The Crystal Structure and Magnetic Properties of Fe₃Pt Martensite Determined by First Principle Calculations*

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The crystal structure and some magnetic properties of Fe₃Pt martensite are investigated by first principle calculations. The crystal structure is optimized in such a way that the atom positions are changed according to the force acting on the nuclei. The positions are repeatedly changed until the forces are all less than 0.257 eV/nm. The final structure obtained is the same as expected from simple Bain distortion of austenite with L₁₂ ordered structure. The magnetic moments of two kinds of Fe atoms in this structure are 2.6 and 2.8 Bohr magneton, and that of a Pt atom is 0.45. The magnetic moments of Fe atoms in Fe₃Pt martensite are considerably larger than those in bcc Fe.

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1. Introduction

Fe–Pt ordered alloys with compositions near Fe₃Pt undergo a thermoelastic martensitic transformation from an L₁₂ type ordered parent phase into an ordered bct martensite.¹ The ordered bct martensite was considered to be formed by Bain distortion² as well as other ferrous martensites. Recently, however, Tadaki et al. have found that anomalous extra reflections exist in electron diffraction patterns taken from fully ordered Fe–24%Pt martensites.³ These extra reflections cannot be explained in terms of the Bain distorted structure. In order to explain these anomalous reflections they have proposed a new structural model with additional atom displacements to the Bain distorted structure. The model proposed is shown in Fig. 1, where the arrows indicate the directions of the atom displacements added to the Bain distorted structure. In this figure, the origin is shifted by [1/2, 0, 1/4] from that in the original figure given by Tadaki et al.⁴ Although Tadaki et al. have considered that the above new crystal model belongs to the space group of I₄m2, Fig. 1 shows that this structural model actually has the mirror symmetry on (001), (100) and (110) planes. This indicates that the structural model proposed by Tadaki et al. belongs to the space group of I₄/mmm.

The proposed model is of great interest, but the magnitude of the displacement is not given. It requires quantitative analysis of reflection intensities to determine the magnitude of displacement experimentally. However, the intensity ratio of very weak reflections to strong ones is difficult to evaluate quantitatively because of the dynamical effect on each reflection. Recent developments of the first principle calculation makes it possible to optimize the crystal structure theoretically by calculating the force acting on the nuclei. The purpose of the present study is to investigate the crystal structure of Fe₃Pt martensite by first principle calculations developed by Blaha et al.⁵ Moreover, some magnetic properties in the Fe₃Pt martensite is also investigated in the present study by the first principle calculation.

2. Methods of Calculation

The calculations has been performed using the WIEN2k program package⁶ which is based on the full-potential augmented plane-wave and local orbitals method (APW+lo) within the generalized gradient approximation. The electronic states below the 3s states for Fe atoms, and those below 5s for Pt are treated as the core states. The muffin-tin radius is 0.1058 nm for any atom. The number of APW is about 230, which is corresponding to the condition of $R/C_h K = 7$, where $R$ and $K$ are the muffin tin radius and maximum wavelength of APW, respectively. The warped electron density in the interstitial region is described by a Fourier series with 1240 coefficients. The maximum $l$ value for partial waves inside atomic spheres was 12. The lattice parameters used in the calculations are $a = 0.573$ nm and $c = 0.634$ nm, which are given by X-ray diffraction.⁵

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Fig. 1 The structure of Fe₃Pt martensite proposed by Tadaki et al. The origin of this figure is located at (1/2, 0, 1/4) of the original figure given by Tadaki et al. The arrows indicate the directions of displacements. The dotted lines show the unit cell of the Bain distorted structure.
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3. Results and Discussion

3.1 Optimization of the crystallographic parameters

Table 1 shows the coordinates of the atoms for the structural model given in Ref. 3) and those of the corresponding atoms under the new coordinate system described in Section 1. Although the expression of the atom positions is different from each other because of the shift of the origin, the atom arrangement is the same. There are two unknown parameters in this structural model, that is, $z$ of the Fe1 atom and $x$ of the Fe2 atom. When both of these parameters are $3/4$ under the new coordinate system, the displacements from the Bain distorted model become zero. At first, the initial values of $z$ and $x$ are set to 0.76 and 0.74, respectively. The atom positions are optimized by moving atoms according to the calculated forces. The changes in the cohesive energy and the two parameters are shown in Figs. 2(a) and (b), respectively. Here, the cohesive energy stands for the difference in energy between the crystal and the free atoms. The cohesive energy decreases with the number of iterations and its change in each step tends to become small. This shows that the optimization was carried out satisfactorily. On the other hand, the parameters, $x$ and $z$, seem to approach the value of $3/4$ with each iteration. This means that the magnitude of displacements indicated by the arrows in Fig. 1 becomes zero, then Fe₃Pt martensite approaches the Bain distorted structure.

This result suggests that another structural model should be needed to explain the electron diffraction patterns. The lattice parameters and atoms included in the unit cell should be the same as those of the structural model shown in Fig. 1. Moreover, the atom positions should be based on the Bain distorted structure because intensities of the extra reflections are very weak. Thus, the directions of atom displacement are only altered from Fig. 1. As mentioned by Tadaki et al., the structure of the martensite should belong to the point groups of $I4/mmm$, $I4m2$, $I42m$, $I4mm$, and $I422$ on the assumption that the electron diffraction pattern has $I4/mmm$ symmetry. If the crystal belong to the space group of $I42m$, the displacement along $c$-axis is allowed for Fe2 atoms. If the crystal belongs to the space group of $I422$, the rotation around the $c$-axis is allowed for Fe2 atoms. These structural models can also explain the extra reflections in electron diffraction patterns. In addition, it should be noted that Tadaki et al. assume that the diffraction pattern has the symmetry of $I4/mmm$. If this assumption is removed, the restriction of the displacement become easy. It may be necessary to postulate that Fe₃Pt martensite has lower symmetry than $I4/mmm$.

3.2 Density of states (DOS) and magnetic properties

The magnetic properties are investigated by the band calculation. In this calculation, the structure is approximated by a Bain distorted one. The unit cell is shown in Fig. 1 by the dotted lines. This structure may not be perfectly correct, but is probably a good approximation of the exact structure because the extra reflections are very weak. Figure 3(a) shows the total DOS and the partial DOS for each atom in Fe₃Pt martensite. In this figure, the origin of the energy axis stands for the Fermi level. Figure 3(b) shows total DOS in bcc pure Fe crystal for reference. As seen in Fig. 3(b), a slight part of $d$ states in the up spin band is above the Fermi level. On the other hand, in Fe₃Pt martensite, the $d$ states in the up spin band are located below the Fermi level. Consequently, the occupied $d$ states in the down spin band decreases compared with those of bcc Fe. Therefore, Fe atoms in the Fe₃Pt martensite can have larger magnetic moments than

Table 1 The correspondence between the coordinates in Ref. 3) and those in the present study. Multiplicity and Wyckoff letters are also shown in this table.

<table>
<thead>
<tr>
<th>Model</th>
<th>Ref. 3</th>
<th>Present study</th>
</tr>
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<td>Space group</td>
<td>$I4/m2$</td>
<td>$I4/mmm$</td>
</tr>
<tr>
<td>Pt</td>
<td>$\pm(0,0,0) + \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$</td>
<td>$\pm(0,0,0) + \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$</td>
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<tr>
<td>Fe1</td>
<td>$2a$: 0, 0, 0</td>
<td>$4d$: 0, $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, 0, $\frac{1}{2}$</td>
</tr>
<tr>
<td>Fe2</td>
<td>$4f$: 0, $\frac{1}{2}, 0, \frac{1}{2}$</td>
<td>$4c$: 0, 0, $\frac{1}{2}$, 0, $\frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>$8b$: $x$, $\frac{1}{2}$, $x$, $\frac{1}{2}$, $\frac{1}{2}$, $x$, $\frac{1}{2}$, $\frac{1}{2}$</td>
<td>$8b$: $x$, $x$, 0, $\bar{x}$, 0, $\bar{x}$, 0, $\bar{x}$</td>
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<td>$x$, $\frac{1}{2}$, $x$, $\frac{1}{2}$, $\frac{1}{2}$, $x$, $\frac{1}{2}$, $\frac{1}{2}$</td>
<td>$x$, 0, $\bar{x}$, 0, $\bar{x}$, 0, $\bar{x}$, 0, $\bar{x}$</td>
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</table>
those in the bcc Fe crystal. In Fig. 3(a), the partial DOS of Pt also has the energy shift between up and down spin bands. Thus, Pt atoms can also have magnetic moments. The difference in magnetic moments between bcc Fe and Fe<sub>3</sub>Pt is concerned with the deference in energy shift between up and down spin band. The center of d states is shifted by 2.64 eV for bcc Fe, while the energy shifts are 3.07 eV for Fe<sub>1</sub> and 2.96 eV for Fe<sub>2</sub>.

The magnetic moment for each atom is shown in Table 2. The magnetic moment of Fe<sub>1</sub> and Fe<sub>2</sub> are considerably larger than bcc Fe in the present calculation. The magnetic moment of Fe<sub>3</sub>Pt has much larger magnetic moment, taking account of the increasing in magnetic moment with S. The discrepancy between theoretical and experimental values is understood by the difference in degree of order.

The hyperfine field is also shown in Table 2. The hyperfine field of Fe<sub>2</sub> is weaker than that of Fe<sub>1</sub> although the magnetic moment of Fe<sub>2</sub>Pt is stronger than that of Fe<sub>1</sub>. It is very often said that the hyperfine field has strong correlation with the magnetic moment. However, in Fe<sub>3</sub>Pt martensite, this empirical law is not satisfied. The decrease in the hyperfine field of Fe<sub>2</sub> is due to the contribution of valence electrons. In general, the hyperfine field is explained by the exchange correlation between 3d band and core 2s orbital. Usually, the effect of the valence band is not so significant. In the case of Fe<sub>2</sub> in Fe<sub>3</sub>Pt martensite, however, the valence electrons have contribution of 10.3 T. Consequently, hyperfine field of −36.2 T formed by the core electrons decreases to −25.9 T. It should be noted that the hyperfine fields formed by the core electrons are −36.2 T for Fe<sub>2</sub> and −33.7 T for Fe<sub>1</sub>. It is found from this fact that hyperfine field formed by the core electrons is strongly correlated to the magnetic moment. The contribution of the valence electrons is very weak at Fe<sub>1</sub> as well as in bcc Fe. It could not be made clear why the contribution of valence electrons is outstanding at Fe<sub>2</sub>, but four Pt atoms enclosing an Fe<sub>2</sub> atom is considered to play an important role in enhancement of density of valence electrons at the nucleus.

REFERENCES

6) 1 eV = 1.60218 × 10<sup>−19</sup> J. The value of 0.257 eV/nm originates from atomic unit, that is, it is equal to 1 mRy/a.u., where 1 mRy = 0.0136 eV and 1 a.u. = 0.05292 nm.