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Composition-dependent elastic properties and electronic structures of off-stoichiometric TiNi from first-principles calculations

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Abstract

The composition-dependent elastic properties and electronic structure of off-stoichiometric TiNi with a B2 structure are investigated by using the first-principles exact muffin-tin orbitals method in combination with coherent potential approximation and first-principles plane-wave pseudopotential method (for computing bonding charge densities). The Zener anisotropy, c_{44}/c', increases with increasing Ni contents, but is quite small, indicating a strong correlation between the softening of c_{44} and c' with decreasing temperature during martensitic transformation (MT). For the Ni-rich TiNi, c_{44} increases with increasing Ni content whereas c' decreases. On the Ti-rich side, both c_{44} and c' are insensitive to the composition. It was observed that larger c_{44} corresponds to higher MT temperature, and the composition dependence of elastic modulus is discussed on the basis of the bonding charge densities and electronic density of states. We propose that the strong composition dependence of the elastic modulus of the Ni-rich TiNi can be attributed to the Coulomb static electronic repulsion between the antisite Ni atoms and their surroundings. The insensitivity of the elastic modulus of the Ti-rich TiNi to the composition is due to the absence of such repulsion between the Ti antisites and their nearest neighbors.

Keywords: TiNi; Martensitic transformation; Elastic constants; First principles; Electronic structure

1. Introduction

TiNi binary alloys are well-known shape memory materials and have been extensively used in industry since 1960s when first reported by Buehler and Wiley [1]. Many aspects of these alloys, however, are still not fully understood, among which are the fundamentals of the strong composition dependence of martensitic transformation (MT) temperature [2]. Considerable experimental effort [3–8] has been devoted to determining the composition dependence of MT in TiNi, and it came to a consensus that the transformation temperature is independent of composition on the Ti-rich side but decreases dramatically with increasing Ni content on the Ni-rich side.

Martensitic transformation in TiNi is heralded by a series of ‘‘precursor” effects and one of these is the elastic softening of the high temperature parent phase, i.e., decreasing of elastic modulus with temperature until the starting point of MT. Ren and Otsuka [9,10] suggested that the critical elastic modulus of a martensitic alloy at which the MT occurs is independent of the composition, and they proposed that the composition dependence of the MT temperature is closely related to the composition dependence of elastic modulus. While the correlation between the elastic modulus and the MT temperature through their composition dependence for TiNi alloys was experimentally studied [9,11,12], the underlying physics for the composition dependence of the elastic modulus in this important alloy system is still to be established. The elastic properties of solids are dominated by their cohesive interactions which in turn are determined by the electronic structure of the system. Therefore, first-principles methods based on electronic structure theory are expected to provide a clue to

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understanding the composition dependence of elastic modulus and consequently of the MT temperature.

In this paper, the elastic modulus of TiNi alloys with B2 structure is calculated by the use of a first-principles exact muffin-tin orbitals (EMTO) method. The obtained results are correlated with the composition-dependent MT temperature. The origin of the composition dependence of elastic modulus is discussed by characterizing the variation of bonding charge and density of states with the composition.

2. Computational details

The high-temperature phase of binary TiNi alloys are of cubic B2 (CsCl) ordered structure. Two elastic moduli are critical to the MT of this phase, namely, $c' = (c_{11} - c_{12})/2$ and c_{44}, for the $\{110\}\langle 1\bar{1}0\rangle$ basal plane and the $\{001\}\langle 1\bar{1}0\rangle$ or $\{001\}\langle 100\rangle$ non-basal plane shear, respectively. Both elastic moduli can be calculated readily and reliably from first-principles theory based on density functional theory [13]. The theoretical equilibrium volume V_0 and bulk modulus B_0 of the alloy are first determined by fitting the total energies versus the volume according to Murnaghan equation. With the equilibrium volume, the elastic modulus $c' = (c_{11} - c_{12})/2$ and c_{44} are obtained by using the volume conserving orthorhombic and monoclinic deformations, i.e.,

$$\varepsilon_{\mathrm{o}}(\delta) = \begin{pmatrix} \delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & \delta^2/(1-\delta^2) \end{pmatrix} \tag{1}$$

and

$$\varepsilon_{\mathrm{m}}(\delta) = \begin{pmatrix} 0 & 0 & \delta \\ 0 & \delta^2/(1-\delta^2) & 0 \\ \delta & 0 & 0 \end{pmatrix} \tag{2}$$

and then fitting the total energies $E_{\mathrm{o}}(\delta)$ and $E_{\mathrm{m}}(\delta)$ of the deformed crystal according to

$$E_{\mathrm{o}}(\delta) = E(0) + 2V_0 c' \delta^2 \tag{3}$$

and

$$E_{\mathrm{m}}(\delta) = E(0) + 2V_0 c_{44} \delta^2 \tag{4}$$

respectively. In this paper, six strain steps of δ starting from 0 with interval of 0.01 are used to calculate the total energies of the deformed crystals.

The first-principles exact muffin-tin orbitals (EMTO) method with full charge-density (FCD) technique [14,15] is adopted to calculate the elastic modulus and electronic density of states (DOS) of the off-stoichiometric TiNi. In this method, the effective potential in the one-electron equation is treated with optimized overlapping muffin-tin approximation [15]. This method, implemented with Green Function technique, is very convenient for the coherent potential approximation (CPA) [16,17] calculations, which provides accurate description of the random alloys [15]. In the current calculations, the one-electron equation was solved within the scalar-relativistic and soft-core approximations. The Ti-3d^{2}4s^2 and Ni-3d^{8}4s^2 are treated as valence states. The Green Function was calculated for 16 complex energy points distributed exponentially on a semi-circular contour. Our test calculations on stoichiometric TiNi showed that further increasing the number of the complex energy points does not change the equilibrium volume and elastic modulus. The *s*, *p*, *d*, and *f* orbitals are included in the EMTO basis set. In the one-center expansion of the full charge density, we used the number of orbitals of 10. The conventional Madelung energy was calculated for the number of orbitals of 8. The generalized-gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) [18] was used to describe the electronic exchange-correlation (XC) potential. For the Brillouin zone sampling, we used a uniform *k*-mesh without any smearing technique. The convergence of the elastic modulus with respect to the *k* point mesh has been carefully tested for stoichiometric TiNi as shown in Fig. 1. It is seen that the elastic modulus converges very well with *k*-point mesh beyond 25 × 25 × 25. Therefore, this *k*-point mesh is adopted throughout this work.

There are two sublattices in B2 structured TiNi that are occupied by Ti and Ni atoms at stoichiometric composition. Our previous work [19] demonstrated that, for the off-stoichiometric TiNi, the excess Ti or Ni atoms exist as antisite defects on the sublattice of the deficient component instead of forming vacancies. We assume that the excess Ti or Ni atoms (antisite defects) are distributed randomly on the sublattice of the deficient component, which is treated with CPA in the current calculations. Namely, the geometry of the off-stoichiometric TiNi remains ideal B2 type with one sublattice solely occupied by the atoms of the rich component and the other by the "mixed atoms" of the antisite defects and the atoms of the deficient component according to the composition. This assumption is reasonable for the Ni-rich TiNi because our previous study showed that excess Ni atoms are mutually repulsive when they are close to each other [19]. For Ti-rich TiNi, the excess Ti atoms attract each other so that Ti-rich precipi-

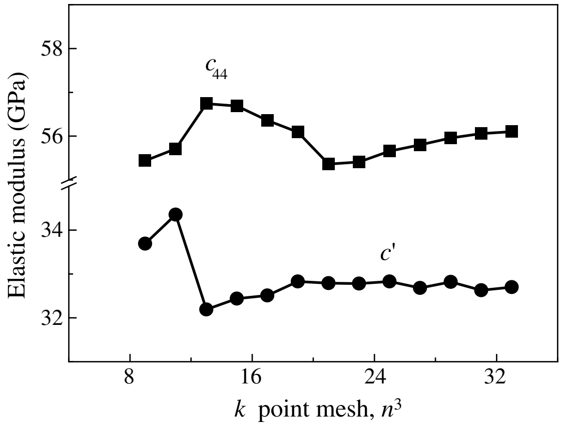

Fig. 1. Elastic moduli c_{44} and c' of the stoichiometric TiNi with respect to k point mesh.