An Interpretation of Martensitic Transformation in L12-Type Fe3Pt from Its Electronic Structure

Takuya Yamamoto1,*,1, Masatake Yamamoto1,*,2, Takashi Fukuda1,*,3, Tomoyuki Kakeshita1 and Hisazumi Akai2

1Department of Materials Science and Engineering, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan
2Department of Physics, Graduate School of Science, Osaka University, Toyonaka 560-0043, Japan

Partly ordered Fe3Pt is one of ferromagnetic shape memory alloys exhibiting a large magnetic field-induced strain in its martensite phase formed by a second-order-like martensitic transformation from the L12-type structure to the so-called FCT martensite (L60-type structure). We have investigated the origin of this transformation from their electronic structures calculated in the present study. A characteristic feature in the electronic structure is the existence of a relatively high peak in the density of states of the minority spin band just below the Fermi energy. This peak splits into two peaks by tetragonal distortion, and one of them shifts to lower energy by the distortion, suggesting that the band Jahn-Teller effect is the main cause for the transformation. [doi:10.2320/matertrans.M2009400]

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1. Introduction

The binary Fe-Pt system exhibits a disorder-order transformation from the A1-type structure to the L12-type structure in the vicinity of composition Fe3Pt. The alloy with the composition near Fe3Pt exhibits a martensitic transformation from the L12-type structure to the L60-type structure, and the transformation behavior depends strongly on the long range order parameter S of the L12-type structure.1,2,3 That is, in the case that S is nearly equal to zero, the martensitic transformation is a burst type, but it changes to a thermoelastic type with increasing S, and the alloy with S ≈ 0.8 exhibits a second-order-like transformation. The product phase formed by the second-order-like transformation is frequently referred to as the FCT martensite although the Bravais lattice is simple tetragonal.

Among these different martensites in Fe3Pt alloys, the so-called FCT martensite is of special interest partly because it exhibits a large magnetic field-induced strain of several percent due to the rearrangement of martensite variants under a magnetic field.5,6 It is now well understood that a large magnetocrystalline anisotropy energy and small twinning shear of the FCT martensite are important for realizing the rearrangement of martensite variants under a magnetic field. However, the origin of such second-order-like transformation and the resulting small twinning shear are not clarified yet. In order to design an alloy with superior properties of magnetic field-induced strain, it is of importance to understand the origin of the L12-FCT transformation in Fe3Pt alloys. In the present study, therefore, we investigate the origin of the L12-FCT transformation observed in Fe3Pt alloys from the electronic structure of the parent phase by calculating its band structure.

2. Method of Calculation

The electronic structure of perfectly ordered Fe3Pt was calculated within the density-functional-theory using the all-electron full potential (linearized) augmented plane wave plus local orbitals (L/APW+lo) method.7 The generalized gradient approximation (GGA) was employed for exchange-correlation interactions. The cut-off parameter Kmax used was 9.0. The energy calculation was made at 550 k-points in the irreducible 1st Brillouin zone. Self-consistency was considered to be achieved when the total energy variation from iteration to iteration did not exceed 10−5 Ry/cell.

3. Results and Discussion

First of all, we have calculated the total energy at 0 K of the perfectly ordered Fe3Pt by changing tetragonality c/a and the volume of the unit cell V, in order to know the ground state. Figure 1 shows the calculated total energy plotted in a contour map. We know from the figure that the total energy is minimum at c/a = 1 and V = V0 = 352.9 a.u.3/cell. This result means that the ground state of the perfectly ordered Fe3Pt is cubic. Similar result was obtained previously by a different band calculation method.9,10 Incidentally, the equilibrium lattice parameter obtained from V0 is 0.374 nm, and the Bulk modulus is calculated to be 176 GPa. These values are in good agreement with experimentally obtained values of 0.375 nm11 and 179.2 GPa,12 respectively, for a highly ordered Fe3Pt.

We plot the total energy as a function of c/a in Fig. 2 with a fixed volume of 340 a.u.3/cell, 352.9 a.u.3/cell (≈ V0), and 360 a.u.3/cell. Obviously, the total energy is the lowest for c/a = 1 with V = V0, as described above. However, we notice in Fig. 2 that the energy increase by tetragonal distortion is quite small, especially when c/a < 1. We also notice in Fig. 2 that the total energy curve for the fixed volume of V = 360 a.u.3/cell has two local minima located at c/a = 1 and c/a ≈ 0.85. Such a small increase of...
energy by tetragonal distortion and the existence of two local minima in the energy curve suggest that a tetragonal structure could be stabilized by giving a slight change in the present system such as introducing defects or changing composition. From the \( c/a \) dependence of total energy shown in Fig. 2, the elastic modulus \( c' = 1/(c_{11} - c_{12}) \) is calculated to be 11.6 GPa by using the method reported by Mehl et al. \(^\text{13}\). This value of \( c' \) is significantly small compared with that of normal metals (for example 48 GPa \(^\text{14}\) for BCC-Fe and 52 GPa \(^\text{15}\) for FCC-Pt).

In order to understand the origin of the instability for the tetragonal distortion observed experimentally in Fe\(_3\)Pt, we have calculated the density of states (DOS) of the perfectly ordered Fe\(_3\)Pt, and the result for the cubic phase (\( c/a = 1 \)) is shown in Fig. 3. In the figure, the majority and minority spin bands are shown separately and the Fermi Energy \( E_F \) is shown by a horizontal dotted line. Incidentally, the total magnetic moment calculated from the DOS profile is 2.13 \( \mu_B/\text{atom} \), being in good agreement with experimentally obtained value of 2.15 \( \mu_B/\text{atom} \). \(^\text{16}\) A characteristic feature in Fig. 3 is the existence of a sharp peak in the DOS of minority spin band slightly below \( E_F \) as indicated with an arrow. As seen from the magnification of this peak shown in Fig. 4(a), the peak top is located at about 0.01 Ry below \( E_F \).

Then, we have examined how the peak shown in Fig. 4(a) changes by giving a tetragonal distortion while fixing the volume of the unit cell to \( V_0 \), and the result is shown in Fig. 4(b)–(d). Obviously, the single peak seen in the DOS profile of \( c/a = 1 \) (Fig. 4(a)) splits into two peaks in that of \( c/a = 0.99 \) (Fig. 4(b)), and the separation becomes larger with increasing \( c/a \). This result suggests that the band Jahn-Teller effect appears strongly in Fe\(_3\)Pt. That is, the split of the peak by the tetragonal distortion shifts the energy of states near \( E_F \) lower. However, the decrease in electronic energy by the shift is not large enough to stabilize the so-called FCT structure as seen in Figs. 1 and 2 in the case of the perfectly ordered Fe\(_3\)Pt.

Considering the fact that the FCT martensite appear in a partly disordered Fe\(_3\)Pt while not in the perfectly ordered Fe\(_3\)Pt, it is speculated that the band Jahn-Teller effect will be enhanced by partial disordering (i.e., by decreasing \( S \)). This speculation is explained qualitatively from the local band structure of Fe\(_3\)Pt shown in Fig. 5. As seen in the local DOS

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Fig. 1 Contour map of total energy plotted as a function of tetragonality \( c/a \) and the volume of the unit cell.

Fig. 2 Total energy plotted as a function of tetragonality \( c/a \) for three fixed volumes. The inset shows the magnification with fixed volume of \( V_0 = 352.9 \text{ a.u.}^3/\text{cell} \).

Fig. 3 Total density of states of ordered Fe\(_3\)Pt. The dotted line indicates the Fermi energy.

Fig. 4 Total density of states of minority spin of Fe\(_3\)Pt in the vicinity of Fermi energy \( E_F \). The tetragonality is changed form \( c/a = 1 \) to \( c/a = 0.945 \).
profile, a significant hybridization exists between $d$-band of Fe (solid curve) and $d$-band of Pt (dashed curve) in the L1$_2$-type Fe$_3$Pt. With decreasing $S$, a part of the Fe-Pt pairs in the first nearest neighbor is replaced by the Fe-Fe pairs and Pt-Pt pairs. This replacement will reduce a part of the hybridization between the $d$-bands of Fe and Pt. At the same time, the number of Pt $d$-states lying in the low energy region is expected to increase because of the increase in the number of the Pt-Pt pairs. Thus, we can speculate that the number of low energy states increases by introducing partial disorder. If such a change in DOS profile is realized in the cubic phase, $E_F$ should approach the peak indicated with an arrow in Fig. 3, and enhances the band Jahn-Teller effect. In this way, the introduction of partial disorder will stabilize the FCT martensite in Fe$_3$Pt. To make a quantitative discussion, a band calculation with partially disordered state should be made, and it is the subject in future.

### 4. Conclusions

A band calculation has shown that the cubic L1$_2$-type structure is the ground state for the perfectly ordered Fe$_3$Pt. The density of states of the minority spin of the L1$_2$-structure has a peak just below the Fermi energy $E_F$, and it splits by tetragonal distortion ($c/a < 1$). The splitting of the peak causes the band Jahn-Teller effect, and stabilizes the tetragonal martensite phase when the degree of order decreases.

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### REFERENCES