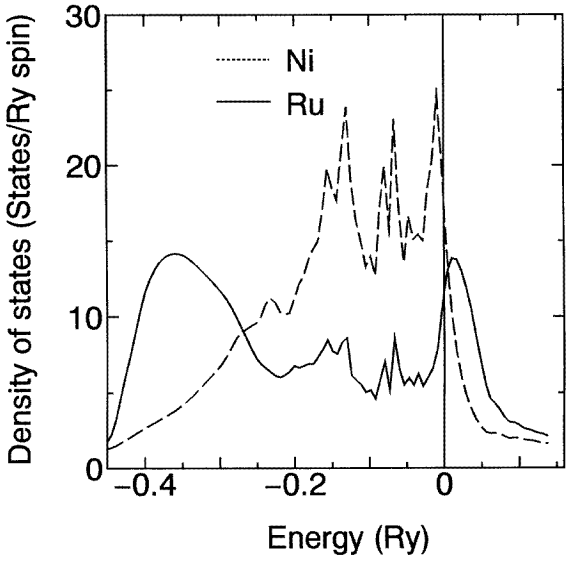

Figure 5. DOS calculated in a paramagnetic state of $Ni_{90}Ru_{10}$. The solid curve shows the DOS at the Ru site and the broken curve shows the DOS at the Ni site.

The increase in Ru concentration causes the decrease in the peak of DOS near the Fermi energy at a Ni site, which is different from the Fe–Ru alloy system [2]. The difference in the Ru concentration dependence of the d–d hybridization can be understood from the crystal structure. The previous work showed that BCC Ru is nearly ferromagnetic and FCC Ru is non-magnetic. So, the Ru in the BCC structure easily becomes ferromagnetic. The

Fermi energy of Ru in the FCC structure moves from the peak, although the ferromagnetic environment induces spin splitting in Ru in the diluted alloy. Figure 6 shows the DOS at the Fermi energy as a function of Ru concentration. The circle and square show the values for Fe in Fe–Ru and for Ni in Ni–Ru, respectively. As the Ru concentration increases, the DOS at the Fermi energy of the Fe site in Fe–Ru increases, although the Fermi energy at the Ni site in Ni–Ru decreases. This leads to an enhancement in the magnetic moment at the Fe site in Fe–Ru and a diminution at the Ni site in Ni–Ru.

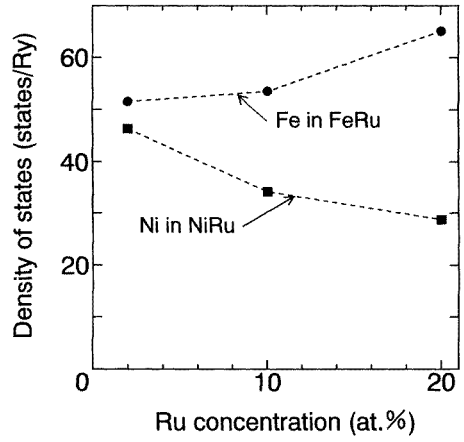

Figure 6. The DOS at the Fermi energy at various Ru concentrations: The circle and square show the values for Fe in FeRu and for Ni in NiRu, respectively.

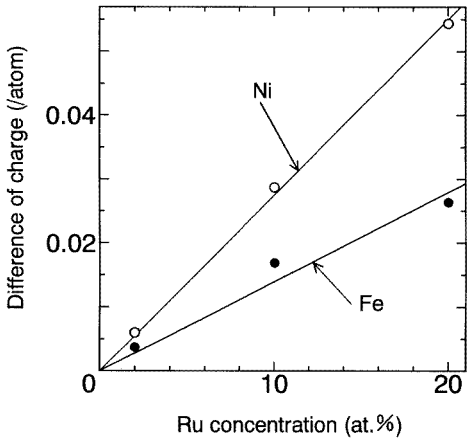

Figure 7. The charge transferred from Ru to the Fe and Ni sites. The full and open circles show the Fe and Ni sites, respectively.

It could be thought that the decrease in DOS at the Fermi energy is partly due to the charge transfer. Figure 7 shows the charge transferred from Ru to the Fe or Ni site. As the Ru concentration increases, the charge at the Ni site increases. In the DOS of Ni calculated

in the paramagnetic state, the Fermi energy is on the edge of the DOS. An increase in the charge of the Ni site causes a decrease in the DOS at the Fermi energy.

4. Conclusions

The first-principle KKR CPA calculation clarifies the reason why the Ru addition to Ni causes the average magnetic moment to decrease, although the Ru addition to Fe scarcely reduces the average magnetic moment. The local magnetic moment of Ru has a non-zero value of about 0.6 μ_B in the low-Ru-concentration region of Ni–Ru owing to the ferromagnetic environment. However, the moment of Ru decreases as the Ru concentration increases. The local magnetic moment of Ni decreases on Ru addition because of the large charge transfer from Ru to Ni. The increase in Ru concentration causes a decrease in the peak of the DOS near the Fermi energy at the Ni site.

Acknowledgments

We would like to thank Professor M Fukuchi for helpful discussions. We acknowledge the kind computing support of the Keio University Computer Centre.

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