

Ab initio dynamical stability of tungsten at high pressures and high temperatures

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ABSTRACT

Considering the phonon-phonon interactions, the temperature-dependent phonon dispersion curves of bcc and fcc W are derived at high pressures. Both the fcc and bcc phases are dynamically stable in a wide range of pressures and temperatures. The bcc-fcc phase boundary is obtained by comparing the Gibbs free energy in their dynamically stable regions and the bcc-fcc phase boundary is located above 1200 GPa in the temperature range 300–8000 K.

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1. Introduction

Extensive experimental [1–7] and theoretical [8–13] investigations have been performed for transition metals because of their importance in condensed-matter physics, geophysics, and so on. As for tungsten (W), the melting temperature obtained from the shock-wave experiments [4] is extremely high, while the results [5,6] obtained from the diamond anvil cell (DAC) measurements are lower and increase only a few hundred Kelvin (K) over the pressure range 0–100 GPa. An enormous discrepancy exists in extrapolating the DAC experimental results of W to the shock melting pressure [6,7]. The same problem also emerges in other transition metals [6,7,14]. A possible explanation [6,7,10] is that a solid-solid phase transition occurs at high pressures and high temperatures, and this high-pressure and high-temperature phase may result in a large slope of the melting curve.

Actually, at room temperature, it is known that bcc W is very stable. The DAC experiment has determined the absence of the room-temperature phase transitions for the bulk W up to 423 GPa [15]. Total energy calculations [16,17] indicate that bcc W is stable to very high pressures and the fcc structure is a potential high pressure phase. The dynamical stability of bcc and fcc W has been studied in detail at high pressures [16], together with

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the Bain's transition paths between bcc and fcc W [16,17]. The bcc phase will be dynamically stable up to 1200 GPa [16]. The fcc phase is dynamically unstable at lower pressures and will be dynamically stable at higher pressures [16]. However, the temperature is not taken into account for the phonon calculations in Ref. [16] and the dynamical stability of bcc and fcc W at high temperatures is unknown.

Anharmonic contributions to the free energy are very important and will change the results from the quasi-harmonic approximation for the closely analogous element Mo [18,19]. If the anharmonic effect from the phonon-phonon interactions is taken into account, fcc Mo will be the dynamically stable in a wide range of pressures and temperatures, and the bcc-fcc phase boundary will also change markedly compared with the bcc-fcc boundary derived from the quasi-harmonic approximation [18]. The importance of the anharmonic effect is also apparent in the bcc phases of the group-IIIB (Sc, Y, La) and group-IVB (Ti, Zr, Hf) transition metals [20–22]. However, in the case of W, whether the anharmonic effect is of great importance remains to be demonstrated at high pressures and high temperatures.

The self-consistent *ab initio* lattice dynamics (SCAILD) method [20,21] includes the effect of phonon-phonon interactions and can determine anharmonic phonon dispersion curves at high temperatures. In this work, we perform the SCAILD calculations to investigate the dynamical stability at high pressures and high temperatures for bcc and fcc W.

2. Computational details

The temperature-dependent phonon dispersion curves were computed using the SCAILD method [20,21]. In this approach, the displacements $\mathbf{U}_{\mathbf{R}}$ of the atoms located at equilibrium Bravais lattice sites \mathbf{R} , are regarded as superpositions of all the phonon modes s with wave vectors \mathbf{q} and the displacements are given by

$$\mathbf{U}_{\mathbf{R}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q},s} A_{\mathbf{q}s} \boldsymbol{\epsilon}_{\mathbf{q}s} e^{i\mathbf{q}\cdot\mathbf{R}} \quad (1)$$

where N is the number of atoms in the supercell and $\boldsymbol{\epsilon}_{\mathbf{q}s}$ is the eigenvector of the phonon mode s . The mode amplitude $A_{\mathbf{q}s}$ can be derived from different phonon frequencies $\omega_{\mathbf{q}s}$ through

$$A_{\mathbf{q}s} = \pm \sqrt{\frac{\hbar}{M\omega_{\mathbf{q}s}} \left[\frac{1}{2} + n\left(\frac{\hbar\omega_{\mathbf{q}s}}{k_B T}\right) \right]} \quad (2)$$

where $n(x) = 1/(e^x - 1)$ is the Planck function, M is the mass of atoms, and T is the temperature of a system. The phonon frequencies

$$\omega_{\mathbf{q}s} = \left[-\frac{1}{M} \frac{\boldsymbol{\epsilon}_{\mathbf{q}s} \cdot \mathbf{F}_{\mathbf{q}}}{A_{\mathbf{q}s}} \right]^{1/2} \quad (3)$$

are obtained from the Fourier transform $\mathbf{F}_{\mathbf{q}}$ of atomic forces. The SCAILD method first needs to calculate a starting guess for phonon dispersion curves using a standard supercell calculation. Then because the displacements, forces and phonon frequencies are interdependent, this method can calculate the temperature-dependent phonon frequencies self-consistently according to Eqs. (1)–(3). Because all the commensurate phonons simultaneously present in the same force calculation, the interaction between different lattice vibrations is included. The phonon frequencies are also renormalized by this interaction.

The Hellmann-Feynman forces required for the SCAILD calculations were computed using the VASP package [23]. The PBE form of the generalized gradient approximation (GGA) was employed to the exchange-correlation functional [24]. The projector augmented wave (PAW) method was used to describe electron-ion interactions, and 5p, 5d, and 6s states were treated as valence electrons. The energy cutoff was set to 400 eV throughout. The total energy was converged to 1×10^{-6} eV/atom. Our calculations used the $4 \times 4 \times 4$ supercells of 64 atoms ($3 \times 3 \times 3$ Γ -centered k -point grid) for the bcc and fcc phases. The electronic temperature was also taken into account through the Fermi smearing width in the SCAILD calculations. The vibrational free energy $F_{\text{ph}}(V, T)$ can be calculated from the self-consistent phonon dispersion curves at volume V and temperature T , through the following equation

$$F_{\text{ph}}(V, T) = \int_0^\infty d\omega g(\omega, V, T) \left[\frac{\hbar\omega}{2} + k_B T \ln(1 - e^{-\hbar\omega/k_B T}) \right], \quad (4)$$

where k_B is the Boltzmann constant, \hbar is the Planck constant divided by 2π , ω is the phonon frequency, and $g(\omega, V, T)$ is the density of states of the phonons. In the SCAILD calculations, the vibrational free energy was converged to less than 1 meV/atom. In the total energy calculations, the $25 \times 25 \times 25$ Γ -centered k -point meshes were employed for the primitive cells of bcc and fcc phases.

3. Results and discussion

The bcc and fcc phases of W are fully relaxed at zero pressure and zero temperature. For the bcc W, the predicted equilibrium volume is $V_0^{\text{bcc}} = 16.230 \text{ \AA}^3/\text{atom}$, which accords with the recently experimental value of $15.855 \text{ \AA}^3/\text{atom}$ [25]. At room temperature (300 K), the phonon dispersion curves of the bcc phase at the equilibrium volume V_0^{bcc} are shown in Fig. 1. Our result agrees with the

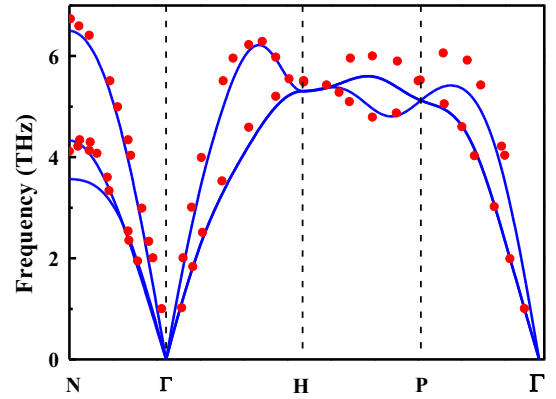


Fig. 1. Experimental [26] (circle symbols) and calculated (solid lines) phonon dispersion curves of bcc W at the volume V_0^{bcc} and temperature 300 K.

experimental result [26], which implies the SCAILD method is reliable. The phonon dispersion curves of the bcc phase at volumes of V_0^{bcc} , $0.65V_0^{\text{bcc}}$ and $0.44V_0^{\text{bcc}}$ (approximately corresponding to pressures of 0 GPa, 318 GPa and 1350 GPa) are shown in Fig. 2 at different temperatures. At the volume of V_0^{bcc} , the bcc phase is dynamically stable up to the melting temperature of 3695 K [27] and the frequencies in the H–P direction slightly soften with the increase of temperature. As the pressure increases at a fixed temperature T , the softening mode in the H–P direction becomes more obvious. Under ultra-compression, the bcc phase will dynamically unstable at lower temperatures, while it will be dynamically stable again at higher temperatures. For example, we can find that the phonon dispersion curves appear imaginary frequencies in the N– Γ direction at the volume $0.44V_0^{\text{bcc}}$ and the temperature 300 K, and then the imaginary frequencies become real at higher temperatures.

We also present the phonon dispersion curves of the fcc phase in Fig. 3 at volumes of V_0^{fcc} ($16.519 \text{ \AA}^3/\text{atom}$), $0.65V_0^{\text{fcc}}$ and $0.58V_0^{\text{fcc}}$ corresponding to approximate pressures of 0 GPa, 287 GPa and 457 GPa, respectively. Contrary to the bcc phase, the fcc phase is dynamically unstable up to 3695 K at the equilibrium volume V_0^{fcc} , though the imaginary frequency regions decrease obviously with the increase of temperature. As the pressure increases at a fixed temperature, the imaginary frequency regions will decrease in size. Noticeably, the fcc phase is dynamically stable at all temperatures for the volume of $0.58V_0^{\text{fcc}}$. Under compression such as the volume of $0.65V_0^{\text{fcc}}$, as the temperature increases, the imaginary frequencies disappear around the gamma point and the fcc phase become dynamically stable at high temperatures. Einarsdotter et al. [16] reported that at ~ 300 GPa and 0 K, there were large number of imaginary frequencies in the phonon dispersion curves of the fcc phase, but our calculations (see Fig. 4) indicate that at ~ 300 GPa and higher temperatures ($T \geq 4000$ K), the imaginary frequencies disappear and the fcc phase becomes dynamically stable. Thus, the anharmonic effect from the phonon-phonon interactions is important and must be taken into account.

The dynamical stability of bcc and fcc phases are investigated in a wide range of pressures and temperatures (Fig. 4). The SCAILD calculations are performed at different volumes and temperatures. The Helmholtz free energy $F(V, T)$ of a system can be written as a sum of three parts [21]:

$$F(V, T) = E_0(V) + F_{\text{el}}(V, T) + F_{\text{ph}}(V, T). \quad (5)$$

Here, $E_0(V)$ is the total energy at 0 K with the fixed ionic positions. The second part $F_{\text{el}}(V, T)$ is the thermal free energy from the electronic excitations and the last term $F_{\text{ph}}(V, T)$ is the vibrational free energy obtained from Eq. (4). The sum of $E_0(V)$ and $F_{\text{el}}(-$

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