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Investigations on the structural, electronic, elastic and thermodynamic properties of niobium silicide under high temperature and pressure

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ABSTRACT

A first principles investigation on the structural, electronic and elastic properties of $NbSi_2$ has been calculated using the plane wave pseudo-potential density functional theory (DFT) method. The lattice constants and elastic constants are obtained. The characters of the band structure and the density of states of niobium silicide ($NbSi_2$) are analyzed, which shows that $NbSi_2$ is metallic. The bulk, shear and Young's modulus for $NbSi_2$ are also calculated. The Debye temperature is calculated from the average elastic wave velocity obtained from the shear and bulk modulus. The thermodynamic properties including the heat capacity C_V and C_P, thermal expansion α, entropy S and Grüneisen parameter γ have been calculated at temperatures from 0 to 2100 K and pressures from 0 to 30 GPa using the quasi-harmonic Debye model. We also found that the present work can give a reference to those not to be experimentally investigated.

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1. Introduction

Transition metal disilicide are of much interest due to the variety of their physical properties and practical applications. These have also two crystal structures: i.e. the tetragonal $C1l_b$ structure and the hexagonal C40 structure. The $C1l_b$ structure has a comprehensive mechanical properties at high temperatures, but low fracture toughness at low temperatures [1,2]. C40 structure compounds are attractive material for microelectronic devices, due to their desirable physical properties, such as high melting temperature, low density and high temperature anomalous yield behavior [3,4]. Among these C40 compounds,

$NbSi_2$ is a typical transition metal disilicide compounds. In recent years, there are many experimental and theoretical studies on the $NbSi_2$. In experimental studies, Chu et al. have studied the elastic properties of hexagonal C40 transition metal disilicides $NbSi_2$ and $TaSi_2$ at room temperature and low temperature using Resonant Ultrasound Spectroscopy (RUS) [5,6]. Laborde et al. have studied the phonon spectra of metallic disilicides VSi_2, $NbSi_2$ and $TaSi_2$ at 300 K and specific heat measurements between 10 K and 250 K by inelastic neutron scattering [7]. Antonov et al. have investigated the optical properties of $NbSi_2$ experimentally and theoretically [8]. Lasjaunias et al. have been also extensively studied the specific heat of $NbSi_2$ [9].

tHowever, there are few reports on the elastic and thermodynamic properties of C40 structure $NbSi_2$ with space group $P6_422(D_6^5)$ at high temperature and high pressure in theory. Therefore, the aim of this work is to

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give a systematic theoretical study of elastic and thermo-dynamic properties of NbSi$_2$.

2. Method of calculations

The present first principles DFT calculations are done by means of the CASTEP code [10,11]. The interactions between the electrons and core ions are treated by using ultrasoft pseudopotentials [12]. For the geometry optimizations and property calculations, the exchange–correlation effects are mainly taken into account using the Ceperley–Alder data as parameterized by Perdew–Zunger (CA-PZ) of local density approximation (LDA) [13]. Kinetic-energy cutoff is 600 eV for the plane waves and Brillouin zone integration is performed using a $8 \times 8 \times 8$ Monkhorst–Pack k-point sampling for a primitive cell. The self-consistent convergence of the total energy is 1×10^{-5} eV atom^{-1}. Both the k-point sampling and cutoff have been tested to provide sufficient precision in our calculations.

In order to investigate the thermal properties of NbSi$_2$ at high temperature and high pressure we have used the quasi-harmonic Debye model as implemented in the Gibbs code [14]. The non-equilibrium Gibbs function $G^*(V; P, T)$ takes the form of

$$G^*(V; P, T) = E(V) + PV + A_{Vib}(\Theta(V); T) \tag{1}$$

where $E(V)$, PV, and $\Theta(V)$ are the total energy per unit cell, the constant hydrostatic pressure condition, the Debye temperature, respectively. The Helmholtz free energy A_{Vib} can be written as [15]

$$A_{Vib}(\Theta; T) = nkT \left[\frac{9}{8}\frac{\Theta}{T} + 3 \ln(1 - e^{-\Theta/T}) - D(\Theta/T) \right] \tag{2}$$

where $D(\Theta/T)$ and n are the Debye integral and the number of atoms per formula unit, respectively. Θ is expressed by [16]

$$\Theta = \frac{\hbar}{k} \left[6\pi^2 V^{1/2} n \right]^{1/3} f(\sigma)\sqrt{\frac{B_S}{M}} \tag{3}$$

M being the molecular mass per unit cell and B_S is the adiabatic bulk modulus, approximated by the static compressibility

$$B_S \cong B(V) = V \left\{ \frac{d^2E(V)}{dV^2} \right\} \tag{4}$$

$f(\sigma)$ is given by Refs. [17,18], and σ is the Poisson ratio. Therefore, the non-equilibrium Gibbs function $G^*(V; P, T)$ as a function of $(V; P, T)$ can be minimized with respect to volume V

$$\left(\frac{\partial G^*(V; P, T)}{\partial V} \right)_{P,T} = 0 \tag{5}$$

By solving the Eq. (5), one can get the thermal equation of state $V(P, T)$.

The constant volume heat capacity C_V and the constant pressure capacity C_P, the thermal expansion coefficient$\alpha$and entropy S are taken as

$$C_V = 3nk \left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right] \tag{6}$$

$$C_P = C_V(1 + \alpha\gamma T) \tag{7}$$

$$\alpha = -\frac{\gamma C_V}{B_S V} \tag{8}$$

$$S = nk[4D(\Theta/T) - 3 \ln(1 - e^{-\Theta/T})] \tag{9}$$

γ is the Grüneisen parameter, which is defined as

$$\gamma = -\frac{d \ln \Theta(V)}{d \ln V} \tag{10}$$

3. Results and discussions

3.1. Structural properties

NbSi$_2$ was refined to be a hexagonal crystal with the space group P6$_4$22(D_6^5). The atomic positions are Nb 3c (0.5, 0, 0), Si 6i (0.167, 0.334, 0) [19]. The crystal structure is shown in Fig. 1.

All physical properties are in connected with the total energy. For instance, the equilibrium structural of a crystal is the lattice constants when the total energy obtains its minimum. Once the total energy is obtained, any physical property concerning the total energy can be determined. In a first step a set of calculations were done around optimized minima to obtain the equilibrium ground state energy–volume (E–V) data, where V_0 is the equilibrium volume at zero pressure, which are fitted to the Murnaghan equation of state [20]

$$\Delta E(V) = E - E_0 = B_0 V_0 \left[\frac{V_n}{B_0'} + \frac{1}{1 - B_0'} + \frac{V_n^{1-B_0'}}{B_0'(B_0' - 1)} \right] \tag{11}$$

where E_0 is the equilibrium energy at zero pressure.

The pressure P versus the normalized volume $V_n = V/V_0$ (where V_0 is the equilibrium volume at zero pressure) is obtained through the following relationship:

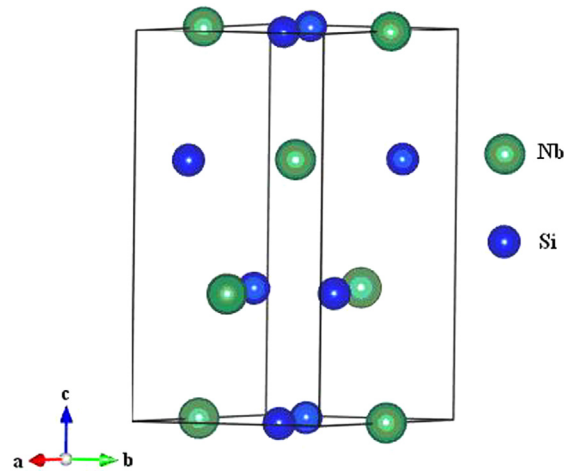$$P = -\frac{dE}{dV} = \frac{B_0}{B_0'} \left[V_n^{-B_0'} - 1 \right] \tag{12}$$

Fig. 1. Crystal structure of NbSi$_2$.