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Phase diagram, mechanical and thermodynamics properties of metallic Co under high temperature and high pressure

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ABSTRACT

The phase diagram, mechanical and thermodynamic properties of metallic Co are investigated extensively using first-principles calculations in conjunction with a quasi-harmonic Debye model. The simulations indicate that metallic Co is a ferromagnetic hcp (ε) structure at 0 K and 0 GPa, and transforms to a nonmagnetic fcc (β) structure at about 120 GPa under compression, the transition is consistent with the experimental results (crystallographic transition) and other theoretical calculations. Particularly, from the calculated Gibbs free energy, the phase boundary between the ferromagnetic hcp (ε) phase and the ferromagnetic fcc (γ_f) phase is drawn, it is close to the conjecture of Yoo et al. (2000) (the phase boundary between the ferromagnetic hcp phase (ε) and the mixed phases ($\varepsilon+\beta/\gamma$) of the ferromagnetic hcp (ε) structure and the ferromagnetic or paramagnetic fcc (γ), or nonmagnetic fcc (β) structure) as well as the part of experimental data under high temperature and high pressure. The elastic constants of the ferromagnetic hcp- and fcc-Co under temperature are presented for the fist time in theory, they are in reasonable agreement with experiments at zero temperature and zero pressure, and decrease slightly with increasing temperature at $V/V_0 = 1$ or $V/V_0 = 0.97$. In addition, the heat capacity C_V, thermal expansion coefficient α and Grüneisen parameter γ for the ferromagnetic hcp- and fcc-Co are also acquired and predicted successfully in an extended temperature and pressure range.

1. Introduction

The study of 3*d* magnetic metals under pressure and temperature is useful and important for a better understanding of the composition and structure of the Earth's interior. Among these elements Fe is the most widely studied both by experiments and theory [1], as it is the major constituent of the Earth's inner core. Cobalt (Co), being the metal following iron in the periodic table, is potentially important as regards the properties of the Earth's inner core, in term of the fact that the behavior of Co at high pressure and high temperature are closely associated with the physical properties of Fe metal [1–5]. For example, *ab initio* calculations [2] have shown that the elastic modulus of hcp (hexagonal-close-packed) Fe and hcp-Co display a very similar pressure evolution at 0 K; while the hcp phase of cobalt is stable at ambient temperature up to 100 GPa, so the knowledge of the elasticity of cobalt can be utilized to address the issue of the elastic anisotropy of hcp-Fe [3]. The structural behavior of Co at high pressure and high temperature also may shed light on the phase diagram of iron in general [4,5]. Therefore, many experimental and theoretical works have been carried out on the phase diagram or phase transition, elastic constants and magnetism of metallic Co [1–9,11–21].

In experiments, Yoo et al. [4,5] investigated the phase diagram of metallic Co in 1998 and 2000 by X-ray diffraction; they found that hcp-Co transforms to fcc (face-centered cubic) structure in the pressure range of 105–150 GPa at room temperature or at 700 K and ambient pressure. In 2004, Goncharov et al. [6] investigated the anomalies of the elastic and vibrational properties of hcp-Co under pressure by Raman spectroscopy measurements; from 2004 to 2006, the high-pressure elasticity of hcp-Co attracted continuously the experimental working groups' attentions and were measured using inelastic X-ray scattering (IXS) [3], impulsive stimulated light scattering (ISLS) [7] and radial X-ray diffraction (XRD) [8]. In 2008, the elastic constants of hcp-Co at high temperature and high pressure were also measured by IXS [9], which was motivated by the conflicting experimental [10] and theoretical [11] results about the quasiharmonic behavior of hcp-Fe (the compressional and shear velocities are, at constant density,

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temperature dependent in experiment; but temperature independent in *ab initio* finite-temperature molecular-dynamics simulations). The experiment reported in Ref. [9] supported the quasiharmonic behavior of hcp-Fe [9], and indicated that the elasticity of hcp-Co is well described within the quasiharmonic approximation, and the anharmonic high-temperature effects on the elastic modulus, sound velocities, and elastic anisotropies of hcp-Co are minimal at constant density. This is particularly interesting and also is a reason for the present investigation. Recently, Ishimatsu et al. [12] and Torchio et al. [13] studied extensively the magnetism and structure of metallic Co under high pressure using K-edge X-ray magnetic circular dichroism (XMCD) and X-ray absorption near edge spectroscopy (XANES) [12,13], but they obtained some different conclusions about the magnetism of metallic Co under high pressure.

While in theory, in early stage, Min et al. [14] and leung et al. [15] investigated the ground state properties, and magnetic moment of metallic Co using LSDA (former), GGA and LDA approaches (later); In 1996, Uhl et al. [16] found the free energy of fcc-Co intersects that of hcp-Co at 590 K and 0 GPa using spin-fluctuation theory; in 1999, Steinle-Neumann et al. [2] calculated the elastic constants of ferromagnetic hcp-Co under pressure with GGA and LDA approaches; in 2003, Yamamoto [17] studied the structural properties of hcp- and fcc-Co over a wide pressure range using the full-potential linearized augmented plane-wave method with the generalized gradient approximation; in 2008, Steinle-Neumann [18] investigated systematically the elastic properties (ferromagnetic and nonmagnetic, hcp and fcc), magnetic moment and phase transition of metallic Co under pressure with Yamamoto's method [17]; in 2010, Shang et al. [19] calculated the elastic constants of both metallic Co and other some elements via VASP code; the magnetism and phase transition of metallic Co under pressure were also simulated by Mohammed et al. [20] and Saal et al. [21] using first-principles calculations with GGA or LDA approximation; the anomaly in the E_{2g} mode phonon frequency variation under pressure was also affirmed theoretically [1].

However, for our best knowledge, few theoretical studies dealt with the elastic, thermodynamics properties and phase transition of metallic Co under high pressure and high temperature. Given the importance of metallic Co in general and some curious properties of metallic Co, in the paper, we focus on the phase transitions, mechanical and thermodynamics properties of metallic Co under high pressure and high temperature using first-principles calculations in conjunction with a quasi-harmonic Debye model. The rest of this paper is organized as follows. Section 2 briefly elaborates the computational details. The results and detailed discussions are presented in Section 3. A short conclusion is given in the last section.

2. Theoretical methods

2.1. Total energy electronic structure calculations

The previous theoretical calculations [14,15] and experiments [4,5,12,13] have shown that metallic Co belongs to ferromagnetic (FM) hcp (hexagonal-close-packed) structure at ambient conditions; but with increasing pressure, the ferromagnetic hcp-Co will transform to fcc structure [5,12], in order to explore the transition from ferromagnetic structure (FM) to nonmagnetic structure (NM) under compression, spin-polarized case (FM) and non-spin-polarized case (NM) for both hcp- and fcc-Co were considered in the present work.

We calculated the electronic structures of metallic Co using the plane-wave pseudopotential density functional theory method [22,23] together with generalized gradient approximation (GGA-PBE) [24] for the exchange–correlation function. The Kohn–Sham equation was solved by means of the ultrasoft pseudopotentials introduced by Vanderbilt [25]. Pseudo-atomic calculations were performed for Co $3d^7 4s^2$. A plane-wave basis set with energy cut-off 500 eV was applied. We used $13 \times 13 \times 10$, $15 \times 15 \times 15$ Monkhorst–Pack meshs for the Brillouin zone samplings of hcp and fcc (primitive cell) structures respectively. The self-consistent convergence of the total energy was 10^{-6} eV/Atom.

A full optimization of the cell structure was performed to acquire the equilibrium structure and enthalpy at each target external pressure, and the optimizing method adopted the Broyden–Fletcher–Goldfarb–Shenno (BFGS) minimization technique [26]. Then the energy versus volume dependence $E(V)$ was obtained. The calculated total energies as a function of volume were fitted to spinodal equation of state [27] under a quasi-harmonic Debye model [28], and the equilibrium volume, bulk modulus and its pressure derivative, Gibbs free energy and other thermodynamic properties at different pressures and temperatures were extracted.

Under the corresponding equilibrium volume (different temperature and pressure conditions), we took a series of different values of a to compute the total energies E, hence the lowest energy $E_{\min}$ and the corresponding equilibrium structure were obtained under the corresponding equilibrium volume. With the corresponding equilibrium structure, the elastic constants of the ferromagnetic hcp- or fcc-Co were calculated via the static finite strain technique [29] using CASTEP code. The maximum strain amplitude was set from −0.003 to 0.003 with the step of 0.001, all forces on atoms were converged to less than 0.002 eV/Å. With the calculated elastic constants, we computed other some mechanical qualities, such as bulk modulus, shear modulus, using the method introduced in Ref. [30].

Combining first-principles calculations with the quasi-harmonic Debye model [28], one could calculate the thermodynamic quantities of metallic Co. By the means, the thermodynamic properties of some materials, such as c-BN [31], MgB2 [32] and MgF_2 [33] have been successfully drawn, and the phase transitions and mechanical properties of some materials (such as metallic Ti [34] and Fe [35]) under pressure and temperature have been also simulated and discussed.

3. Results and discussion

3.1. The ground structure, and phase transition under high temperature and high pressure for metallic Co

The experimental structural information for both hcp- and fcc-Co [36,37] was used as initial input. The $E-V$ curves of the ferromagnetic hcp and nonmagnetic hcp, ferromagnetic fcc as well as nonmagnetic fcc structures of metallic Co are presented in Fig. 1. From the point of view of energy, it is seen that the ferromagnetic hcp structure has the lowest energy and should be the most stable structure in all structures at 0 K and 0 GPa, while the ferromagnetic fcc structure is a metastable phase at the conditions, these are consistent with the experiments [4–5,12–13] and other theoretical calculations [14,15]. With the methods introduced in Section 2, the obtained structural parameters, bulk modulus and its pressure derivative at 0 GPa and 0 K for the ferromagnetic hcp- and fcc-Co are listed in Table 1, together with the available experimental and other theoretical data. It is noted that the different experiments [5,38,39] and the present theory, as well as other theories [1,2] present the different results, but the differences of these results are in a accepted range. On the other hand, as the results of GGA calculations, lattice constants are overestimated a little;