

Magnetic Properties and Electronic Structures of (Ru,Fe) and (Rh,Fe) Alloys

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We studied $\text{Ru}_x\text{Fe}_{1-x}$ ($x = 0.30, 0.50,$ and 0.75), $\text{Rh}_{0.75}\text{Fe}_{0.25}$, and $\text{Rh}_{0.25}\text{Fe}_{0.75}$ alloys in order to investigate how the electronic structures and the magnetic properties of those alloys changed depending on the crystallographic structures; *e.g.*, hcp, fcc, and bcc. Magnetization and ac susceptibility measurements showed that $\text{Rh}_{0.25}\text{Fe}_{0.75}$ (bcc) was ferromagnetic even at room temperature while $\text{Rh}_{0.75}\text{Fe}_{0.25}$ (fcc) was weakly antiferromagnetic with $T_N \simeq 80$ K. On the other hand, $\text{Ru}_{0.30}\text{Fe}_{0.70}$ (hcp) was antiferromagnetic below about 130 K while $\text{Ru}_x\text{Fe}_{1-x}$ with $x = 0.50$ and 0.75 (both hcp) remained paramagnetic down to 5 K. From the Fe 3d partial spectra obtained using the Cooper minimum phenomena of the Ru 4d and the Rh 4d bands, we found that the Fe 3d partial spectra were almost the same for all the alloys, regardless of the different structures and the magnetic ground states.

I. INTRODUCTION

The magnetic properties of fcc and hcp Fe have been of some interest because of their potential importance to the understanding of the magnetic properties of the Earth's core. The hcp Fe is stable under the extreme conditions of both high temperature and high pressure and has been theoretically predicted to have magnetic properties different from that of ferromagnetic bcc Fe. On the other hand, fcc Fe is expected to have three possible ground states, depending on the Wigner-Seitz radius (r_{ws}), according to calculations by Moruzzi *et al.* [1]: a paramagnetic state, a high-spin state, and a low spin state. According to another group [2], fcc Fe can have an antiferromagnetic state, too. The latter calculations show an antiferromagnetic state with a total energy, which is very close to that of the ferromagnetic state. The difference between the total energies of a ferromagnetic state and an antiferromagnetic state is only

0.28 eV/Fe-atom.

Unfortunately, however, it is very difficult to study experimentally the magnetic properties of fcc and hcp Fe because the stabilization of these Fe phases requires very extreme experimental conditions, as noted above. Instead, experiments using Fe alloys with the desired fcc and hcp structures have been carried out in order to understand the correlation between the magnetic properties and the structure of Fe. For example, noble metal-Fe alloys with fcc structures, (Ag,Fe), (Au,Fe), and (Cu,Fe), have been studied theoretically, as well as experimentally [3-7]. According to these studies, all noble metal-Fe alloys are ferromagnetic, and the sizes of their magnetic moments are approximately proportional to the Wigner-Seitz radius. In fact, that the magnetic-moment values depend on the Wigner-Seitz radius is consistent with theoretical results [8], which show that the size of the magnetic moments varies with the Wigner-Seitz radius (r_{ws}) for fcc Fe. In this work, we studied (Rh,Fe) and (Ru,Fe) alloys with fcc and hcp structures, respectively, in order to investigate possible relations between the electronic structures and the magnetic properties of fcc and hcp Fe.

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Table 1. Summary of X-ray diffraction results from the samples studied here.

Sample	lattice structure	lattice constants		r_{ws} (Å)
		a (Å)	c (Å)	
Ru _{0.30} Fe _{0.70}	hcp	2.60	4.18	1.429
Ru _{0.50} Fe _{0.50}	hcp	2.60	4.17	1.429
Ru _{0.75} Fe _{0.25}	hcp	2.70	4.27	1.476
	hcp	2.65	4.24	1.455
Rh _{0.25} Fe _{0.75}	bcc	2.94		1.450
Rh _{0.75} Fe _{0.25}	fcc	3.78		1.476

II. EXPERIMENTAL DETAILS

We prepared Ru_xFe_{1-x} with $x = 0.30, 0.50,$ and 0.75 and Rh_yFe_{1-y} with $y = 0.25$ and 0.75 . All the samples were made by arc-melting high purity components under an argon atmosphere and subsequently annealing them at 1000 °C for 5 days in vacuum. After annealing, we took the samples from the furnace and left them to cool in air. In the case of Rh_{0.25}Fe_{0.75}, we quenched the sample from 1000 °C by dipping it into liquid nitrogen to avoid the formation of the α' phase, which is stable at low temperatures according to the published phase diagram for Fe-Ru [9].

We measured the X-ray diffraction (XRD) from all the samples. From the XRD results, we found that all the (Ru,Fe) alloys formed in the hcp structure and Rh_{0.75}Fe_{0.25} in the fcc structure. That our Ru_{0.30}Fe_{0.70} was found to be a single phase with a hcp structure reinforced our view [10] that the phase boundary between the mixed phase and the Ru solid-solution phase was steeper than in the published phase diagram [9]. However, Rh_{0.25}Fe_{0.75} turned out to have a bcc structure after quenching although it was expected to form in a fcc structure according to the Fe-Rh binary phase diagram [9]. It was found that the major phase of Ru_{0.75}Fe_{0.25} formed in a hcp structure ($r_{ws}=1.476$ Å), but it contained a small amount of another hcp phase with a slightly smaller lattice constant ($r_{ws}=1.455$ Å). We estimated that the second phase was about 28 % of the total volume.

Considering the published phase diagram of Fe-Ru [9], we cannot think of any possible reason for the phase problem with Ru_{0.75}Fe_{0.25}. According to the phase diagram, this composition is well inside the stable hcp phase. Nevertheless, we do not think that the second-phase problem of Ru_{0.75}Fe_{0.25} is critical to our discussion in the paper because the second phase also formed in the same hcp structure. Thus, our aim of studying the effects of structure on the electronic structure and the magnetic properties of the alloys is still well served with the alloy. All our XRD results are summarized in Table 1.

Photoelectron spectroscopy (PES) experiments were performed using the 2B1 VUV beamline of the Pohang

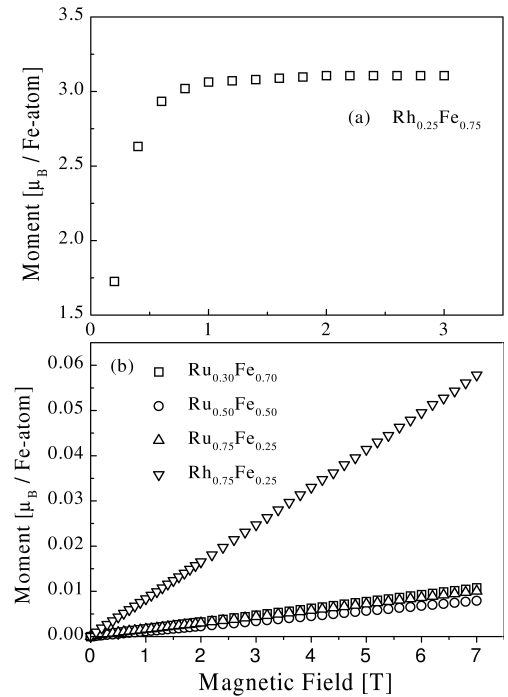


Fig. 1. Field dependence of the magnetic moment of (a) bcc Rh_{0.25}Fe_{0.75} at room temperature, and (b) fcc Rh_{0.75}Fe_{0.25} and three hcp (Ru,Fe) samples at 5 K.

Light Source, Korea. The pressure inside the experimental chamber was monitored throughout the whole experiment and found to be in the low 10^{-10} Torr region. Sample surfaces were cleaned by scraping with diamond file *in situ*. Photon energies used here were in the range of 100 ~ 200 eV. The overall resolution of the photoemission experiment was about 0.3 eV. In order to obtain the Fe 3d partial spectra of the alloys, we took advantage of the Cooper minimum phenomena of the Ru and the Rh 4d bands. (The Cooper minimum phenomenon refers to the large reductions in the photoionization cross sections of 4d or 5d transition metals at some specific photon energy.)

In order to study the magnetic properties, we used a commercial magnetometer equipped with a 9 T superconducting magnet (PPMS9, Quantum Design). The magnetization measurements were performed at 5 K and room temperature with increasing magnetic field. The ac susceptibilities were measured as functions of temperature from 5 to 300 K with a 4 Oe and 150 Hz driving field.

III. EXPERIMENTAL DATA AND ANALYSIS

We present the magnetization data in Figs. 1(a) and (b). The Rh_{0.25}Fe_{0.75} with a bcc structure shows a rapid saturation behavior in the magnetization, indicating that it is already ferromagnetic at room temperature. The

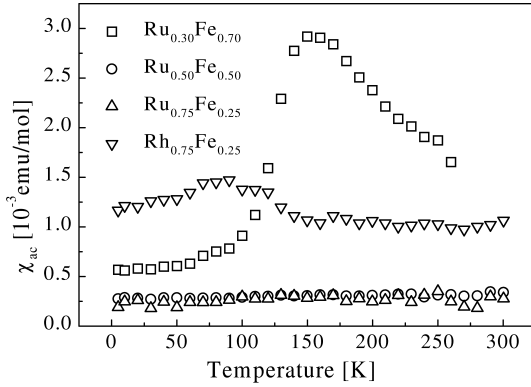


Fig. 2. ac susceptibility data of fcc $\text{Rh}_{0.75}\text{Fe}_{0.25}$ and three hcp (Ru,Fe) alloys as functions of temperature.

value of its saturation magnetic moment is $3.1 \mu_B/\text{Fe-atom}$, *i.e.*, $2.33 \mu_B/\text{f.u.}$, which is very close to the theoretical prediction of $2.38 \mu_B/\text{f.u.}$ [11]. On the other hand, all other samples show a linear increase in the magnetization with field, indicative of either paramagnetic or antiferromagnetic states down to 5 K (see Fig. 1(b)). It is noticeable that $\text{Rh}_{0.75}\text{Fe}_{0.25}$ has a slightly larger field dependence and, thus, a bigger susceptibility value. Figure 2 shows the ac susceptibilities for three hcp (Ru,Fe) alloys and fcc $\text{Rh}_{0.75}\text{Fe}_{0.25}$ as functions of temperature. That the susceptibilities of $\text{Ru}_{0.50}\text{Fe}_{0.50}$ and $\text{Ru}_{0.75}\text{Fe}_{0.25}$ are virtually temperature independent indicates that they are Pauli paramagnetic. However, the susceptibility of $\text{Ru}_{0.30}\text{Fe}_{0.70}$ shows a typical antiferromagnetic behavior, and its Néel temperature is about 130 K. In the case of $\text{Rh}_{0.75}\text{Fe}_{0.25}$, there is a very broad hump at around 80 K, suggesting that it is very weakly antiferromagnetic. Interestingly enough, according to Ref. 11, bcc $\text{Rh}_x\text{Fe}_{1-x}$ alloys are expected to be ferromagnetic up to $x = 0.50$ while all fcc $\text{Rh}_x\text{Fe}_{1-x}$ alloys are paramagnetic, which is, in fact, what we have found in our (Rh,Fe) samples except for the fact that $\text{Rh}_{0.75}\text{Fe}_{0.25}$ is very weakly antiferromagnetic, not Pauli paramagnetic.

In connection to our magnetization studies, it is worthwhile to compare our data with previously published results on similar systems. Unlike Ohno [12], we found that Fe of a fcc structure is more magnetic than Fe of an hcp structure. Experimental evidence may be found in the fact that the (Ru,Fe) samples with 25 and 50 % Fe are paramagnetic down to 5 K while $\text{Rh}_{0.75}\text{Fe}_{0.25}$ appears to have an antiferromagnetic transition around 80 K. Another piece of experimental evidence is in fact that the magnetization value at 5 K is larger for the Rh alloy than for the Ru alloys. The other difference between our data and Ohno's is that our $\text{Ru}_{0.30}\text{Fe}_{0.70}$ clearly shows an antiferromagnetic transition at 130 K in the ac susceptibility while Ohno's susceptibility data are almost temperature independent although his Mössbauer data show a weak sign of an antiferromagnetic transition below 100 K. Having seen how weak the magnetic signal is in our data taken with a state-of-the-art machine, we are

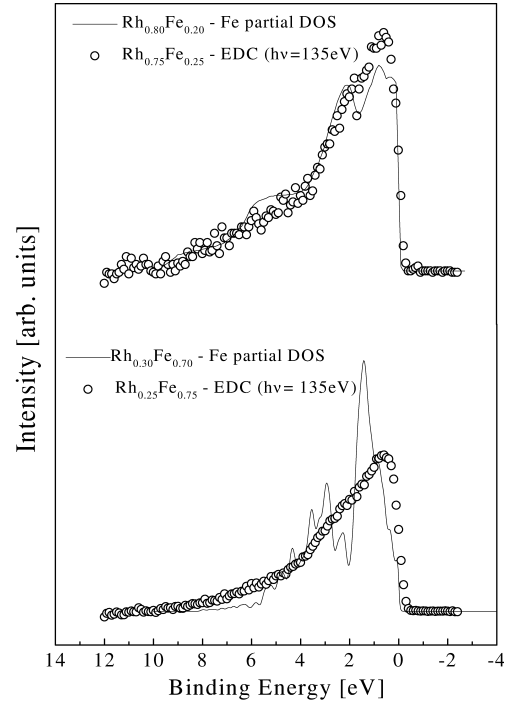


Fig. 3. Fe $3d$ partial DOS was obtained at the experimentally determined Cooper minimum of the Rh $4d$ bands. The line in the upper panel is for the theoretical DOS of paramagnetic fcc $\text{Rh}_{0.80}\text{Fe}_{0.20}$, taken from Ref. 11. The line in the lower panel is the result of our calculations for ferromagnetic bcc $\text{Rh}_{0.25}\text{Fe}_{0.75}$ (see the text).

not surprised that his susceptibility looked temperature independent.

All PES spectra were normalized by using a mesh current, which was proportional to the incident photon flux. Subsequently the inelastic background was removed by using the Shirley method [13]. As the photon energy increased, we found that the intensity at the Fermi level decreased with respect to that at high binding energy and that the intensity ratio had a maximum at 135 eV. According to the theoretical photoionization cross sections for Fe, Ru, and Rh atoms calculated by Yeh and Lindau [14], this maximum is at about 110 eV. This kind of shift in the Cooper minimum energy is due to the solid-state effect: that is, the experimental PES results are taken from alloy samples while Lindau's theoretical results are for isolated atoms. A similar phenomenon was previously observed in the PES experiments on (Cu,Pd) alloy systems [15]. Thus, we conclude that the spectra at the Fermi edge taken with a photon energy of 135 eV are predominantly from the Fe $3d$ band.

In Fig. 3, the Fe $3d$ partial spectra obtained using the Cooper minimum are compared with the theoretical Fe $3d$ partial density of states (DOS) of $\text{Rh}_{0.80}\text{Fe}_{0.20}$ given in Ref. 11. We have also carried out first-principles band calculations for $\text{Rh}_{0.25}\text{Fe}_{0.75}$ [16]. In our calculations, we used a precise all-electron FLAPW (full-potential lin-

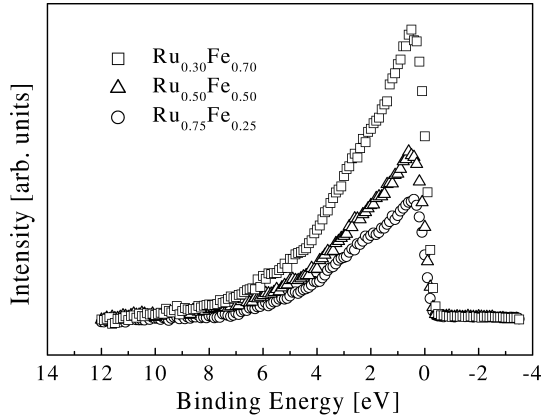


Fig. 4. Fe 3d partial DOS of hcp (Ru,Fe) alloys taken at the experimentally determined Cooper minimum of the Ru 4d bands.

earized augmented plane wave) method [17] based on the local spin-density approximation [18]. Note that the calculations have been made for a paramagnetic fcc structure in the case of $\text{Rh}_{0.80}\text{Fe}_{0.20}$ and for a ferromagnetic bcc structure in the case of $\text{Rh}_{0.25}\text{Fe}_{0.75}$, in accord with our experimental findings. The experimental Fe partial DOS for the fcc $\text{Rh}_{0.75}\text{Fe}_{0.25}$ is very similar to the theoretical DOS whereas in the case of the bcc $\text{Rh}_{0.25}\text{Fe}_{0.75}$, some discrepancy exists between the experimental and the theoretical values of the DOS. The experimental data show a clearly enhanced density of states near the Fermi level compared with the theoretical results. This discrepancy between the experimental results and the theoretical calculations for the bcc $\text{Rh}_{0.25}\text{Fe}_{0.75}$ is noteworthy. (Although the actual interpretation of the PES results would require careful considerations of the matrix elements, many body effects, convolution with the experimental resolution, *etc.*, PES does usually reflect the dominant features of the DOS.) It is also interesting to note that within our experimental errors, the experimental Fe 3d partial DOS is more or less the same for both samples. Related to this, we should note that $\text{Rh}_{0.25}\text{Fe}_{0.75}$ is already ferromagnetic at room temperature. The width (FWHM) of the 3d DOS is about 3.1 eV.

The Fe 3d partial spectra of (Ru,Fe) alloys were also obtained at an incident energy of 135 eV, as described before. The results are given in Fig. 4. It is interesting to note that the three spectra look quite similar; in fact, once the spectra are normalized to appropriate Fe concentrations, they all collapse onto one curve. Thus, the only difference in the spectra results mainly from the Fe concentrations of the samples. What is more surprising is that the three spectra are also quite similar to those of the (Rh,Fe) alloys (see Fig. 3). If we normalize the spectra by Fe concentrations, the five spectra become very similar. Thus, the Fe 3d partial spectra of the samples studied here do not seem to change, despite the fact that the (Ru,Fe) and the (Rh,Fe) samples form in three different structures, bcc, fcc, and hcp. How-

Table 2. Summary of the physical properties of fcc Fe-noble metal alloys and $\text{Rh}_{0.75}\text{Fe}_{0.25}$. Data are taken from Ref. 3 ($\text{Cu}_{0.70}\text{Fe}_{0.30}$), Ref. 4 ($\text{Ag}_{0.60}\text{Fe}_{0.40}$ and $\text{Ag}_{0.80}\text{Fe}_{0.20}$), and Ref. 5 ((Au,Fe) alloys). $\text{Rh}_{0.75}\text{Fe}_{0.25}$ has $T_N=80$ K.

Sample	r_{ws} (Å)	magnetic moment ($\mu_B/\text{Fe atom}$)	T_c (K)
$\text{Cu}_{0.70}\text{Fe}_{0.30}$	1.418	1.4	200
$\text{Ag}_{0.60}\text{Fe}_{0.40}$	1.582	2.5	600
$\text{Ag}_{0.80}\text{Fe}_{0.20}$	1.582	2.5	250
(Au,Fe)	1.566	2.8 ~ 3.0	≤ 300
$\text{Rh}_{0.75}\text{Fe}_{0.25}$	1.476		80

ever, we do not think that these similarities seen in the Fe 3d partial spectra are entirely due to surface effects. To our best knowledge, there is no known surface segregation problem with scraping the samples. That all our samples form in a wide solid-solution region of the phase diagram [9] also rules out possible surface problems. Furthermore, our Fe 3d partial DOS for all five samples scale well with nominal Fe concentrations.

A surprising and very puzzling finding in our data is an apparent discrepancy between the magnetization and the photoemission data. Despite all the alloys of the bcc, the fcc, and the hcp structures showing different magnetic ground states, we have not succeeded in finding any significant difference between the Fe 3d partial DOS of all the samples. Instead, they seem to be quite similar to one another. In this connection, we would like to point out that although fcc $\text{Rh}_{0.75}\text{Fe}_{0.25}$ has a larger r_{ws} ($=1.476$ Å) than fcc $\text{Cu}_{0.70}\text{Fe}_{0.30}$, the former is only weakly antiferromagnetic while the latter is ferromagnetic with $T_c=200$ K. This is an unexpected result since the Wigner-Seitz radius has been theoretically regarded as the single most important parameter in determining the magnetic ground state of Fe alloys [1,2]. This theoretical view seems to be consistent with magnetic moment behaviors in other Fe alloys with noble metals (see Table 2). However, our results for $\text{Rh}_{0.75}\text{Fe}_{0.25}$ are an exception. Our data, therefore, imply that in order to understand the moment formation of Fe in (Rh,Fe) alloys, we need to go beyond a simple band picture. One obvious correction to a simple band picture would be to take into account probable hybridization effects between Fe 3d bands and Rh 4d bands. Thus, we suggest that Fe 3d hybridizes more strongly with Rh 4d bands than with the 3d bands of the noble metals. This proposition is consistent with the relative position of the d bands with respect to the Fermi level: the d bands of noble metals are located farther below the Fermi level than the d bands of Rh, hence farther away from the Fe 3d bands. In a systematic study of the electronic structures of noble metal-Pd alloys systems, it was found that the hybridization between constituent atoms becomes stronger when their relative energy positions are closer [19].

Regarding the structural effect on the magnetism of

Fe, it is worth noting the following two points. Firstly, $\text{Ru}_{0.30}\text{Fe}_{0.70}$ (hcp) is antiferromagnetic while $\text{Rh}_{0.25}\text{Fe}_{0.75}$ (bcc) is ferromagnetic. Secondly, $\text{Rh}_{0.75}\text{Fe}_{0.25}$ (fcc) is weakly antiferromagnetic whereas $\text{Ru}_{0.75}\text{Fe}_{0.25}$ (hcp) is paramagnetic down to 5 K. Closely related to this is the observation that all the samples have similar values for r_{ws} . Therefore, we think that the differences in the magnetic properties are mainly due to structural effects, as theoretically predicted. On the other hand, there is very little structure effect on the experimental electronic structures of Fe 3d partial DOS, unlike theoretical band calculations. Although we admit that photoelectron spectroscopy is sensitive to the surface, especially in the energy range we studied, we do not think that the similarities seen in our Fe 3d partial spectra are entirely due to surface states. We acknowledge that it is very difficult to understand the absence of strong structure effects in the experimental Fe 3d DOS at the moment. However, from our data, we can say that in order to understand the magnetic moment formation in the (Ru,Fe) and the (Rh,Fe) alloys, we need to go beyond a simple band picture. One obvious correction term to the simple band picture would be a term describing the hybridization between the Fe 3d bands and the 4d bands of Ru and Rh.

In summary, we have found that in the (Ru,Fe) and the (Rh,Fe) alloys, there is a clear structure effect on the moment formation of Fe, as seen in the magnetization and the susceptibility measurements. However, what is surprising and puzzling is that our experimentally obtained Fe 3d partial DOS does not agree with the results of theoretical band calculations.

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