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Magneto-elastic effects and thermodynamic properties of ferromagnetic hcp Co

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ABSTRACT

Using first principles projector augmented wave (PAW) potential method, the magneto-elastic effects and thermodynamic properties of ferromagnetic hcp Cobalt at high pressure and temperature are investigated. The calculated elastic constants from PBE+U method demonstrate a noticeable improvement with regard to experimental data. Various physical quantities under high pressure also present significant improvements, such as the bulk modulus, shear modulus, Young's modulus, Debye temperature, various sound velocities and the normalized acoustic velocities in the meridian plane. That is due to the fact that Cobalt system possesses large correlation effects. Meanwhile, the phonon dispersion curves are in excellent agreement with experimental data. It is not observed any anomaly or instability under compression. However, according to the E_{2g}-phonon frequencies, the obtained pressure variation of C_{44} elastic modulus also suggests that the system has miraculous magneto-elastic effects. Moreover, the pressure and temperature dependence of thermodynamic properties are derived within the *quasi*-harmonic approximation for the first time. The obtained Grüneisen ratio, Anderon–Grüneisen parameter and the volume dependence of Grüneisen ratio display manifestly temperature and pressure dependences.

1. Introduction

The magnetic 3d transition metal under compression and expansion is an outstanding model system to understand the composition and structure of the Earth's core better. For instance, the study of hexagonal close-packed (hcp) Fe under high pressure and temperature is of great geophysical and high-pressure physical interest. However, the hcp Fe has been considered to be nonmagnetic and no single crystal of hcp Fe has been grown to date. Since studying of elasticity under compression on ferromagnetic hcp Fe are inundated with challenges, more and more attention are focused on the metal adjacent to Fe in the Periodic Table, i.e. hcp Cobalt. The study of Co provides a number of advantages over Fe to study the hcp structure of 3d transition metals. Because the pressure–temperature (P–T) phase diagram of Co shows that the ferromagnetic hcp Co has no phase transition until temperature goes higher than 695 K at ambient pressure and can be stable up to 100 GPa at room temperature. Recent experiment has proved that the magnetic moment of hcp Co can be even stable up to higher temperature under certain chemical conditions [1].

Elastic constants directly describe the response of the crystal to external stresses and are essential for many practical applications related to the mechanical properties of materials, such as load deflection, thermo-elastic stress, fracture toughness, etc. Since modern high-pressure advances in diamond-anvil-cell techniques [2], there were lots of experimental techniques on the high-pressure elasticity of single hcp Co, such as inelastic x-ray scattering (IXS) [3], impulsive stimulated light scattering (ISLS) [4], and radial x-ray diffraction (XRD) [5] and so on. Nevertheless, these studies did not reach the critical pressure region above 60 GPa. Using ISLS and Raman scattering methods to investigate the elastic and vibrational properties of hcp Co up to 120 GPa, Goncharov et al. discovered that the Raman active transverse optic (TO) phonon mode showed a change in slope near 60 GPa [6]. The anomalous behavior was confirmed by Antonangeli et al. through determining the longitudinal acoustic phonon dispersion of polycrystalline Co by IXS [7]. It is observed that the slope of the linear variation of sound velocities immediately as the pressure above 75 GPa. But this change occurred well below the phase transition pressure, it was attributed to magneto-elastic effects, which were supported by the onset of a loss of magnetic moment in hcp Co predicted by the density functional theory (DFT) computations [8–10]. Generally, first-principles calculations have been improved in reliability and accuracy and have been widely used to predict the high pressure–temperature behavior, deepening the fundamental

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understanding of the experiments. However, direct DFT calculations are often difficult to represent the magnetic properties of Co and thus cause a considerable change in aggregate elastic properties. In this case, the high pressure elastic properties agree qualitatively with experimental data, while they have greatly deviations from experimental values in the quantitative. In this paper, using different computational methods based on first-principles, the problem of how to obtain accurately elastic properties of ferromagnetic hcp Co is solved.

Despite that the thermodynamic properties of ferromagnetic hcp Co were studied experimentally in considerable details, there was less work on thermodynamic properties of hcp Co using increasingly pervasive DFT. Most of theoretical thermodynamic studies on ferromagnetic hcp Co were performed by semi-empirical theory. They were used to choose a model that was particularly useful for the treatment of the thermodynamic properties of the 3d ferromagnetic elements. The model was always based upon the phenomenological description of the magnetic and the nonmagnetic contributions to the Gibbs energy of the substance. Recently, the supercell method is established as a good method for calculating the vibrational and thermodynamic properties. Therefore, investigating the magneto-elastic effects from lattice vibrations is another aim of our work. Furthermore, under *quasi*-harmonic approximation (QHA), the study of thermodynamic properties at high temperature and high pressure is also the fundamental understanding of the experiments.

This paper is organized as follows: in Section 2, we are outlining the method used for the first-principles calculations, along with practical details of the calculations. In Section 3, we apply PAW method based on DFT at high pressure and high temperature of ferromagnetic hcp Co by expanding on previous computational work. The calculated results of elastic, vibrational and thermodynamic properties of ferromagnetic hcp Co are reported and discussed. Finally, in Section 4, we present our summary and conclusions.

2. Theoretical and computational details

2.1. Theory

2.1.1. Elastic properties

Aggregate elastic properties, such as the bulk modulus B, the shear modulus G and the Young's modulus Y can be derived from the single-crystal elastic constants by Voigt–Reuss–Hill average [11,12]. Combining with the density ρ, the aggregate compressional sound velocity v_L, shear sound velocity v_T and bulk sound velocity v_B are readily obtained from standard relations. The average sound velocity v_m can be accurately estimated [13]. Once the v_m is determined, the Debye temperature Θ_D can be expressed [14]. The acoustic vibrational modes of a solid in the long-wavelength limit are obtained from the Christoffel equation [15]

$$\rho\omega^2 u_i - C_{ijkl}k_j k_k k_l = 0, \tag{1}$$

where ω is the vibrational angular frequency, u_i is the displacement amplitudes and summation convention is used for repeated Cartesian indices, C_{ijkl} is the elastic constant, and k_j is the wave vector components of the vibrational wave. In case of a hexagonal crystal, the acoustic anisotropy can be described as

$$\Delta i = M_i[n_k]/M_i[1\ \ 0\ \ 0] \tag{2}$$

where $M=\rho\omega^2$ and hence $\omega=C_n(k)k$ with $C_n(k)$ the sound velocity for polarization n and direction k, and i denotes the three types of elastic wave (one longitudinal and two polarizations of the shear wave). By solving the Cristoffel equation for hcp Co, the anisotropy of the compressional wave (P) can be obtained from $\Delta P=C_{33}/C_{11}$, and the anisotropies of the wave polarized perpendicular to the basal plane (S_1) and the polarized one in the basal plane (S_2) by followed: $\Delta S_1=(C_{11}+C_{33}-2C_{13})/4C_{44}$, $\Delta S_2=2C_{44}/(C_{11}-C_{12})$.

2.1.2. Thermodynamic properties

Under *quasi*-harmonic approximation (QHA), the Gibbs function $G(V; p, T)$ takes the form

$$G(V;p,T)=E_0(V)+F_{vib}(T;V)+F_{elec}(T;V)+pV. \tag{3}$$

In Eq. (3), the $E_0(V)$ is the static contribution to the internal energy at volume V and is easily obtained from standard DFT calculations. The pV corresponds to the constant hydrostatic pressure condition, $F_{elec}(T;V)$ is the thermal free energy arising from electronic excitations that is also evaluated from first-principles calculations directly, and $F_{vib}(T;V)$ is the vibrational free energy that comes from the phonon contribution. Within the QHA, $F_{vib}(T;V)$ is given by

$$F_{vib}(T;V)=k_BT\sum_{q,\lambda}\ln\left[2\sinh\left(\frac{h\omega_{q,\lambda}(V)}{4\pi k_BT}\right)\right]. \tag{4}$$

In Eq. (4), the sum is over all three phonon branches λ and over all wave vectors q in the first Brillouin zone. k_B is the Boltzmann constant, h is the Planck constant and $\omega_{q,\lambda}(V)$ is the frequency of the phonon with wave vector q and polarization λ, evaluated at constant volume V. Once the phonon spectrum is obtained, the temperature dependence of the entropy $S_{vib}=-(\partial F_{vib}/\partial T)_V$ and the internal energy $U_{vib}=F_{vib}+TS_{vib}$ at constant volume are easily computed. Thenceforth the specific heat capacity is $C_V^{vib}=(\partial U_{vib}/\partial T)_V$. The electronic specific heat at low temperature is obtained from

$$C_V^{elec}=\gamma_{elec}T, \tag{5}$$

where γ_{elec} is the electronic heat capacity coefficient. The total specific heat at constant volume as $C_V=C_V^{vib}+C_V^{elec}$. The specific heat at constant pressure C_p is computed by using the relation

$$C_p=C_V+\alpha_V B_T VT, \tag{6}$$

where the coefficient of volume thermal expansion coefficient α_V and the isothermal bulk modulus B_T are obtained from Vinet equation of state (EOS) [16] fitting.

2.2. Details of the calculations

The static total energy and elastic properties were calculated using the projector augmented wave (PAW) potential method with three different exchange correlation potentials, namely, the local density approximation (LDA) in the scheme of Ceperley and Alder [17] as parameterized by Perdew and Zunger [18], generalized gradient approximation (GGA) of Perdew–Wang (PW91) [19] and Perdew–Burke–Ernzerhof (PBE) [20], as implemented in the Viena Ab Initio Simulation Package (VASP) [21–23]. All pseudopotetials based on the projector augmented wave method explicitly included the Co $3d^84s^1$ electrons in the valence states. To properly describe the magnetic behavior of hcp Co phase, an accurate treatment of the electron correlation in the localized d orbital is crucial. Thus, several typical interactions were employed, such as spin polarization (SP), spin–orbit coupling (SOC) and Hubbard U correction. Hubbard U correction is shown to provide a quite accurate description of the electronic structure and properties of several transition metal and rare-earth systems [24–26]. In present work, the Dudarev implementation with on-site coulomb interaction $U=2.8$ eV and on-site exchange interaction $J=1.0$ eV were used which was close to the value used for bulk Co [27]. A plane wave basis set with a cut-off of 500 eV was used and specific