First-Principles Calculation of Curie Temperature Tuning in L1₀-Type FePt by Element Substitution of Mn, Cu, Ru, and Rh

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We studied the Curie temperature $T_C$ variation in L1₀-type FePt ordered alloys that were partially substituted with other transition metal elements, such as Mn, Cu, Ru, and Rh, by first-principles calculations. For the theoretical evaluation of $T_C$, a disordered local moment approach based on the coherent potential approximation was employed. The calculated results reveal that the most significant reduction in $T_C$ was observed for FePt where some Pt was substituted by Ru, while a large uniaxial magnetic anisotropy constant on the order of $10^7 \text{erg/cm}^3$ was maintained. An analysis of the electronic structure demonstrates that the stability of the ferromagnetic state is degraded by the substitution of Ru.

**Key words:** Curie temperature, L1₀-type FePt, element substitution, first-principles calculation, coherent potential approximation, disordered local moment

1 Introduction

L1₀-type FePt alloy is a key material for magnetic recording media because of its strong magnetocrystalline anisotropy.¹⁻⁴) Heat-assisted magnetic recording is a promising technology for achieving further increases in recording density in harddisk drives.⁵,⁶) However, the high Curie temperature $T_C$ of FePt of approximately 750 K causes energy dissipation and also can lead to serious damage by heating in writing operations. Thus, reducing $T_C$ while maintaining a large uniaxial magnetic anisotropy constant $K_u$ in FePt is required.

Element substitution is one of practical ways for controlling $T_C$. Several studies have found that the reduction of $T_C$ in FePt is achieved by the substitution of 3d elements such as Mn⁷,⁸) and Cu⁹⁻¹₂) and 4d elements such as Ru¹³) and Rh¹⁴,¹⁵) However, it is unclear which element is the most effective as the substitution element for reducing $T_C$ in FePt. In this letter, we perform first-principles calculations of $T_C$ for L1₀-type FePt alloys that are partially substituted with other transition metal elements, Mn, Cu, Ru, and Rh. The composition dependence of $T_C$ is investigated systematically, and a possible mechanism of $T_C$ variation is discussed through an analysis of the electronic structure.

2 Calculation Details

Electronic structure calculations were performed using the tight-binding linear muffin-tin orbital (TB-LMTO) method in conjunction with the atomic sphere approximation.¹⁶,¹⁷) The exchange-correlation functional was described within the local spin-density approximation. We considered two substitution patterns in an L1₀-type ordered structure, as shown in Fig. 1. In Fig. 1(a), some Fe is substituted with other transition elements X, where X is Mn, Cu, Ru, and Rh, and in Fig. 1(b), some Pt is substituted with X. To treat the substitutional alloy disorder, the coherent potential approximation (CPA)¹⁹,²⁰) was employed. The range of the amount of substitution, $\sigma$, was set to $0 \leq \sigma \leq 0.2$ for (Fe₁₋$\sigma$X₀)Pt and Fe(Pt₁₋$\sigma$X₀). We set the lattice constants of L1₀-type FePt ($\sigma = 0$) to $a = 3.85 \text{Å}$ and $c = 3.71 \text{Å},²¹)$ and the variation of the lattice volume due to the element substitution was considered with reference to the experimental equilibrium radius of each atom in Ref. 16. The axial ratio was fixed to $c/a = 0.96$ for the whole composition range. In all calculations, $1.1 \times 10^5$ k-points were sampled in the full Brillouin zone for the primitive cell of the L1₀-type lattice.

We calculated the composition dependence of the magnetic properties, such as saturation magnetization $M_s$, $K_u$, and $T_C$. For the evaluation of $M_s$, the electron number difference in the majority- and minority-spin states, i.e., $M_s = N_+ - N_-$, was calculated. For the evaluation of $K_u$, we calculated the band energies $E_\uparrow$ and $E_\downarrow$ where the magnetization aligns along the $a$- and $c$-axis directions, respectively, including the spin–orbit interaction.²²,²³) Based on the magnetic force theorem,²⁴,²⁵) $K_u$ was evaluated from

$$K_u = \frac{E_\uparrow - E_\downarrow}{V},$$

where $V$ is the volume of the unit cell. For the evaluation of $T_C$, the disorder local moment (DLM) state in which the directions
We calculated the total energy in the ferromagnetic ground state $E_{FM}$ and that in the DLM state $E_{DLM}$ without the spin–orbit interaction, and evaluated $T_C$ from

$$T_C = \frac{2}{3} \frac{E_{DLM} - E_{FM}}{\epsilon_B k_B}$$

within the mean field approximation.\(^{29,30}\) Note that $k_B$ and $\epsilon_B$ denote the Boltzmann constant and the total concentration of magnetic atoms, respectively. We counted Fe and Mn as the magnetic atoms to which the DLM treatment was applied.

### 3 Results and Discussion

Let us first confirm the composition dependence of $M_s$ and $K_u$. Figures 2 and 3 show $M_s$ and $K_u$, respectively, as a function of the substitution amount $\sigma$ of the magnetic moments are randomly distributed like paramagnetic states was considered.\(^{26,27}\) The CPA is also applicable to the magnetic disorder, in addition to the alloying disorder mentioned above. For example, the collinear DLM state of pure-Fe can be treated as an $\text{Fe}_2\text{Pt}$ alloy, where half of the Fe moments point in the $\parallel$ direction and the others point in the $\perp$ direction.\(^{28}\) We calculated the total energy in the ferromagnetic ground state $E_{FM}$ and that in the DLM state $E_{DLM}$ without the spin–orbit interaction, and evaluated $T_C$ from

$$T_C = \frac{2}{3} \frac{E_{DLM} - E_{FM}}{\epsilon_B k_B}$$

within the mean field approximation.\(^{29,30}\) Note that $k_B$ and $\epsilon_B$ denote the Boltzmann constant and the total concentration of magnetic atoms, respectively. We counted Fe and Mn as the magnetic atoms to which the DLM treatment was applied.

**Fig. 2** Magnetization $M_s$ as a function of the substitution element X and its amount $\sigma$ in (a) $(\text{Fe}_1-x\text{X})\text{Pt}$ and (b) Fe$(\text{Pt}_{1-x}\text{X})_x$.

**Fig. 3** Uniaxial anisotropy constant $K_u$ as a function of the substitution element X and its amount $\sigma$ in (a) $(\text{Fe}_1-x\text{X})\text{Pt}$ and (b) Fe$(\text{Pt}_{1-x}\text{X})_x$.

For $X = \text{Mn}, \text{Cu}, \text{Ru}, \text{Rh}$, in FePtMn exhibits a ferromagnetic magnetic structure for $\sigma \leq 0.2$. Although the collinear magnetic structure is assumed in the present study, we consider that the obtained result is related to previous studies in which the canting ferromagnetic order was observed in $(\text{Fe}_1-x\text{Mn})\text{Pt}$ (0.1 $\leq \sigma \leq 0.2$) by neutron diffraction\(^7\) and first-principles calculations.\(^{33}\) If the substitution amount of Mn is increased further, an antiferromagnetic order appears due to complex magnetic interactions.

In Fig. 3, $K_u$ tends to decrease, although it is almost constant in the case of the substitution of Rh for Pt. However, strong perpendicular magnetic anisotropy on the order of $10^7$ erg/cm$^3$ is maintained for $\sigma \leq 0.2$. The magnetocrystalline anisotropy in $\text{L}_10$-type FePt originates from the synergy between the strong spin–orbit interaction in Pt atoms and the large exchange splitting in Fe atoms. In particular, the 5d states of Pt located near the Fermi level have an important role in inducing the large $K_u$.\(^{32,33}\) Therefore, the substitution of X for Fe and Pt degrades this synergistic effect, because the spin–orbit interaction is relatively weak in 3d and 4d elements, and also because Cu, Ru, and Rh are non-magnetic in their simple substances. Figure 3 also indicates that enhancement of $K_u$ in FePt is not expected by substitution with Mn, Cu, Ru, and Rh.

Next, we investigate the variation of $T_C$. Figure 4 shows $T_C$ as a function of $\sigma$. For $\sigma = 0$, $T_C$ is 982 K, which is quantitatively consistent with the previous result of 935 K calculated in a similar framework based on the Korringa–Kohn–Rostoker method by Staunton et al.\(^{34}\) However, the calculated $T_C$ values are approximately 30% larger than the experimental value (750 K). One possible reason for the discrepancy between the theoretical and ex-
In consideration of applications, the substitution of Ru for Pt, Fe(Pt$_{1-x}$Ru$_x$), are also remarkable, since $T_C$ can be reduced without lowering $K_u$. Comparing with experiments, 15% and 16% reductions of $T_C$ were reported for (Fe$_{0.95}$Ru$_{0.05}$)(Pt$_{0.06}$Ru$_{0.04}$) and Fe(Pt$_{0.03}$Rh$_{0.01}$), respectively (corresponding to a 5–6 at.% substitution of Ru and Rh). The calculations for these compositions give 17% and 13% reductions of $T_C$ [the data for (Fe$_{0.95}$Ru$_{0.05}$)(Pt$_{0.06}$Ru$_{0.04}$) is not shown in Fig. 4]. The calculated results are in good agreement with the experimental data, though they are different from each other by a few percent. This fact implies that $T_C$ reduction is more efficient if site-specific substitution of Ru can be achieved.

We now discuss the behavior of the $T_C$ variation in Fig. 4. In Fig. 4(a), the variation is not dependent on X in (Fe$_{1-x}$X$_x$)Pt. By substituting X for Fe, the number of Fe–Fe pairs in the system decreases, and the effective exchange field, which is the molecular field around one Fe atom induced by the exchange interaction with the other Fe atoms, is weakened. Therefore, $T_C$ decreases with $\sigma$ regardless of X. On the other hand, the $T_C$ variation strongly depends on X in Fe(Pt$_{1-x}$X$_x$), i.e., $T_C$ is significantly reduced for X = Ru, whereas $T_C$ is not greatly changed for X = Cu, as shown in Fig. 4(b).

To clarify the behavior in Fig. 4(b) qualitatively, we analyze the electronic structure of each atom. Figure 5 shows the local density of states (LDOS) for FePt, Fe(Pt$_{0.3}$Cu$_{0.2}$), and Fe(Pt$_{0.3}$Ru$_{0.2}$). The overall shapes of each LDOS of Fe and Pt are similar. However, focusing on the region around the Fermi level, we observe the broadening of the upper edge of the LDOS in the majority-spin state of Fe through the hybridization with the Ru state located around the Fermi level $E_F$, as shown by the bold arrow in Fig. 5(c), compared to the edge of the LDOS in FePt and Fe(Pt$_{0.3}$Cu$_{0.2}$). This broadening results in the increase of the band energy in the system (the band energy is expressed as $E = \int_{-\infty}^{E_F} \rho(E) dE$, where $\rho(E)$ is the density of states). Because ferromagnetism is considered to emerge when the decrease of the Coulomb energy by exchange splitting is greater than the increase of the band energy, the additional band energy by the Ru substitution is expected to degrade the stability of the ferromagnetic state. Thus, the effective exchange field is weakened and $T_C$ decreases by the substitution of Ru for Pt, although the amount of Fe is constant in Fe(Pt$_{1-x}$Ru$_x$). In contrast, since the LDOS of Fe in Fe(Pt$_{0.3}$Cu$_{0.2}$) is not influenced by the Cu state, the $T_C$ of Fe(Pt$_{1-x}$Cu$_x$) in Fig. 4(b) is almost constant.

4 Summary

The tuning effect on $T_C$ in L1$_0$-type FePt by the substitution of Mn, Cu, Ru, and Rh was studied by first-principles calculations based on the DLM-CPA approach using the TB-LMTO method. The obtained results revealed that the behavior of $T_C$
was strongly dependent on the substitution sites and elements. In particular, the most significant reduction in $T_C$ was observed for the substitution of Ru for Pt. Specifically, about 32% lowering of $T_C$ was achieved in Fe$(\text{Pt}_{0.79}\text{Ru}_{0.21})$, while maintaining a large $\kappa_n$ of $10^3$ erg/cm$^3$ order. Through the analysis of the electronic structure, we found that the substitution of Ru possibly degrades the ferromagnetism in Fe$(\text{Pt}_{1-x}\text{Ru}_x)$, because of the increase of the band energy in the system.

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