metals

Article

Lattice Softening in Fe_3Pt Exhibiting Three Types of Martensitic Transformations

Takashi Fukuda * and Tomoyuki Kakeshita

Department of Materials Science and Engineering, Graduate School of Engineering, Osaka University, 2-1, Yamada-oka, Suita, Osaka 565-0871, Japan; kakeshita@mat.eng.osaka-u.ac.jp
* Correspondence: fukuda@mat.eng.osaka-u.ac.jp; Tel.: +81-6-6879-7483

Academic Editor: Volodymyr A. Chernenko
Received: 24 March 2017; Accepted: 26 April 2017; Published: 27 April 2017

Abstract: We have investigated the relation between the softening of elastic constants and martensitic transformation in Fe_3Pt, which exhibits various kinds of martensitic transformation depending on its long-range order parameter S. The martensite phases of the examined alloys are BCT (S = 0.57), FCT1 (S = 0.75, $c/a < 1$) and FCT2 (S = 0.88, $c/a > 1$). The elastic constants C' and C_{44} of these alloys decrease almost linearly with decreasing temperature. Although the temperature coefficient of C' decreases as S increases, C' at the transformation temperature is the smallest in the alloy with S = 0.75, which transforms to FCT1. This result implies that softening is most strongly related to the formation of the FCT1 martensite with tetragonality $c/a < 1$ among the three martensites.

Keywords: elastic constants; band Jahn–Teller effect; disorder–order transformation

---

1. Introduction

The relation between softening of elastic constants and martensitic transformation has attracted considerable attention for many years and has been discussed by many researchers [1–10]. In some alloys exhibiting martensitic transformation, softening of elastic constants $C' = (C_{11} - C_{12})/2$ and large elastic anisotropy (C_{44}/C') was observed in the parent phase, but the significance of the softening is largely different between the alloys. For example, the value of C' near the transformation start temperature is approximately 0.01 GPa in In–27Tl (at %) alloy [3], 1 GPa in Au–30Cu–47Zn (at %) alloy [2], 5 GPa in Fe–30Pd (at %) alloy [7], 8 GPa in Cu–14Al–4Ni (at %) alloy [10], and 14 GPa in Ti–50.8Ni (at %) [8] and Al–63.2Ni (at %) alloys [4]. Because of such a large distribution of C' at the M_s temperature, the influence of softening of C' on martensitic transformation is expected to be significantly different between these alloys. Martensitic transformation in some alloys is probably strongly related to the softening of C', while that in others is weakly related despite the fact that the softening appears before the transformation.

In some alloys, several kinds of martensite phases appear by slightly changing the composition or long-range order parameter (degree of order). We consider that a study on elastic softening in such alloys will help us understand the relation between softening and martensitic transformation. Iron–platinum alloys are one such alloy system. An iron–platinum alloy with Pt content of 25 at % (Fe_3Pt) exhibits disorder–order transformation from the A1-type disordered structure to the $L1_2$-type ordered structure. Depending on the degree of order S of the $L1_2$-type structure, Fe_3Pt exhibits various kinds of martensitic transformations. (Here, S is the Bragg–Williams long-range order parameter [11]). The disordered alloy transforms to the BCC (body-centered-cubic) martensite like iron–nickel alloys. As the degree of order increases, the structure of the martensite phase changes to BCT (body-centered-tetragonal) and then to FCT (face-centered-tetragonal) with $c/a < 1$ [12–15]. Recently, another type of FCT martensite with $c/a > 1$ and also an orthorhombic martensite were found in highly ordered Fe_3Pt [16,17]. We call the former FCT ($c/a < 1$) martensite FCT1 and the latter FCT

($c/a > 1$) martensite FCT2 in the following. Incidentally, the Strukturbericht symbol for the BCT, FCT1 and FCT2 martensites are $L6_0$-type, but we use the traditional names in this paper for convenience.

As mentioned above, at least five kinds of martensite phases appear in Fe_3Pt depending on degree of order S. Among the five, three (BCT, FCT1 and FCT2) have tetragonal structures. When the BCT martensite is formed, the tetragonality c/a changes drastically from 1 to 0.79 at the transformation start temperature. This means that the $L1_2$-BCT transformation is an obvious first order. On the other hand, the jump in c/a at the transformation temperature is undetectable by conventional X-ray techniques for the FCT1 and the FCT2 martensites; c/a changes gradually in the cooling process from 1 to 0.94 when the FCT1 martensite is formed and from 1 to 1.005 when the FCT2 martensite is formed [16]. This means that the $L1_2$-FCT1 and the $L1_2$-FCT2 transformations are very weak first order. Because of the difference in transformation behavior, we may expect different softening behavior in elastic constants of the $L1_2$-type parent phase.

Several reports have been made on elastic constants of Fe–Pt alloys with Pt content near 25%. Huash [18] examined the elastic constants of a disordered Fe–28Pt (at %) alloy. Although the alloy does not show a martensitic transformation, it exhibits significant softening in elastic constants C' and C_{44} below its Curie temperature. Influence of degree of order S on elastic constants was examined by Ling and Owen [19] using an Fe–25Pt alloy. According to their report, the softening becomes less significant as S increases. They discussed the behavior from the view point of Invar effect. At the time of their report, the various types of martensites in Fe–25Pt alloys were not identified; therefore, the relation between the softening and martensitic transformations was not discussed there. The relation between elastic constant and martensitic transformation was discussed by Kawald et al. [20] in an Fe–25Pt (at %) with $S = 0.6$. They observed that C' approaches nearly zero in Fe–25Pt alloy, but the structure of the martensite phase and the transformation start temperature was not identified in the report. Owen [21] discussed the relation between softening and martensitic transformations in Fe–Pt alloys, and suggested that the softening affects the growth of the martensite phase. However, the structure of the martensite phase was not mentioned and it seems that only the BCC martensite was considered.

The elastic properties of Fe–Pt alloys were also examined by constructing phonon dispersion curves [22–24]. Tajima et al. [22] reported that [110] TA_1 mode of an ordered Fe–27.8Pt (at %) alloy exhibits significant softening near the Γ-point (center of the Brillourin zone) with decreasing temperature. Kästner et al. [23] found that softening at the Γ-point of the ordered Fe–28Pt is less significant compared with the disordered Fe–28Pt alloy. However, the alloys they examined do not show a martensitic transformation; therefore, the relation between the softening and martensitic transformations are not discussed there.

As mentioned above, although there exist several reports on the elastic properties of Fe–Pt alloys, the relation between the softening of elastic constant and martensitic transformations is not clear. The present study is motivated to make progress on the interpretation of the relation between the softening in elastic constant and martensitic transformation using several Fe–25Pt alloys, which transform to three types of tetragonal martensite phases (BCT, FCT1 and FCT2) depending on degree of order.

2. Materials and Methods

An ingot of Fe–25.0Pt (at %) was prepared by melting an iron bar (99.99 mass %) and a platinum plate (99.95 mass %) in an arc melting furnace (DIAVAC, Chiba, Japan) under an argon gas atmosphere. By using the ingot, a boule (single crystal) was grown by a floating zone method in an argon gas atmosphere with a growth rate of 3 mm/h. Three parallelepiped specimens (Specimen-A, Specimen-B, Specimen-C) with all faces parallel to {100} were cut from the boule and subjected to homogenization heat treatment at 1373 K for 1 h. Then, three kinds of ordering heat treatment were applied to obtain different degrees of order S of the $L1_2$-type structure.

Specimen-A ($3.07 \times 3.06 \times 3.03$ mm^3) was cooled from 1373 to 973 K with a cooling rate of 1 K/min, and then kept at 973 K for 10 h followed by quenching into iced water. Specimen-B ($3.03 \times 3.01 \times 3.00$ mm^3) was cooled from 1373 to 923 K with a cooling rate of about 1 K/min, and then kept at 923 K for 100 h followed by quenching into iced water. Specimen-C (3.28 × 3.23 × 3.10 mm^3) was cooled from 1373 to 1103 K with a cooling rate of about 1 K/min, and then cooled to 773 K with a cooling rate of 10 K/day followed by furnace cooling to room temperature. The degree of order S ($L1_2$-type) of the three specimens was determined by comparing the intensity of 100 and 200 reflections obtained by X-ray diffraction. Details of the method were described elsewhere [25], and the obtained value of S was 0.57, 0.75 and 0.88 with an error of approximately ±0.05 for Specimens-A, -B and -C, respectively; in the following, we refer to the three specimens as S57, S75 and S88 in order to clearly indicate the degree of order.

All three specimens exhibit ferromagnetic transition, and the Curie temperature, T_c, increases with increasing degree of order (S) and the value is 353, 394 and 441 K for S57, S75 and S88, respectively [15]. The specimen S57 (S = 0.57) transforms to the BCT martensite at 145 K, S75 transforms to the FCT1 martensite with $c/a < 1$ at 85 K, and S88 transforms to the FCT2 martensite with $c/a > 1$ at 60 K [15].

The elastic constants of the three specimens were measured by a rectangular parallelepiped resonance (RPR) method [26,27]. More than 40 resonance peaks in the frequency range of 200 and 800 Hz were used to optimize the elastic constants. During the measurements, a magnetic field of 1 T was applied to the [111] direction of the specimen to avoid the movement of magnetic domains. The experimental setup is shown in Figure 1a, and an example of the spectra obtained for the S88 specimen at 300 K is shown in Figure 1b with indexes of modes.

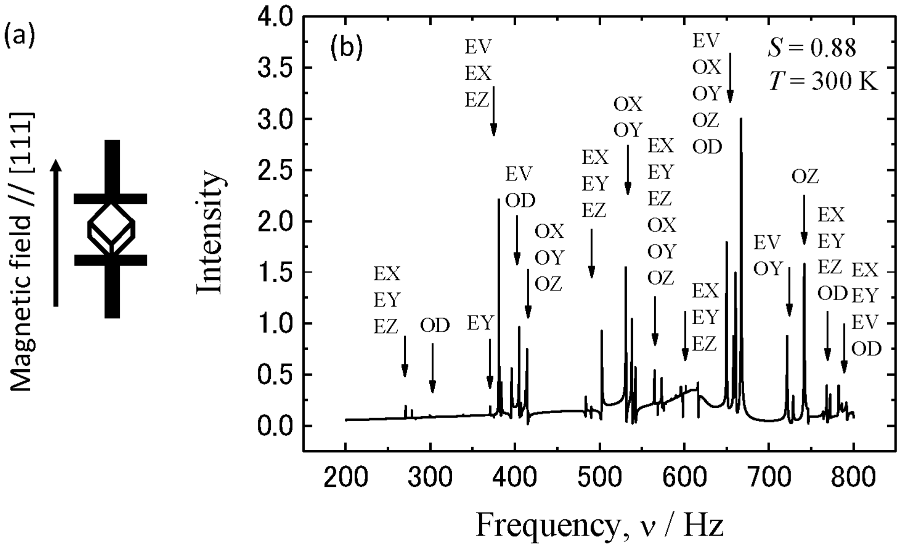

Figure 1. Schematic illustration showing the setting of the specimen for rectangular parallelepiped resonance (RPR) measurements under a magnetic field (**a**), and an example of the spectra of S88 at 300 K (**b**).

3. Results and Discussion

Figure 2 shows the temperature dependence of elastic constants $C_L = (C_{11} + C_{12} + 2C_{44})/2$, C_{44} and $C' = (C_{11} - C_{12})/2$. The errors of data are estimated to be the size of the marks. The temperature dependence of C_L is small, and C_L increases as the degree of order S increases. The value of C_{44} decreases almost linearly in the examined temperature range for all the specimens. The value of C' decreases almost linearly for all the specimens, but it slightly deviates from the linear relation below about 200 K for S75 and S57. This deviation could be due to the formation of tweed microstructure reported previously [12]. The bulk modulus B, which is given by $B = (C_{11} + 2C_{12})/3 = C_L - C_{44} - C'/3$, increases as temperature decreases; the value of B is between 85 and 100 GPa for S57, between 105 and 125 GPa for S75, and between 125 and 150 GPa for S88 in the examined temperature range.

Since C_{44} and C' decrease almost linearly in a wide temperature range, we fitted C_{44} and C' by linear functions of T, and the results are shown in Figure 2 by dashed lines. On each line, Curie temperature is shown by a double arrow. We notice that the value of C_{44} and C' at T_c on the extrapolated line is nearly the same for all the specimens: $C_{44}(T_c)$ ~100 GPa and $C'(T_c)$ ~30 GPa. This result supports a previous discussion that the softening of C' and C_{44} is caused by the band structure of the ferromagnetic phase [27–29].

The martensitic transformation temperature is also shown by a single arrow on each line in Figure 2. The extrapolated value of C' at M_s is 1.7 GPa for S57, 0.6 GPa for S75 and 6.9 GPa for S88. The value of C' is the smallest when the martensite phase is FCT1 with $c/a < 1$. The present result suggests that the softening in C' is most strongly related to the formation of FCT1 martensite with $c/a < 1$ compared with other martensites.

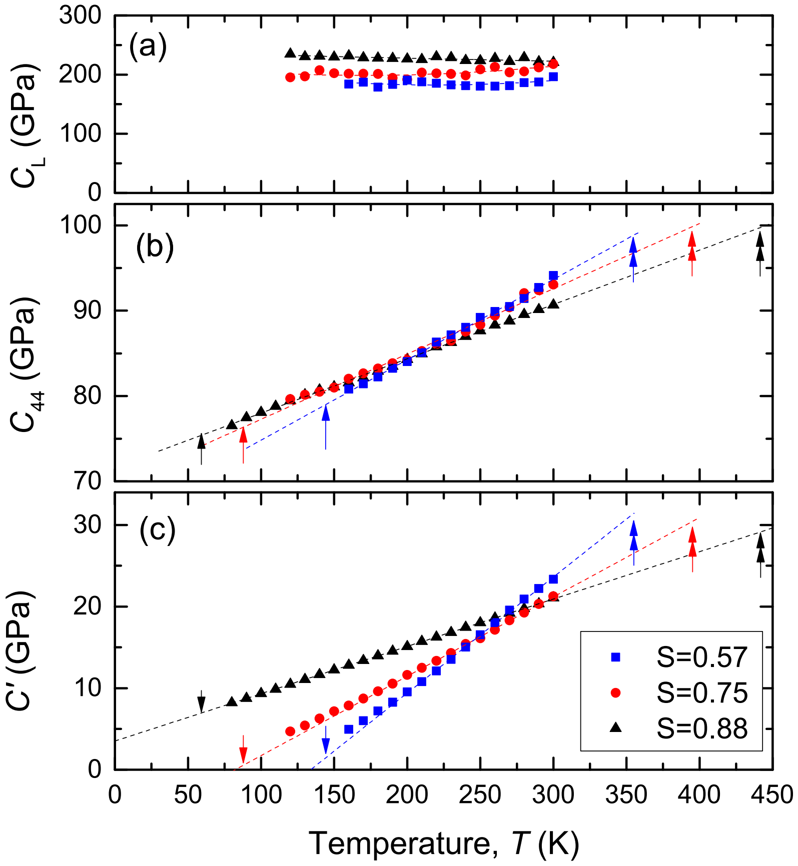

Figure 2. Elastic constants C_L (**a**), C_{44} (**b**) and C' (**c**) of Fe_3Pt with different degrees of order S. Single arrows indicate the martensitic transformation start temperature. Double arrows indicate the Curie temperature.

The anomalies in elastic anisotropy $A = C_{44}/C'$ are frequently discussed in alloys exhibiting thermoelastic martensitic transformations. Figure 3 shows the elastic anisotropy evaluated from Figure 2. The vertical lines indicate the martensitic transformation temperature. If we simply extend the experimental data, the approximate value of A at M_s temperature is expected to be 10 for S88, 30 for S75 and 20 for S57. The elastic anisotropy at M_s is the largest for S75 which transforms to FCT1 with $c/a < 1$. This again suggests that softening in C' is most strongly related to the formation of FCT1 martensite. Presumably, the band Jahn–Teller effect is the main reason for the softening of C' as previously reported [30]. Incidentally, the solid curve in Figure 3 is the calculated anisotropy using the linear relation shown by the dotted lines in Figure 2. If the linear relations were satisfied to M_s, the anisotropy at M_s would be 50 in S57 and 280 in S75.

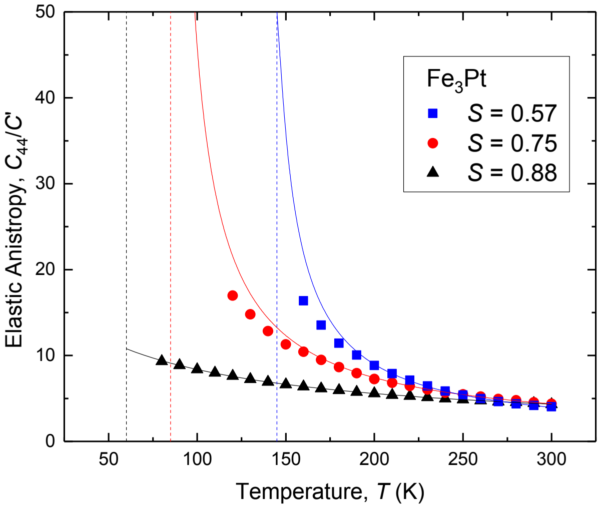

Figure 3. Temperature dependence of the elastic anisotropy of Fe$_3$Pt with different degrees of order S. The vertical lines indicate the martensitic transformation temperature.

4. Conclusions

The three alloys of Fe$_3$Pt (S = 0.57, 0.75, 0.88) all exhibit softening of elastic constant C'. Although the temperature coefficient of C' is largest for S = 0.57, which transforms to the BCT martensite, the value of C' at M_s is the smallest for S = 0.75, which transforms to the FCT1 martensite. In addition, the elastic anisotropy is the largest for S = 0.75. The softening in C' is probably most strongly related to the formation of the FCT1 martensite.

Acknowledgments: We appreciate technical advices by Katsushi Tanaka (Kobe University) on the measurements and analysis of PRP method. We also appreciate Masataka Yamamoto, Sayaka Sekida and Motoyoshi Yasui, who were students of Osaka University, for their support on sample preparation, measurements and analysis on the raw data. The present work was supported by JSPS KAKENHI Grant Number JP26289230 and JP25249086.

Author Contributions: Takashi Fukuda designed the experiments and prepared the manuscript; Tomoyuki Kakeshita supervised the research.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Nakanishi, N. Elastic constants as they relate to lattice properties and martensite formation. *Prog. Mater. Sci.* **1980**, *24*, 143–265. [CrossRef]
2. Murakami, Y. Lattice softening, phase stability and elastic anomaly of the β-Au-Cu-Zn alloys. *J. Phys. Soc. Jpn.* **1972**, *33*, 1350–1360. [CrossRef]
3. Gunton, D.J.; Sanuders, G.A. The elastic behavior of In-Tl alloys in the vicinity of the martensitic tansformation. *Solid State Commun.* **1974**, *14*, 865–868. [CrossRef]
4. Enami, K.; Hasunuma, J.; Nagasawa, A.; Nenno, S. Elastic softening and electron-diffraction anomalies prior to the martensitic transformation in Ni-Al β_1 alloy. *Scr. Metall.* **1976**, *10*, 879–884. [CrossRef]
5. Nagasawa, A.; Ueda, Y. Elastic Soft Mode Preceeding Martensitic Phase Transition in β Phase Alloys. *J. Phys. Soc. Jpn.* **1978**, *45*, 1249–1252. [CrossRef]
6. Verlinden, B.; Delay, L. On the elastic constants and Ms-temperatures in β-Hume-Rothery alloys. *Acta Metall.* **1988**, *36*, 1771–1779. [CrossRef]
7. Muto, S.; Oshima, R.; Fujita, F.E. Elastic softening and elastic strain energy consideration in the fcc-fct transformation of FePd alloys. *Acta Metall. Mater.* **1990**, *38*, 685–694. [CrossRef]
8. Ren, X.; Miura, N.; Zhang, N.; Otsuka, K.; Tanaka, K.; Koiwa, M.; Suzuki, T.; Chumlyakov, Yu.I.; Asai, M. A comparative study of elastic constants of Ti-Ni based alloys prior to martensitic transformation. *Mater. Sci. Eng. A* **2001**, *312*, 196–206. [CrossRef]

9. Sedlák, P.; Seiner, H.; Landa, M.; Novák, V.; Šittner, P.; Mañosa, L.I. Elastic constants of bcc austenite and 2H orthorhombic martensite in CuAlNi shape memory alloy. *Acta Mater.* **2005**, *53*, 3643–3661. [CrossRef]
10. Graczykowski, G.; Mielcarek, S.; Breczewski, T.; No, M.L.; San-Juan, J. Martensitic phase transition in Cu-14%Al-4%Ni shape memory alloys studied by Brillouin light scattering. *Smart Mater. Struct.* **2013**, *22*, 085027. [CrossRef]
11. Warren, B.E. X-ray studies of order-disorder. In *X-ray Diffraction*; Dover: New York, NY, USA, 1990.
12. Muto, S.; Oshima, R.; Fujita, F.E. Electron microscopy study on martensitic transformations in Fe–Pt alloys: General features of internal structure. *Metall. Trans. A* **1988**, *19*, 2723–2731. [CrossRef]
13. Dunne, D.P.; Wayman, C.M. The effect of austenite ordering on the martensite transformation in Fe–Pt alloys near the composition Fe_3Pt: I. Morphology and transformation characteristics. *Metall. Trans.* **1973**, *4*, 137–152. [CrossRef]
14. Tadaki, T.; Shimizu, K. High tetragonality of thermoelastic Fe_3Pt martensite and small volume change during the transformation. *Scr. Metall.* **1975**, *9*, 771–776. [CrossRef]
15. Umemoto, M.; Wayman, C.M. The effect of austenite ordering on the transformation temperature, transformation hysteresis, and thermoelastic behavior in Fe–Pt alloys. *Metall. Trans. A* **1978**, *9*, 891–897. [CrossRef]
16. Yamamoto, M.; Sekida, S.; Fukuda, T.; Kakeshita, T.; Takahashi, K.; Koyama, K.; Nojiri, H. A new type of FCT martensite in single-crystalline Fe_3Pt Invar alloy. *J. Alloys Compd.* **2011**, *509*, 8530–8533. [CrossRef]
17. Yamamoto, M.; Fukuda, T.; Kakeshita, T.; Takahashi, K. Orthorhombic martensite formed in $L1_2$-type Fe_3Pt Invar alloys. *J. Alloys Compd.* **2013**, *577*, S503–S506. [CrossRef]
18. Hausch, G. Elastic constants of Fe–Pt alloys. I. Single crystalline elastic constants of $Fe_{72}Pt_{28}$. *J. Phys. Soc. Jpn.* **1974**, *37*, 819–823. [CrossRef]
19. Ling, H.C.; Owen, W.S. The magneto-elastic properties of the invar alloy, Fe_3Pt. *Acta Metall.* **1983**, *31*, 1343–1352. [CrossRef]
20. Kawald, U.; Zemke, W.; Bach, H.; Pelzl, J.; Saunders, G.A. Elastic constants and martensitic transformations in FePt and FeNiPt Invar alloys. *Physica B* **1989**, *161*, 72–74. [CrossRef]
21. Owen, W. The influence of lattice softening of the parent phase on the martensitic transformation in FeNi and FePt alloys. *Mater. Sci. Eng. A* **1990**, *127*, 197–204. [CrossRef]
22. Tajima, K.; Endoh, Y.; Ishikawa, Y. Acoustic-phonon softening in the invar alloy Fe_3Pt. *Phys. Rev. Lett.* **1976**, *37*, 519–522. [CrossRef]
23. Kästner, J.; Petry, W.; Shapiro, S.M.; Zheludev, A.; Neuhaus, J.; Wassermann, E.F.; Bach, H. Influence of atomic order on $TA_1[110]$ phonon softening and displacive phase transition in $Fe_{72}Pt_{28}$ Invar alloys. *Eur. Phys. J. B* **1999**, *10*, 641–648. [CrossRef]
24. Noda, Y.; Endoh, Y. Lattice dynamics in ferromagnetic Invar alloys, Fe_3Pt and $Fe_{65}Ni_{35}$. *J. Phys. Soc. Jpn.* **1988**, *57*, 4225–4231. [CrossRef]
25. Fukuda, T.; Yamamoto, M.; Yamaguchi, T.; Kakeshita, T. Magnetocrystalline anisotropy and magnetic field-induced strain of three martensites in Fe_3Pt ferromagnetic shape memory alloys. *Acta Mater.* **2014**, *62*, 182–187. [CrossRef]
26. Migliori, A.; Sarrao, J.L.; Visscher, W.M.; Bell, T.M.; Lei, M.; Fisk, Z.; Leisure, R.G. Resonant ultrasound spectroscopic techniques for measurement of the elastic moduli of solids. *Physica B* **1993**, *183*, 1–24. [CrossRef]
27. Tanaka, K.; Okamoto, K.; Inui, H.; Minonishi, Y.; Yamaguchi, M.; Koiwa, M. Elastic constants and their temperature dependence for the intermetallic compound Ti_3Al. *Philos. Mag. A* **1996**, *73*, 1475–1488. [CrossRef]
28. Gruner, M.E.; Adeagbo, W.A.; Zayak, A.T.; Hucht, A.; Entel, P. Lattice dynamics and structural stability of ordered Fe_3Ni, Fe_3Pt and Fe_3Pt alloys using density functional theory. *Phys. Rev. B* **2010**, *81*, 064109. [CrossRef]
29. Sternik, M.; Couet, S.; Łażewski, J.; Parlinski, P.T.; Vantomme, A.; Temst, K.; Piekarz, P. Dynamical properties of ordered Fe-Pt alloys. *J. Alloys Compd.* **2015**, *651*, 528–536. [CrossRef]
30. Yamamoto, T.; Yamamoto, M.; Fukuda, T.; Kakeshita, T.; Akai, H. An interpretation of martensitic transformation in $L1_2$-type Fe_3Pt from its electronic structure. *Mater. Trans.* **2010**, *51*, 896–898. [CrossRef]