Structure and Magnetism of Fe(Rh,Pd) Alloys

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First-principle band calculations of ordered 3d and 4d transition-metal alloys FeRh and FePd with the CsCl and CuAu-I type structures are carried out by a linear muffin-tin orbital method within an atomic sphere approximation, where Rh and Pd atoms are treated as virtual 4d-atoms with the atomic number averaged over the concentration. A generalized gradient correction for exchange-correlation potential is taken into account. Total energies for paramagnetic, ferromagnetic and three kinds of antiferromagnetic states are estimated as a function of lattice constants, a and c. Observed lattice constants and spin structures for the present alloys are well described by the present calculations.

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1. Introduction

It is well known that ordered 3d and 4d transition-metal alloys of equiatomic composition show various kinds of magnetic states. For instance, FeRh with the CsCl-type structure is antiferromagnetic at low temperature. At 340 K, a first-order transition takes place from the antiferromagnetic structure is antiferromagnetic at low temperature. At 340 K, a first-order transition takes place from the antiferromagnetic structure to the ferromagnetic one without changing the structure. On the other hand, FePd with the CuAu-I type structure is ferromagnetic. Yuasa et al. have studied the crystalline structures and magnetic properties for pseudobinary alloy FeRh$_{1-x}$Pd$_x$. Substitution of Pd for Rh stabilizes a strongly distorted CsCl type structure with increasing axial ratio $c/a$. In the range $x = 0.53-0.61$, the alloys exhibit a temperature-induced first-order transition from antiferromagnetic to ferromagnetic state, while the alloys with $x < 0.53$ exhibit a first-order transition from antiferromagnetic to paramagnetic state. Both axial ratio and volume increase abruptly at the transitions. A ferromagnetic phase with orthorhombic structure was found in a narrow concentration range around $x = 0.6$.

Band structure calculations for the ordered alloys FeRh and FePd have so far been performed in a local density approximation (LDA). A good agreement with the observed results of the magnetic state and lattice constant was obtained for FeRh. For FePd, however, the calculated total energy in the ferromagnetic state becomes higher than that in the antiferromagnetic one, being incompatible with the observed results. Moreover, the calculated value of the ratio $c/a$ between lattice constants $a$ and $c$ in the ferromagnetic state is far from the observed one. Such a discrepancy between the calculated and observed lattice constants is often obtained when LDA is used combined with a linear muffin-tin orbital (LMTO) method with an atomic sphere approximation (ASA). A generalized gradient approximation (GGA) improves the difference between the calculated and observed lattice constants. Yamada et al. have recently calculated the electronic structures for FeRh, FePd, MnRh and MnPd by using the LMTO-ASA with GGA. They have obtained total energies for some magnetic states as a function of lattice constants, $a$ and $c$. The observed lattice constants and spin structures have been shown to be well described by their calculations.

In this paper, the LMTO-ASA band structure calculations with GGA are performed for ordered FeRh(Pd) alloys, where Rh and Pd are treated as virtual 4d-atoms with the atomic number averaged over the concentration of Rh and Pd. Total energies are calculated as a function of lattice constants, $a$ and $c$, for the non-magnetic (NM), ferromagnetic (FM), and three kinds of antiferromagnetic states (AF1, AF2, AF3), which are shown in Fig. 1. In AF1 the magnetic moments of Fe atoms on the basal $c$-plane are coupled ferromagnetically. Between the nearest neighbor layers, the Fe moments are coupled antiferromagnetically, as shown in Fig. 1(a). In AF2 and AF3, the Fe moments on a basal $c$-plane are coupled antiferromagnetically. Between the nearest neighbor layers Fe atoms are coupled ferromagnetically and antiferromagnetically as shown in Figs. 1(b) and (c), respectively. The antiferromagnetic state of FeRh observed by neutron diffraction measurements is the AF3. In the AF2, 4d atom may have a magnetic moment. The total energies in these five magnetic states are calculated at various values of lattice parameters $a$ and $c$, and the equilibrium values with the lowest energy are obtained as a function of the concentration of Rh and Pd. In §2, the method of our band structure calculations is given. The calculated results are shown in §3. Summary and discussion are given in §4.

2. Method of Band-Structure Calculation

CuAu-I type lattice structure is characterized by two types of unit cell, as illustrated in Fig. 2. One of them is CuAu-I type with lattice parameters $a$ and $c$, which is surrounded by solid lines shown in Fig. 2. Another is a strongly distorted CsCl-type one (bct) with lattice parameters $a^*$ ($=a/2^{1/2}$) and $c$, surrounded by thin lines shown in Fig. 2. When $a^* = c$, this structure is the cubic CsCl-type one. Two ordered structures of the CsCl-type and CuAu-I type can be discussed together, by changing the ratio $c/a^*$ along the Bain path.

Our first-principle band structure calculations are based on the LMTO method with ASA. GGA is used for the exchange-correlation potential. All relativistic effects are included except the spin-orbit interaction. A tetragonal unit cell is used in the present calculations, which contains one Fe atom and one virtual 4d-atom of Rh and Pd. Self-consistent calcula-
tions are carried out at 126 inequivalent \( k \)-points in the irreducible 1/16 Brillouin zone (IBZ) for NM, FM, AF1, and AF3 states, and at 216 \( k \)-points in 1/8 IBZ for AF2 state. These numbers of sampling \( k \)-points are determined so that the total energy is obtained within the difference less than 0.2 \( \times \) \( 10^{-3} \) aJ per formula unit from that obtained at much more large number of sampling \( k \)-points, 726 \( k \)-points, in IBZ (8000 points in the full BZ). The basis set is constructed with angular momenta up to \( l_{\text{max}} = 3 \), \textit{i.e.}, \( spdf \)-linear muffin-tin orbitals.\(^{\text{12}}\) Atomic spheres of Fe and Rh/Pd are taken to be equal to each other. By a simple geometrical consideration, the packing fraction of rigid spheres for the present structure is given by \( (\pi/24)(p^2 + 2)^{3/2}/p \) for \((2/3)^{1/2} < p < 2^{1/2} \), where \( p = c/a^* \). This is always larger than that of the bcc structure, 0.68. Therefore, the ASA used in the calculation is available for the present system.

3. Calculated Results

Total energies are calculated as a function of \( a^* \) and \( c \) in the NM, FM, and three kinds of AF state shown in Fig. 1. For each value of \( c \), a minimum energy with respect to \( a^* \) is estimated. Then, these minimum energies can be plotted as a function of \( c/a^* \). Figures 3(a)–(f) denote the calculated minimum energies for Fe(Rh\(_{1-x}\),Pd\(_x\)) at \( x \) = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0, respectively. The origin of the energy is taken to the lowest energy among the five magnetic states for each \( x \).

Fig. 1  Three kinds of antiferromagnetic spin structures, AF1 (a), AF2 (b), and AF3 (c). Light and dark spheres denote the atomic sites of Fe atom and 4d atoms, Rh or Pd. In the AF2, 4d atom may have a magnetic moment.\(^{\text{10}}\)

Fig. 2  CuAu-I type ordered structure. Light and dark spheres denote the atomic sites of Fe and 4d atom of Rh and Pd.

Figures 3(a) and (f) for FeRh and FePd are those obtained previously.\(^{\text{9}}\) For all concentrations, the total energies in the NM are found to be about 0.06–0.10 aJ per formula unit higher than the lowest energy among the five magnetic states. No self-consistent solutions of the ferrimagnetic state with the antiparallel magnetic moments for Fe and virtual 4d-atom are obtained for all calculations.

As seen in Fig. 3(a), the ground state of FeRh is the AF3 in the CsCl-type structure \((c/a^* = 1)\). The calculated lattice constant \( a^* = c = 0.30 \) [nm], which is very close to the observed one,\(^{\text{25}}\) 0.299 nm. The CsCl-type structure is stable for the concentration \( x \) less than 0.2. To discuss it more precisely, we have calculated the total energies for \( x = 0.10 \) and 0.15. Figure 4 denotes the total energies calculated for AF3 at \( x = 0.10, 0.15 \) and 0.20. The CsCl-type structure is shown to be stable at \( x < 0.15 \). The crossing of the energies of FM and AF3 takes place between \( x = 0.4 \) and 0.6, as seen in Figs. 3(c) and (d). It has been confirmed that the critical concentration between FM and AF3 is 0.55.

In Figs. 5 and 6, the equilibrium lattice constants \( a^* \) and \( c \), where the total energy becomes lowest, and the calculated magnetic moment \( m_{\text{Fe}} \) and \( m_{\text{Rh}} \) in the ferromagnetic state and sub-lattice moment \( m_{\text{Fe}} \), are shown together with the observed results. The agreements between the calculated and observed results are satisfactorily.

4. Summary and Discussion

In this paper, the total energies for pseudo-binary alloys Fe(Rh\(_{1-x}\),Pd\(_x\)) are calculated as a function of lattice constants \( a^* \) and \( c \). By comparing the calculated total energies between the nonmagnetic, ferromagnetic and three kinds of antiferromagnetic states, the ground states are determined. The equilibrium lattice constants \( a^* \) and \( c \) obtained by our calculations well agree with the observed ones. It has been also obtained the antiferromagnetic spin orderings at 0.15 < \( x < 0.55 \) are AF3. At \( x > 0.55 \), the ferromagnetic state was found to be the ground state. The calculated magnetic moments are in good agreement with the observed ones. The observed ferrimagnetic phase with orthorhombic structure\(^{\text{3}}\) at \( x = 0.525–0.61 \) has not been discussed in this paper, which is left in future works.

Finally, we will discuss the large volume changes,
associated with the magnetic field-induced transition from the antiferromagnetic to ferromagnetic state, observed in FeRh\textsuperscript{13,14} and Rh rich Fe(Rh,Pd) alloys.\textsuperscript{15} Figure 7 denotes the calculated result of the concentration dependence of volume change \((V_{\text{FM}} - V_{\text{AF3}})/V_{\text{AF3}}\), where \(V_{\text{FM}}\) and \(V_{\text{AF3}}\) are the calculated unit-cell volumes in the FM and AF3 states, respectively. The calculated volume changes are found to be a little larger than the observed values\textsuperscript{13–15} at room temperature. However, it has been obtained that the volume change decreases as the concentration \(x\) increases for Fe(Rh\textsubscript{1–\(x\)},Pd\textsubscript{\(x\)}) near the critical concentration between the antiferromagnetic state and ferromagnetic one (\(x \sim 0.55\)), the volume change is still large (about 1%). It is pointed out that Fe(Rh,Pd) alloys are prospective as high magnetostrictive materials.

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REFERENCES