Competition of magnetism in iron Laves phase compounds

Competition of magnetism in iron Laves phase compounds

S Asano† and S Ishida‡

† Institute of Physics, College of Arts and Science, University of Tokyo, Meguro-ku, Tokyo 153, Japan
‡ Department of Physics, Faculty of Science, Kagoshima University, Kagoshima 890, Japan

Abstract. To investigate the varied magnetism of Fe Laves phase compounds, the electronic structures were calculated by the LMTO method within the framework of the local-spin-density approximation. Calculating the total energy as a function of the lattice constant and the magnetic moment, we found that two types of ferromagnetism, antiferromagnetism and paramagnetism compete with each other in the $(Sc_{1-x}Ti_x)Fe_2$ and $(Zr_{1-x}Nb_x)Fe_2$ systems. The lattice constant or the concentration x is an important factor in the appearance of these different types of magnetism. The difference between the two types of ferromagnetism is clearly seen in the density of states. One of them is weakly itinerant ferromagnetism.

1. Introduction

In order to investigate the magnetic properties of Laves phase compounds, we calculate the electronic structures by the KKR method within the framework of the local-spin-density (LSD) approximation (Ishida and Asano 1985, Ishida *et al* 1985a, b). It was found that the magnetism can be approximated by the rigid-band model. Furthermore, to investigate the relation between the magnetism and the crystal structure, the total energy was systematically calculated by the LMTO method for the various magnetic states in the hexagonal C14 and the cubic C15 structure (Asano and Ishida 1987, 1988). The results show that the theoretical predictions for the magnetism and the crystal structure are in good agreement with the experimental results. For the Laves phase compounds AB_2 between transition metals, the crystal structure is determined by the B atom; the stable structure is the C15 structure when the B atom is Cr, Co or Ni (Mo, Rh or Pd) and the C14 structure when the B atom is Mn or Fe (Tc or Ru). When this rule does not apply to the compound, the magnetism of the compound is related to the crystal structure. For the Fe Laves phase compound AFe_2, it has also been shown that, when the number of the valence electrons of the A atom increases, the lattice spacing decreases and the magnetism becomes weak. For $TiFe_2$ and $NbFe_2$ the stable states are the anti-ferromagnetic state and the paramagnetic state, respectively, and the other magnetic states are almost degenerate in energy. Therefore, it is expected that the magnetic states of $TiFe_2$ and $NbFe_2$ are sensitive to experimental conditions such as composition and temperature and that these states can be of various types.

In fact, various types of magnetism have been observed under different experimental conditions. $ScFe_2$ exhibits ferromagnetism, and $TiFe_2$ antiferromagnetism. In the $(Sc_{1-x}Ti_x)Fe_2$ system, two ferromagnetic states with different degrees of localisation were observed for $0.3 < x < 0.7$ and a coexistent state of ferromagnetism and antiferromagnetism appears for $x > 0.7$ (Nishihara and Yamaguchi 1984, 1985). The $(Zr_{1-x}Nb_x)Fe_2$ system is ferromagnetic for $x < 0.4$ in the C15 structure, antiferromagnetic for $0.4 < x < 0.8$ and weakly ferromagnetic for $0.8 < x < 1.0$ in the C14 structure (Nakamura and Shiga 1980, Yamada *et al* 1984a, b). In the $Ti_{1-x}Fe_{2+x}$ system, two types of ferromagnetism are induced when the composition deviates from stoichiometry towards Fe-rich or Fe-deficient compounds (Shiga and Nakamura 1987).

In this paper, we consider two types of Fe Laves phase compound: the C14 hexagonal Laves compound and the C15 cubic compound. Although the latter has one kind of Fe atom, the former has two kinds of Fe atom: Fe(2a) atoms at 2a sites with symmetry $\bar{3}m$ and Fe(6h) atoms at 6h sites with symmetry mm (Ishida *et al* 1985a). The electronic structures of $TiFe_2$, $NbFe_2$, YFe_2 and $ZrFe_2$ are calculated to investigate the competition between the various magnetic states. From the total energy for the various magnetic states, we can see how they compete in the Fe Laves phase compounds.

2. Method

The band calculations were carried out by the LMTO method within the framework of the LSD approximation (Andersen *et al* 1985, Janak *et al* 1975). The crystal potentials were assumed to be spherical in the atomic sphere. The radius ratio of each atomic sphere was chosen to be $r_A/r_B = 1.255$. For the hexagonal C14 structure, the c/a ratio was assumed to be $2\sqrt{2}/\sqrt{3}$ and the lattice constant is calculated as that of the C15 structure with the same volume. The maximum angular momenta to describe the wavefunctions were chosen as $l_{max} = 3$ for the A atom and $l_{max} = 2$ for the B atom. Although the frozen-core approximation was used in the previous calculations (Asano and Ishida 1987, 1988), self-consistent iteration was carried out for both core and valence states in this calculation. As the wavefunctions outside the atomic sphere are described by the Hankel function of the first kind, it seems that the repulsion force between electrons is overestimated for the core states. Hence, the lattice spacing widens and it becomes easier for the compound to carry magnetic moments. Therefore, there is a tendency that the total energy for the magnetic state is lower than the real value in this calculation. For instance, although the paramagnetic state is the most stable in $NbFe_2$ using the frozen-core approximation, the antiferromagnetic state becomes stable in this calculation, as seen later.

The calculations were carried out as follows. First, we calculated self-consistently the total energy as a function of the lattice constant and determined the lattice constant of the stable state so as to minimise the total energy (Asano and Ishida 1988). We denote the potentials obtained for a given lattice constant as $V_\uparrow$ and $V_\downarrow$ for the majority and the minority spin. Next, in order to calculate the magnetic moment dependence of the total energy, we estimated the initial potentials using the parameter α as follows:

$$V_{in}^\uparrow = (V_\uparrow + V_\downarrow)/2 + \alpha(V_\uparrow - V_\downarrow)/2$$
$$V_{in}^\downarrow = (V_\uparrow + V_\downarrow)/2 - \alpha(V_\uparrow - V_\downarrow)/2.$$

By carrying out the self-consistent iteration for some α, we could obtain the magnetic
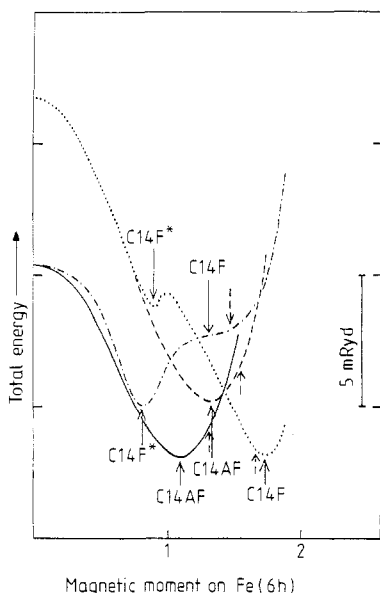
Figure 1. The total energy of $TiFe_2$ as a function of the magnetic moment on Fe(6h) for ferromagnetic and antiferromagnetic states in the C14 structure with lattice constants of 6.7 Å (— · —, ——) and 6.8 Å (· · · · ·, ---). The two minima for the ferromagnetic state are labelled C14F and C14F*. The broken arrows correspond to the stable state determined by only the lattice constant dependence of the total energy.
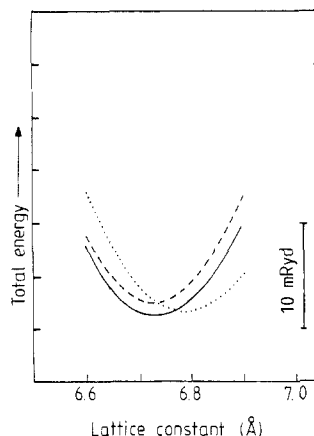
Figure 2. The total energy of $TiFe_2$ as a function of the lattice constant: · · · · ·, C14F; ---, C14F*; ——, C14AF. This is obtained from the minima in figure 1.

moments and the total energies, i.e. the magnetic moment dependence of the total energy.

3. Results and discussion

3.1. TiFe₂

In the $(Sc_{1-x}Ti_x)Fe_2$ system, the compounds exhibit ferromagnetism with the magnetic moment $0.9\mu_B$ per Fe atom for $0 < x < 0.3$ and antiferromagnetism for $0.8 < x$. Furthermore, a strange magnetic behaviour was observed: two types of ferromagnetism and a coexistent state of ferromagnetism and antiferromagnetism (Nishihara 1987). One type of ferromagnetism has a magnetic moment of $(1.2–1.3)\mu_B$ per Fe atom at low temperatures and the other a magnetic moment of $0.9\mu_B$ per Fe atom at high temperatures. These moments were determined from the hyperfine fields without considering the difference between the moments of Fe(6h) and Fe(2a). The lattice spacing of the compounds decreases with increasing x.

In figure 1 the total energy is shown as a function of the magnetic moment on Fe(6h) for the ferromagnetic and the antiferromagnetic states (denoted C14F and C14AF, respectively) in the C14 structure with a lattice constant of 6.7 or 6.8 Å. While there is one minimum for the antiferromagnetic state, there are two minima for the ferro-
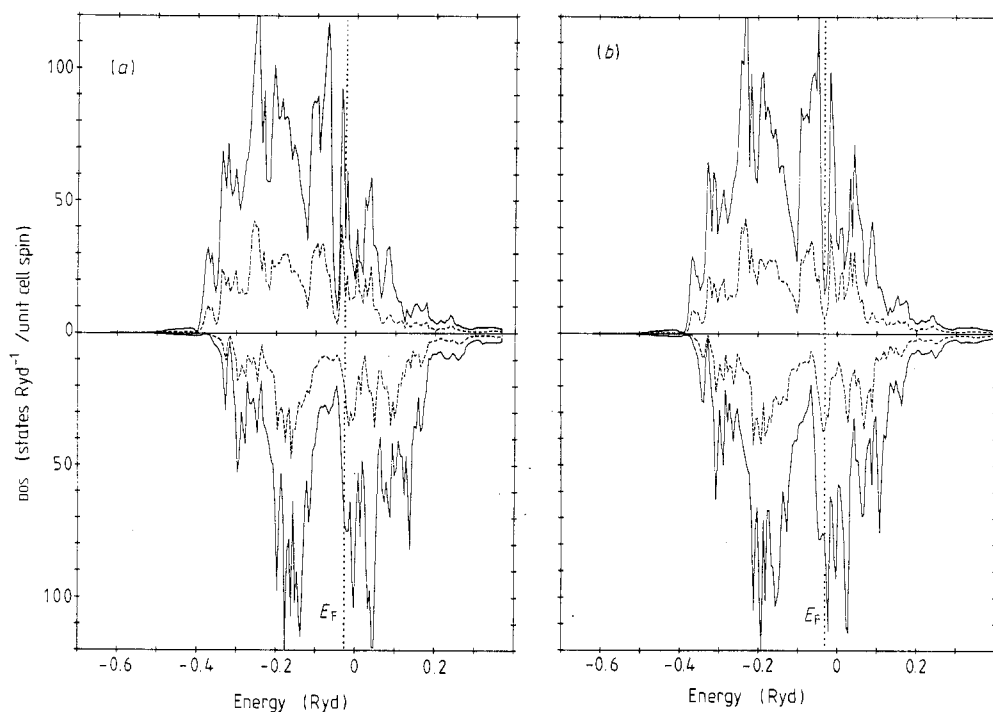
Figure 3. The DOS of the d bands for (a) the C14F state and (b) the C14F* state: ———, Fe(6h); ---, Fe(2a).

magnetic state. The energy at the minima is plotted against the lattice constant in figure 2. The ferromagnetic states with the larger and the smaller magnetic moments are denoted C14F and C14F*, respectively. As we showed the electronic structure for the antiferromagnetic state in our previous paper (Asano and Ishida 1988), it is not given here. However, we should comment on the previous result. The magnetic moment was calculated to be $1.42\mu_B$ per Fe(6h) atom considering only the lattice constant dependence of the total energy. However, to determine the magnetic moment of the truly stable state, we should consider not only the lattice constant dependence but also the magnetic moment dependence of the total energy. The moment was determined to be $1.07\mu_B$ per Fe(6h) atom. Fe(2a) in the antiferromagnetic state does not have a magnetic moment owing to the crystal symmetry.

The density of states (DOS) is shown for C14F and the C14F* in figures 3(a) and 3(b) where the DOSs of the d state of Fe(6h) and Fe(2a) are shown by the solid and the broken curves, respectively. The difference between the two ferromagnetic states is clearly seen in these figures. Although the DOSs are similar to each other for the C14F and the C14F* states, the positions of the Fermi level are different. The peak of the DOS in the majority spin just below 0 Ryd is occupied for the C14F state but unoccupied for the C14F* state. Therefore, the magnetic moments are different; the moments of C14F are $1.4\mu_B$ per Fe(6h) atom and $1.1\mu_B$ per Fe(2a) atom and the moments of C14F* are $0.8\mu_B$ per Fe(6h) atom and $0.4\mu_B$ per Fe(2a) atom for a lattice constant of 6.7 Å; the moments of C14F are $1.7\mu_B$ per Fe(6h) atom and $1.5\mu_B$ per Fe(2a) atom and the moments of C14F* are $0.9\mu_B$ per Fe(6h) atom and $0.3\mu_B$ per Fe(2a) atom for a lattice

constant of 6.8 Å. The C14 and the C14F* states correspond to the two types of ferromagnetism observed in the experiments. From figures 1 and 2, we can see that the three states C14F, C14F* and C14AF compete with each other and that, although the C14AF state is stable when the lattice constant is small, the C14F state becomes stable when the lattice constant increases. The correspondence between the theoretical and the experimental results is qualitatively good considering the difference between Ti and $Sc_{1-x}Ti_x$ as the A atom in AFe_2. When the lattice spacing decreases or the concentration x increases in $(Sc_{1-x}Ti_x)Fe_2$, the magnetism changes in the following order: ferromagnetism (C14F), two types of ferromagnetism (C14F and C14F*), coexistence of ferromagnetism and antiferromagnetism (C14F* and C14AF) and antiferromagnetism (C14AF).

3.2. NbFe₂

$NbFe_2$ is a strongly enhanced Pauli paramagnet with the C14 structure (C14P) and $ZrFe_2$ is a ferromagnet with the C15 structure (C15F). In the $(Zr_{1-x}Nb_x)Fe_2$ system, the compounds exhibit ferromagnetism for $0 < x < 0.4$ in the C15 structure, antiferromagnetism for $0.5 < x < 0.7$ and weak ferromagnetism for $0.85 < x < 0.95$ in the C14 structure. Furthermore, a coexistent state of ferromagnetism and antiferromagnetism was observed at around $x = 0.8$. The weak ferromagnetism is an itinerant electron type and the magnetic moment is about $0.1\mu_B$ per Fe atom (Yamada and Ohira 1983, Yamada *et al* 1984a, b). In the $Nb_{1-x}Fe_{2+x}$ system for $-0.04 < x < 0.04$, ferromagnetism appears in the C14 structure when the concentration deviates from the stoichiometric compound $TiFe_2$ towards both the Fe-rich and the Fe-deficient compounds (Shiga and Nakamura 1987). The Nb-rich compound is a weakly itinerant ferromagnet. On the contrary, in the Fe-rich compounds the ferromagnetism may be due to the impurity effect of Fe in Nb sites.

In figure 4 the total energy is shown as a function of the lattice constant for various magnetic states. Although the C14P state is the most stable when the frozen-core approximation is used (Asano and Ishida 1987, 1988), the C14AF state becomes the most stable in this calculation. Recently Yamada and Sakata (1988) reported that $NbFe_2$ is a weak antiferromagnet. There is a general tendency that the total energy for the C15F state becomes lower than the true value when we use the LSD approximation. In figure 5 the total energy is shown as a function of the magnetic moment on Fe(6h) for the C14F, C14F* and C14AF states. The total energy curve for the ferromagnetic state has two minima as for $TiFe_2$, which correspond to the C14F and the C14F* states with the larger and the smaller magnetic moments. Although the antiferromagnetic state is more stable than the ferromagnetic state for both lattice constants 6.8 and 6.9 Å, the ferromagnetic state is more stable than the antiferromagnetic state for the smaller magnetic moment. This corresponds to the fact that weak ferromagnetism appears for $0.85 < x < 0.95$ in $(Zr_{1-x}Nb_x)Fe_2$. When the lattice constant increases, the total energy for the C14F state decreases but the C14AF state is still more stable. The ferromagnetic state with the large magnetic moment has not been observed in the C14 structure but in the C15 structure for $(Zr_{1-x}Nb_x)Fe_2$ system. In figure 6 the DOS for the C14F* state is shown; this is similar to that of $TiFe_2$. The DOS for the C14F state is not shown here but it is also similar to that of $TiFe_2$. The magnetic moments are $1.5\mu_B$ per Fe(6h) atom and $1.5\mu_B$ per Fe(2a) atom for the C14F state and $0.3\mu_B$ per Fe(6h) atom and $0.1\mu_B$ per Fe(2a) atom for the C14F* state. This difference between the C14F and the C14F* states comes from the different occupations of the peaks in the energy range $-0.1 < E < 0$ Ryd for the majority spin.
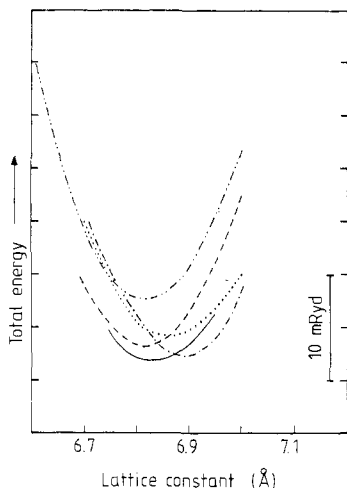
Figure 4. The total energy of NbFe$_2$ as a function of the lattice constant for the paramagnetic (– – –), the ferromagnetic (·····) and the antiferromagnetic (——) states in the C14 structure and the paramagnetic (— · · —) and the ferromagnetic (— · —) states in the C15 structure.
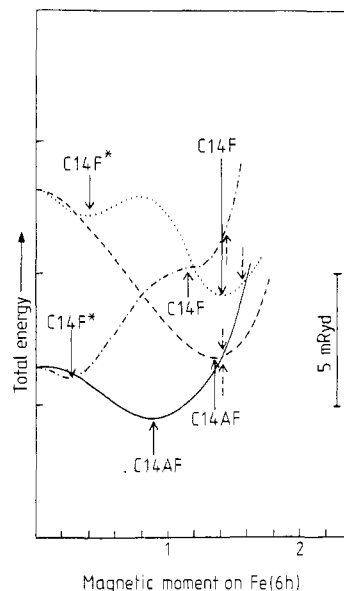
Figure 5. The total energy of NbFe$_2$ as a function of the magnetic moment on Fe(6h), for ferromagnetic and antiferromagnetic states in the C14 structure with lattice constants of 6.8 Å (— · —, ——) and 6.9 Å (· · · ·, – – –). The other symbols are the same as for figure 1.

Although we did not originally find weak ferromagnetism in the work in our previous papers (Asano and Ishida 1987, 1988), by considering the magnetic moment dependence of the total energy here we found that weak ferromagnetism appears in the $(Zr_{1-x}Nb_x)Fe_2$ and $Ti_{1-x}Fe_{2+x}$ systems.

3.3. YFe$_2$ and ZrFe$_2$

YFe$_2$ and ZrFe$_2$ are ferromagnets with the C15 structure (C15F). The total energy for these compounds is shown in figure 7 as a function of the magnetic moment on Fe. These curves for the C15F state have only one minimum in contrast with two minima for the ferromagnetic state in TiFe$_2$ and NbFe$_2$ with the C14 structure. Therefore, we cannot expect the appearance of the weak ferromagnetism seen in the C14 compounds. The stable state determined by only the lattice constant dependence of the total energy is indicated by the broken arrow. The positions of the minima in figure 7 are almost in agreement with the positions indicated by the arrows. On the contrary, in figures 1 and 5, the positions of the broken arrows, which correspond to the stable states obtained by only the lattice constant dependence of the total energy, are different from the positions of the minima. Thus, although the magnetic moments for YFe$_2$ and ZrFe$_2$ determined by only the lattice constant dependence of the total energy have reasonable values, the moments for the C14 compounds must be determined by considering also the magnetic moment dependence.

As described above, the varied magnetic properties of Fe Laves phase compounds are explained well by the total energy and the electronic structures. In particular, we
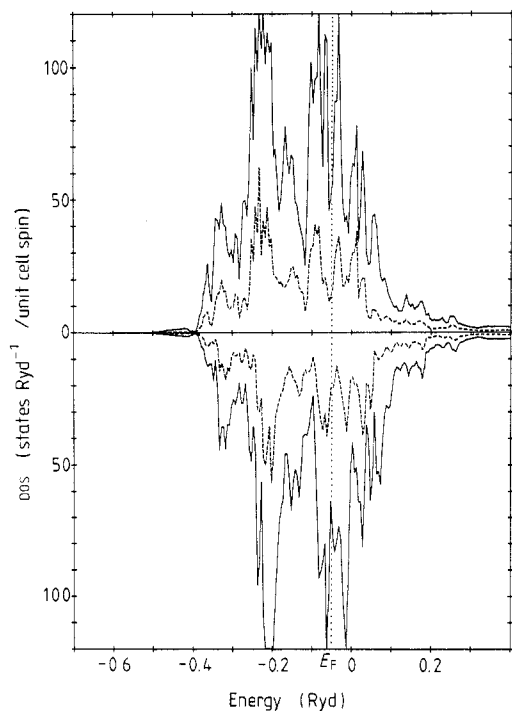
Figure 6. The DOSs of the d bands for the C14F* state of NbFe$_2$: ———, Fe(6h); ---, Fe(2a).
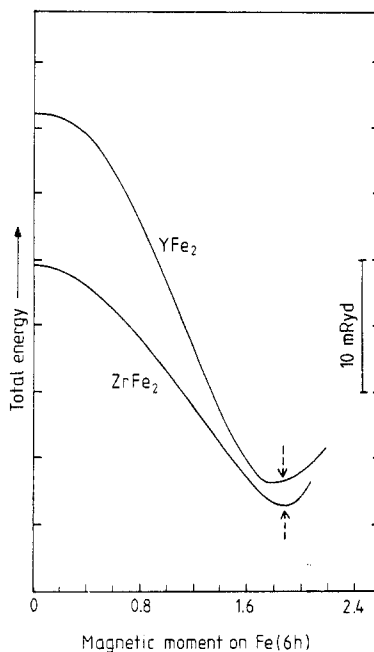
Figure 7. The total energy for YFe$_2$ and ZrFe$_2$ as a function of the magnetic moment on Fe. The total energy is for the ferromagnetic state in the C15 structure. The broken arrows correspond to the stable states determined by only the lattice constant dependence of the total energy.

found in this calculation that the C14F, the C14F* and the C14AF states compete with each other in the (Sc$_{1-x}$Ti$_x$)Fe$_2$ and (Zr$_{1-x}$Nb$_x$)Fe$_2$ systems and cause curious and interesting magnetic properties. It was also found that, to determine the truly stable state theoretically, we should consider not only the lattice constant dependence but also the magnetic moment dependence of the total energy. Weak ferromagnetism (C14F*) was found in the C14 compounds; this had not been found in the previous calculations (Asano and Ishida 1987).

Acknowledgments

References

Andersen O K, Jepsen O and Glotzel D 1985 *Proceedings of the International School of Physics 'Enrico Fermi'* Course 89 (Amsterdam: North Holland) p 59

Asano S and Ishida S 1987 *J. Magn. Magn. Mater.* **70** 39
—— 1988 *J. Phys. F: Met. Phys.* **18** 501
Ishida S and Asano S 1985 *J. Phys. Soc. Japan* **54** 4688
Ishida S, Asano S and Ishida J 1985a *J. Phys. Soc. Japan* **54** 3925
—— 1985b *J. Phys. Soc. Japan* **54** 4695
Janak J F, Moruzzi V L and Williams A R 1975 *Phys. Rev.* B **12** 1757
Nishihara Y 1987 *J. Magn. Magn. Mater.* **70** 75
Nishihara Y and Yamaguchi Y 1984 *J. Phys. Soc. Japan* **53** 2201
—— 1985 *J. Phys. Soc. Japan* **54** 1689
Nakamura Y and Shiga M 1980 *J. Phys. Soc. Japan* **15–18** 629
Shiga M and Nakamura Y 1987 *J. Phys. Soc. Japan* **56** 4040
Yamada Y, Kitaoka Y, Asayama K and Sakata A 1984a *J.Phys. Soc. Japan* **53** 3198
—— 1984b *J. Phys. Soc. Japan* **53** 3634
Yamada Y and Ohira K 1983 *J. Phys. Soc. Japan* **52** 3646
Yamada Y and Sakata A 1988 *J. Phys. Soc. Japan* **57** 46