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Martensitic transition in Fe via Bain path at finite temperatures: A comprehensive first-principles study

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ABSTRACT

Due to the magnetic nature of Fe, various phenomena during structural transitions in Fe-based alloys, including martensitic transition (MT), cannot be accurately interpreted even by the state-of-the-art first-principles methods based on density functional theory (DFT), which is mostly limited to zero Kelvin. In the present work, thermodynamics and kinetics of Bain transition in pure Fe, i.e. the simplest model for fcc/bcc transition, are studied by analyzing the minimum energy path (MEP) at finite temperatures. Energies of various lattices and magnetic configurations at ground state are calculated by the standard DFT methods, which are further fitted by the Birch-Murnaghan equation of state (EOS) to obtain the ground state properties. By combing the quasi-harmonic Debye-Grüneisen model with the magnetic partition function approach (PFA), the Helmholtz energies for the body-centered tetragonal lattices with fixed c/a ratio and volume (V) are calculated, where the PFA accounts for the fluctuations of the magnetic configurations. Using free energy surface in the $\{c/a, V\}$ space, the MEP is searched and a correlation between driving force and energy barrier for the fcc/bcc transition is observed. Further combined with previous heterogeneous nucleation models for MT, the correlation shown in the present work is found to be ubiquitous of MTs, and thus governing the formation of martensite.

1. Introduction

Martensitic transition (MT), occurring in various materials, proceeds by collective movement of atoms by lattice straining and atomic shuffle [1,2]. Due to the unique mechanism of transition, the product of MT, i.e., martensite, plays a special role for tuning the properties of various materials, especially metallic materials [3,4] and ceramics [5]. For example, in the development of advanced steels, the effect of transformation induced plasticity (TRIP), where the retained austenite in bainite matrix transforms to martensite under loading, can significantly enhance mechanical properties of steels, and thus are widely implemented in the automobile industry [6].

In the past, tremendous efforts were devoted to thermodynamics, kinetics and crystallography of martensitic transition [1], which has largely boosted the tuning of the properties of materials by martensite [3–6]. Despite the wide application of materials with MT, the microscopic mechanism of the transition under various conditions is still unclear in the relatively simple systems, such as pure Fe, in which the mechanism of MT is dominated by the magnetic degree of freedom at finite temperatures due to the strongly correlated magnetic ordering and lattice deformation [7–9]. Without the magnetic degree of freedom, bcc Fe would be unstable with respect to tetragonal deformation [10–13], contradicting the common knowledge that bcc Fe is stable at low temperatures. Compared with the pressure-induced hcp/bcc transition in Fe [14], the temperature-induced fcc/bcc transition is particularly interesting due to its wide application in the thermo-mechanical processing of steels [3]. To study such an fcc/bcc transition, various crystallographic models have been proposed [15], among which, the Bain path [16], i.e. a homogenous deformation with contraction along the c-axis and extension along the a-axis of a body-centered tetragonal (bct) cell (see Fig. 1), is most frequently adopted. Taken Fe as an example, if the experimental lattice parameters are used [15], the fcc/bcc transition corresponds to the contraction of c-axis and stretching of a-axis of bct lattice by approximately 20% and 12%, respectively. During the transition, the

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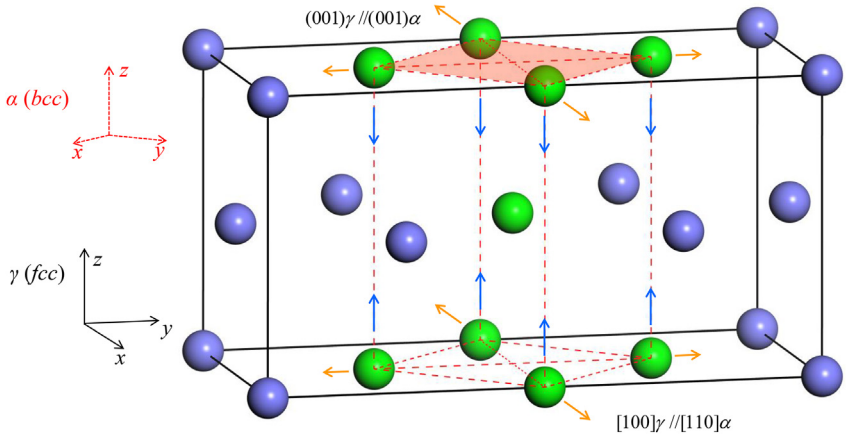

Fig. 1. Schematic diagram of martensitic phase transition from fcc-γ (blue atoms) to bcc-α lattice (green atoms) via Bain path. The martensitic transition occurs by compression of the fcc lattice in the direction [001] (blue arrows), and expansion in the direction <110> (yellow arrows). The orientation relationship is $(001)\gamma//(001)\alpha$ (red plane) and $[100]\gamma//[110]\alpha$. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

orientation relationships are $(001)\gamma//(001)\alpha$ and $[100]\gamma//[110]\alpha$, where α and γ represent bcc and fcc phases, respectively. As the simplest atomic mechanism of MT, Bain path has been applied to analyze the soft mode [17], and combined with various phase-field models to study the microstructure formation upon MT [7–9,18].

As a powerful tool to investigate electronic structure and energetics of materials, density functional theory (DFT) [19] based methods have been applied to the Bain transitions in pure Fe [9–13,20–27]. Following the development of methodologies and computational techniques, DFT is combined with Stoner theory of magnetism [10] and spin polarized calculations [11,13,20–26] to study the energetics of Bain path, with local density approximation (LDA) [20,25], local spin density approximation (LSDA) [11,13,21–24], and general gradient approximation (GGA) [11–13,25,26] being the exchange-correlation (X-C) functionals [19], where the magnetic configurations are modeled using collinear [10,11,13,20–26] and non-collinear magnetic spins [12,25,26]. Despite the significant progress towards understanding the magnetic nature of Fe, the volume of the cell in several calculations of Bain path is fixed using experimental lattice parameters of Fe [11,13,21–23], thus inevitably overestimating the energy due to the restrained degree of freedom. Moreover, the Bain path of relatively simple magnetic states, i.e., the nonmagnetic (NM), ferromagnetic (FM), anti-ferromagnetic (AFM), and double-layered anti-ferromagnetic (AFMD) states were considered using relatively small cells (e.g., 4 atoms), thus cannot consider the long-range magnetic disorder, e.g., the paramagnetic (PM) state.

Although the Bain transition in Fe has been studied extensively using the first-principles methods, all the above calculations were concerned with the ground state transition, which differs from the case at high temperatures due to the fluctuation of magnetic states, hence cannot provide physical insights into the role of magnetism in phase transitions in thermo-mechanical processing of steels. To our knowledge, the only finite temperature first-principles work of fcc/bcc transition along the Bain path was undertaken by Leonov et al. [27], by combining the dynamical mean field theory and DFT with LDA/GGA being the X-C functionals. Although the effects of electronic correlations on magnetism and the fcc/bcc transition were nicely demonstrated in the paramagnetic states, the volume of the lattice was fixed during the Bain transition, which cannot account for the effects of thermal expansion and volume differences between bcc and fcc Fe. Furthermore, the free energy contributed from lattice vibration, which dominates at high temperatures [28,29], was also excluded.

Due to the importance of MT in thermo-mechanical processing of steels, modeling of MT and ultimately controlling the microstructures are of great interest in physical metallurgy [1,3]. Although the Bain transition in Fe is relatively simple as compared with the MT in steels, studies on the Bain transition at finite temperatures can help to understand the effect of magnetic fluctuations on MT, thus provide insights into the role of magnetism in the phase transitions in the processing of steels. Regarding the above, the present work focuses on the Bain transition in Fe at finite temperatures, where the fluctuation of magnetic configurations, in addition to the thermal electrons and lattice vibrations, are considered for the transition. First, with the collinear magnetic spins, the ground state stability and Bain path of various magnetic configurations are calculated. Then, to test the reliability concerning the combination of the quasi-harmonic Debye-Grüneisen model [30] with the magnetic partition function approach (PFA) [31,32] for finite temperature properties of Fe, the thermodynamic properties of bcc and fcc Fe are calculated, with the free energy and iso-baric heat capacity compared to CALPHAD data and experiments. Afterward, the free energies for the lattices along Bain path (i.e. fixed *c/a*) are calculated using the above approach. With the Helmholtz energy surface at finite temperatures, the minimum energy path (MEP) of the Bain path is determined, from which the thermodynamics and kinetics of the Bain path are analyzed.

2. Methodology

In this section, the methodology and computational details for the current study are presented, including the selection of lattices and magnetic configurations (Sec. 2.1), the ground state DFT calculations (Sec. 2.2), the calculations of Helmholtz energy for a given magnetic configuration (Sec. 2.3), the magnetic partition function approach for the fluctuations of magnetic states (Sec. 2.4), and the algorithm to determine the MEP (Sec. 2.5).

2.1. Selection of lattices and magnetic configurations

According to the previous calculations, bcc and fcc Fe are, respectively, FM and AFMD at the ground state [11,13,24]. Above the Curie temperature (T_C, 1043 K [33]), bcc Fe is paramagnetic (PM), where the magnetic spins are mixed randomly and the overall magnetic moment is zero [34]. And fcc Fe is PM in the temperature range of 1185–1667 K [33]. In addition, the energetics of the AFM and NM states of Fe are also widely studied [10–13,20–26].