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First-principles study of the elastic properties and electronic structure of NiTi, CoTi and FeTi

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ABSTRACT

First-principles total-energy electronic structure calculations based on the full-potential linearized augmented plane-wave method have been carried out to study the elastic properties and electronic structure of NiTi, CoTi and FeTi. The calculated values for the equilibrium lattice constants and elastic properties are generally in good agreement with experiments. From the calculated results, it is found that the anisotropy factors are ordered as follows $\text{NiTi} > \text{CoTi} > \text{FeTi}$ and the shear moduli C' are ordered as $\text{FeTi} > \text{CoTi} > \text{NiTi}$. The close relationship between the anisotropy factor and the stability of the B2-type Ti-based alloys has been discussed. It is shown that a lower anisotropy factor is an important factor for the existence of the B19' structure in NiTi. The total electron densities of states (DOSs) and the d DOS of the Ti element of the three alloys have been calculated. The stabilities of NiTi, CoTi and FeTi have been discussed on the basis of the present results on the electronic structure calculations.

§1. INTRODUCTION

Martensitic alloys have been of interest to metallurgists for nearly a century owing to their unique properties, such as the shape memory effect and superelasticity, which are displayed during martensitic transformations (Otsuka and Shimizu 1986, Shabalovskaya 1985). Although much experimental and theoretical work has been devoted to the study of these extraordinary phenomena, many aspects of the transformation are still elusive. Ti-based alloys are important members of this alloy class. Most Ti-based alloys have an ordered B2 structure at high temperatures and transform to a stable low-temperature austenitic phase when the temperature decreases. The transformation temperatures M_s are about 320 and 40 K for NiTi and CoTi respectively; FeTi retains the B2 structure until 0 K. Some of these alloys exhibit curious elastic behaviour near M_s (Ren *et al.* 1999). They can be strained beyond the elastic limit and, when reheated, they can regain their original form, which is known as the shape-memory effect (Perkins 1975). Recently, experimentalists have established some empirical formulae for the temperature to martensitic transformation for some Ti-based alloys. Shabalovskaya *et al.* (1993) found a relationship between the stability and the electronic structure of the Ti-based shape-memory alloy using X-ray photoemission spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) data.

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At the same time, a mechanical explanation of the martensitic transformation invariably is related to a lattice instability due to the softening of the $\{110\}$ $\langle 1\bar{1}0 \rangle$ shear modulus $C' = (C_{11} - C_{12})/2$ of the bcc high-temperature phase, following the idea of Zener (1947). This idea found significant development after Shapiro *et al.* (1986, 1989) discovered a phonon softening (Ohba *et al.* 1998) dip in the $[110][1\bar{1}0]\text{TA}_2$ branch of NiAl alloy above its M_s . Based on this fact the martensitic transformation is generally regarded to be triggered by a softening of the elastic constant C' and TA_2 phonons, which correspond to $\{110\}$ $\langle 1\bar{1}0 \rangle$ shearing and shuffling of the $\{110\}$ close-packed planes in the parent phase. As a result, these close-packed planes become the basal planes of the stacking order structure of martensite (Heheman and Sandrock 1971, Kudoh *et al.* 1985).

In this paper, we report first-principles total-energy electronic structure and elastic constant calculations of the B2-type ordered NiTi, CoTi and FeTi alloys. From the calculated results we interpret why FeTi is the most stable and NiTi is the most unstable of FeTi, CoTi and NiTi, and why the B19' phase exists in NiTi.

§2. ELASTIC CONSTANT CALCULATIONS OF NiTi, CoTi AND FeTi

The elastic constants $C_{\sigma\mu\nu}$ are defined by means of a Taylor expansion of the total energy of the system, $E(V, \varepsilon)$, with respect to a small strain ε of the lattice. The Taylor expansion of the total energy at the equilibrium volume V_0 can be written as

$$E(V, \varepsilon) = E(V_0, 0) - P(V_0)\Delta V + \frac{V_0}{2} \sum_{i,j} C_{i,j} \varepsilon_i \varepsilon_j + O[\varepsilon_i^3]. \quad (1)$$

Here, V_0 is the volume of the undistorted lattice, $P(V_0)$ is the pressure of the undistorted lattice at volume V_0 , ΔV is the change in volume of the lattice due to the strain, and $O[\varepsilon_i^3]$ indicates that the neglected terms in the polynomial expansion are cubic and a higher power of the ε_i .

There are 21 independent elastic constants C_{ij} in equation (1). Symmetry reduces this number to three (C_{11} , C_{12} and C_{44}) for the B2 cubic lattices (Nye 1957). At any volume V , the bulk modulus B is related to the elastic constants by $B = (C_{11} + 2C_{12})/3$. The single-crystal shear moduli for the $\{110\}$ plane along the $[1\bar{1}0]$ direction can be simply given by $G_{\{100\}} = C_{44}$ and $G_{\{110\}} = C' = (C_{11} - C_{12})/2$ respectively. The shear anisotropy factor is defined as $A = 2C_{44}/(C_{11} - C_{12})$.

The relationship between $E(V, \varepsilon)$ and ε is determined by a first-principles electronic structure calculation. The elastic constants are then obtained from the curvature of the total energy versus strain curves. A set of three independent calculations have been performed for each alloy for the following strain conditions:

- (1) uniform hydrostatic pressure to determine the equilibrium lattice constants a_0 and the bulk moduli B , where the strain elements are $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = \varepsilon$ and $\varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0$;
- (2) uniaxial strain to determine C_{11} , with strain elements $\varepsilon_3 = \varepsilon$ and $\varepsilon_1 = \varepsilon_2 = \varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0$;
- (3) pure shear strain to determine C_{44} , with strain elements $\varepsilon_6 = \varepsilon$ and $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = \varepsilon_4 = \varepsilon_5 = 0$, and where the volume is allowed to change in the calculation.

The total energy under each of the above-mentioned conditions was calculated self-consistently using the full-potential linearized augmented plane-wave (FLAPW)

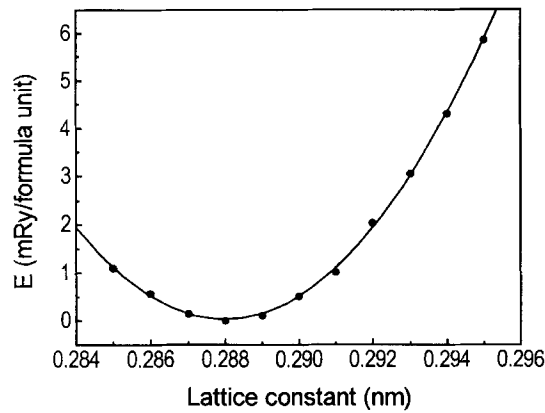
method (Krakauer *et al.* 1979, Wimmer *et al.* 1981, Jansen and Freeman 1984). The FLAPW method is based on the local-density-functional (LDF) theory (Hohenberg and Kohn 1964, Kohn and Sham 1965). In the FLAPW method, no shape approximation is made to the potential and the charge density. The LDF equations, incorporating the Hedin–Lundqvist (1971) exchange–correlation potential, are solved self-consistently for each lattice geometry condition mentioned above. The total energy changes slightly when the crystal is under a small strain. Therefore, a very accurate total-energy calculation is required. The representative points in the Brillouin zone were chosen according to the special points scheme (Monkhorst and Pack 1977). The number of k points was increased until the total energy was converged to less than about 0.1 mRyd. For calculations of the bulk modulus, 126 k points in the irreducible portion of the Brillouin zone were used; the calculations of C_{11} and C_{44} , which involve a lowering of the symmetry, were carried out with 196 k points. Each self-consistent convergence was assumed when the average rms differences between the input and output charge were less than 1×10^{-5} electrons au^{-3} .

The total energy was calculated for different ε values for each of the three strain conditions. As a typical example, the calculated results of $E(V, \varepsilon)$ versus strain ε for FeTi is shown in figure 1. The bulk moduli B and the elastic constants C_{11} and C_{44} can be routinely obtained from these calculated results.

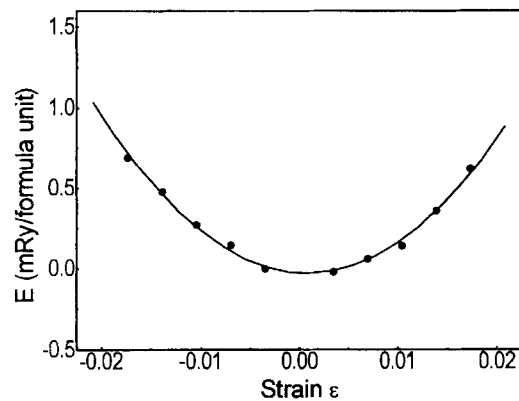
The calculated and the experimental values of the equilibrium lattice constants and bulk moduli of NiTi, CoTi and FeTi are given in table 1. The experimental bulk modulus of FeTi is not known. All the elastic constants were calculated at the theoretical equilibrium volumes. The error in the calculated results compared with the experimental data for the equilibrium lattice constants is about 3–4%, and therefore within the limitation of the local-density approximation calculation. The errors in the bulk moduli of NiTi and CoTi are less than 27%, which is considered to be due to the lower accuracy in the calculation of the electron exchange–correlation energy. It may be improved by using the generalized gradient approximation for the exchange–correlation functional (Perdew 1986, Perdew and Wang 1986).

The calculated elastic constants for NiTi, CoTi and FeTi are compared with available experimental data. Unfortunately, the related experimental data of FeTi are missing, too. The calculations overestimated the elastic constants systematically, especially for the values of C_{44} . It was found that the calculated errors in C_{11} and C_{44} are larger than that of the bulk modulus B . This result was also found in other papers (Iotova *et al.* 1996, Wolf *et al.* 1999) using first-principles calculations. It is thought that there are two reasons for this: one is that the lower symmetry in the C_{11} and C_{44} calculations lead to low precision in the calculations, and the other is that the higher-power terms in equation (1) may have more influence of the C_{11} and C_{44} calculations than on the B calculations. Since the same convergence criterion was adopted in all the calculations, the results can qualitatively reflect the relative elastic properties of these alloys, although the agreement between theoretical and experimental results sometimes is not quite satisfactory.

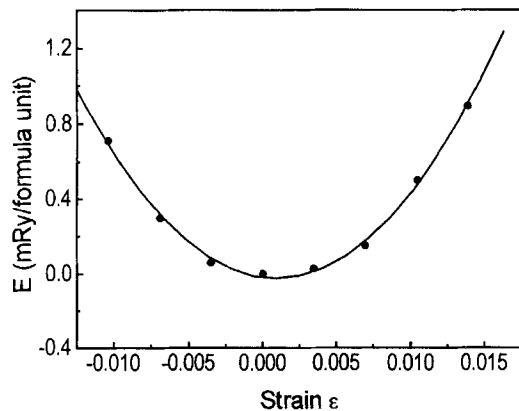
It can be seen from table 2 that the anisotropy factors A of NiTi and CoTi are far smaller than those of the usual martensitic alloys, such as CuZn ($A = 8$) (Prasetyo *et al.* 1976) and NiAl ($A = 14.6$) (Enami *et al.* 1976). It is inferred that the higher A is a sufficient condition for the B2-to-B19 martensitic transformation. However, the smaller anisotropy factor corresponds to the stronger correlation between C_{44} and C' and it is considered that the stronger correlation between C_{44} and C' is responsible for the B2-to-B19' transformation in NiTi just as suggested by Ren and



(a)



(b)



(c)

Figure 1. Calculated total energy as a function of (a) lattice constant, (b) strain of tetragonal deformation and (c) strain of orthorhombic deformation for FeTi.

Table 1. Calculated and experimental values of the equilibrium lattice constants and bulk moduli.

Compounds	Experiment		Calculation	
	a_0 (nm)	B (10^{11}Nm^{-2})	a_0 (nm)	B (10^{11}Nm^{-2})
NiTi	0.3010	1.42 ^a	0.294	1.91
CoTi	0.2996	1.52 ^b	0.290	2.04
FeTi	0.2975	—	0.288	1.92

^a From Mecier and Melten (1980).^b From Hideyuki *et al.* (1991).Table 2. Calculated and experimental elastic constants C_{11} , C_{12} , C_{44} and C' and anisotropy factors A .

Compound	C_{11} (10^{11}Nm^{-2})	C_{12} (10^{11}Nm^{-2})	C_{44} (10^{11}Nm^{-2})	C' (10^{11}Nm^{-2})	A
NiTi	2.18	1.78	0.71	0.19	3.68
Experiment ^a	1.62	1.32	0.36	0.15	2.40
CoTi	2.61	1.76	0.99	0.43	2.29
Experiment ^b	2.03	1.29	0.68	0.37	1.83
FeTi	3.04	1.36	1.38	0.84	1.64
Experiment	—	—	—	—	—

^a From Mecier and Melten (1980).^b From Hideyuki *et al.* (1991).

Kazuhiro (1998). It can be seen in table 2 that the anisotropy factor A of CoTi is also small, and there also exists a B2-to-B19' transformation in CoTi (Shabalovskaya *et al.* 1993). This further supported our suggestion. In addition, it is thought that the martensitic transformation involves shearing along the $\langle 1\bar{1}0 \rangle$ direction; so the transformation should be easy if there are a large anisotropy factor A and a small C' . From table 2 it can be seen that the order of the martensitic transformation, or the stability of B2 structure, of the three alloys from difficult to easy is FeTi > CoTi > NiTi. This order is in accordance with the experimental observations.

§3. ELECTRONIC STRUCTURE ANALYSIS

Shabalovskaya *et al.* (1993) investigated the electronic structure and the stability of Ti-based B2 shape-memory alloys by XPS and UPS. Both XPS and UPS reflect the valence-band structure of the alloys. Using their experimental results, they introduced an empirical formula to determine the M_s of Ti-based B2 shape-memory alloys and believed that the M_s of the alloys is directly proportional to the d density of states (DOS) of the Ti element at the Fermi level in B2 alloys. In addition, the lower total DOS at the Fermi level means the higher structural stability of the alloy. The total DOS and the Ti d DOS of NiTi, CoTi and FeTi at the equilibrium lattice constants were calculated in the present study to investigate the relationship between the electronic structure and the stability of the alloys. The calculated results of the total DOSs and the d DOSs of Ti for the three alloys are shown in figure 2.

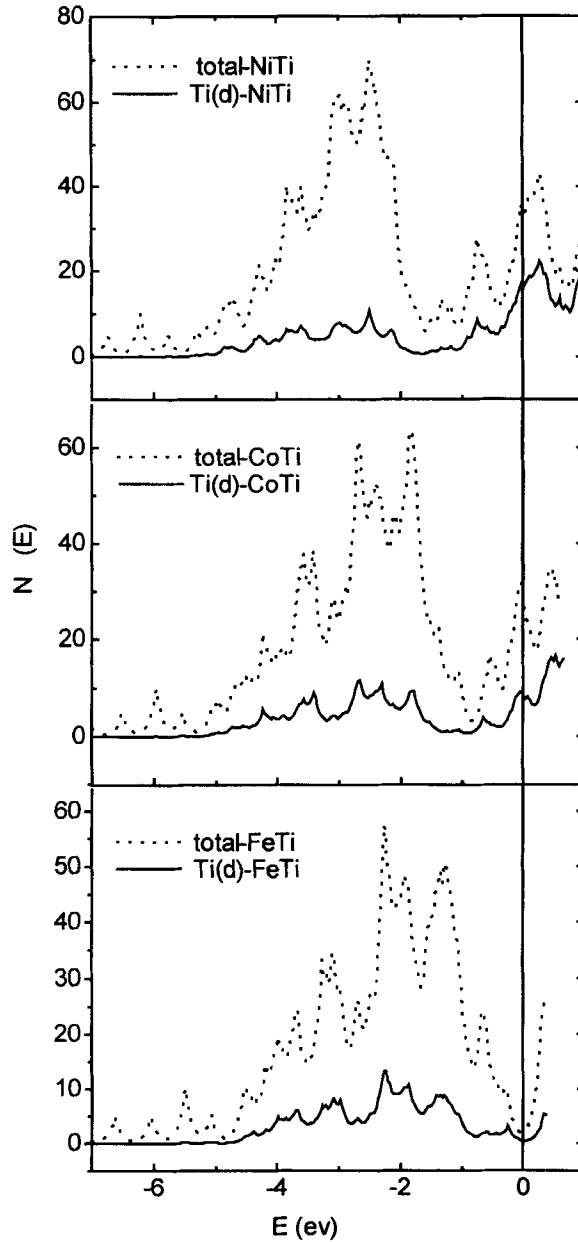


Figure 2. The calculated total and d DOSs of FeTi, CoTi and NiTi. The Fermi level is at 0 eV.

From figure 2 it can be seen that the shapes of the three total DOS curves are similar and all of them comprise two sets of peaks separated by a valley. Table 3 lists the calculated values of the DOSs at the Fermi level for the alloys. The values of the Ti d DOSs at the Fermi level for FeTi, CoTi and NiTi are 0.46, 8.27 and 17.05 states Ryd^{-1} respectively. They are in the order $\text{FeTi} > \text{CoTi} > \text{NiTi}$. This is in accordance with experimental observation.

Table 3. DOSs at the Fermi level.

Compound	Total DOS (states Ryd ⁻¹)	Ti d DOS (states Ryd ⁻¹)
FeTi	1.84	0.46
CoTi	28.21	8.27
NiTi	33.08	17.05

The DOS at the Fermi level of Ti-based B2 alloys is primarily offered by the Ti element. The contributions of the second element are much smaller than those of the Ti element, and it is negligible sometimes (Shabalovskaya *et al.* 1993). The centres of gravity of the d DOSs for Fe, Co and Ni shift towards the bottom of the valence band. At the same time, the d-DOSs at the Fermi level of the Ti element increase in the order FeTi < CoTi < NiTi. The d DOS increase will result in a decrease in the degree of hybridization of the d-d orbits between Ti and M (=Fe, Co or Ni) atoms. In other words, the strength of the d-d bond will decrease (Shabalovskaya *et al.* 1993). Therefore the stability of the alloys will decrease owing to the degeneracy of the d orbit of Ti and the Fermi level.

§ 4. SUMMARY AND CONCLUSIONS

The elastic properties and the electronic structures of FeTi, CoTi and NiTi have been studied by first-principles total-energy electronic structure calculations based on the FLAPW method. The results are in overall agreement with experimental data. The following conclusions are obtained by the study.

- (1) The values of the anisotropy factor A change in the order NiTi > CoTi > FeTi.
- (2) The shear moduli C' change in the order FeTi > CoTi > NiTi.
- (3) Both the total DOS and the Ti d DOS at the Fermi level change in the order NiTi > CoTi > FeTi.

These results indicate that FeTi is the most stable while NiTi is the most unstable of the three alloys. The calculated results show that the anisotropy factors A of NiTi and CoTi are anomalous when they are compared with the usual martensitic alloys. This result is thought to be an important factor for the B2-to-B19' transformations in NiTi and CoTi alloys.

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