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Pseudo-potential investigations of structural, elastic and thermal properties of tungsten disilicide*

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The plane-wave pseudopotential method using the generalized gradient approximation within the density functional theory is used to investigate the structure and bulk modulus of WSi_2. The quasi-harmonic Debye model, using a set of total energy versus cell volume obtained with the plane-wave pseudopotential method, is applied to the study of the elastic properties and vibrational effects. We have analysed the bulk modulus of WSi_2 up to 1600 K. The major trend shows that the WSi_2 crystal becomes more compressible when the temperature rises and the increase of compressibility leads to the decrease of Debye temperature. The predicted temperature and pressure effects on the thermal expansion, heat capacity and Debye temperatures are determined from the non-equilibrium Gibbs functions and compared with the data available.

Keywords: density functional theory, elastic modulus, Debye temperature, WSi_2
PACC: 6220D, 6550, 7155D

1. Introduction

The refractory metal disilicide WSi_2 has found important technological applications in silicon-based microelectronics because of its high-temperature stability and low electrical resistivities.[1] Its stability, resistance to oxidation and great tensile strength at high temperatures naturally lead to its use in high-temperature furnaces, coatings, integrated circuits, heating elements and ceramic reinforcements in metal matrices.[2−7] Battacharyya *et al*[8] have carried out full relativistic band structure calculations of WSi_2, using norm-conserving pseudopotentials. Weng *et al*[9] have measured the photoemission, Auger spectroscopy, and work functions of room-temperature deposition of Si on a W (001) surface. Antonov *et al*[10] have investigated the optical properties of WSi_2 using the most-localized linear muffin-tin orbital atomic sphere approximation (LMTO-ASA) method.[11] Mattheiss has calculated the valence-electron contribution to the total energy of the hexagonal and tetragonal phases of WSi_2 by means of the linear augmented plane wave (LAPW) method.[12] Itoh *et al*[13] used the LMTO-ASA method to calculate the electronic structure of the (001) surface of WSi_2. Moreover, many scientists have investigated the WSi_2 alloy by different experiments.[14−17] Nevertheless, as far as we know, no theoretical investigation of the elastic and thermal properties at high temperature and pressure has been published up to now.

A study of the elastic properties for materials is well motivated by, for example, the understanding it thereby gains about the cohesion of materials. Knowledge of the heat capacity of a crystal not only provides essential insight into its vibrational properties but is also mandatory for many applications. At intermediate temperatures, however, the temperature dependence of the heat capacity is governed by the details of vibrations of the atoms and for a long time could only be determined from experiments. It is worthwhile noting that many theoretical calculations only gave material properties at zero temperature, without any thermal effects included. So, this has motivated us to explore the structure and elastic properties of tungsten disilicide at high temperature and pressure.

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2. The model and methodology

The WSi_2 crystal has a body-centered $C11_b$ structure (space group $I4/mmm$). The W atom occupies the $2a$ (0, 0, 0) Wyckoff site; the Si atom occupies the $4e$ (0, 0, 1/3+Δ) site, where Δ is the internal structural parameter. We find the optimized internal parameter $\Delta = 0.0013$, which is in agreement with the experimental values ($\Delta = 0.0013$) and $\Delta = 0.0014$).[18] This result has been described in another paper (see Ref.[19]). Firstly, we make a first-principles total energy electronic structure calculation. First-principle calculations are performed using density functional theory incorporated with the plane-wave pseudopotential technique, as implemented in the CASTEP code.[20] The generalized gradient approximation (GGA) of the revised Perdew–Burke–Ernzerhof[21] is used for describing the exchange-correlation interaction. Our tests guided the choice of 450 eV for the energy cutoff, $E_{\rm cut}$. A 13×13×6 gird of k points is adopted for sampling the Brillouin zone.[22] The total energy is converged to within 5×10^{-7} eV/atom.

Then, a recently developed Debye-like model (quasi-harmonic Debye model)[23] is implemented. This method has been described in detail elsewhere (see Ref.[23]), here we give only a brief overview for completeness. In this method, the isotropic approximation is used to determine the Debye temperature given by

$$\theta_{\rm D} = \frac{h}{2\pi}(6\pi^2 V^{1/2} n)^{1/3} f(\sigma)\sqrt{\frac{B_S}{k_{\rm B}^2 M}}. \qquad (1)$$

In this equation, V, M, n, B_S, $f(\sigma)$, and $k_{\rm B}$ are the molar cell volume, the mass, the number of atoms per unit cell, the adiabatic bulk modulus, a function that depends on the Poisson ratio σ of the solid, and the Boltzmann constant, respectively. A simple way to use the Debye model is to consider that B_S is equal to isothermal bulk modulus B_T, leading to the following equation:

$$B_S \approx B_T = V\left(\frac{{\rm d}^2 E}{{\rm d}V^2}\right), \qquad (2)$$

where E is the total energy. The non-equilibrium Gibbs function G^* $(V; P; T)$ can be described as:

$$G^*(V; T; P) = E(V) + PV + A_{\rm vib}(T, \theta(V)), \qquad (3)$$

where $A_{\rm vib}$ is the vibrational Helmholtz free energy given by the Debye model. Then, the Gibbs function is minimized and the thermal equation of state is calculated. In this method, phonon contributions and anharmonic effects are also considered. A detailed description of this procedure can be found in Ref.[23] and references there in.

3. Results and discussion

3.1. Elastic properties

The pressure and temperature dependences of the relative volume V/V_0 of WSi_2 are plotted in Fig.1. As the pressure increases, the relative volume V/V_0 decreases, which means that the cell volume V decreases rapidly. It is noted that as the pressure P increases, the relative volume V/V_0 decreases at a given temperature. The value V/V_0 at higher temperatures is less than that of lower temperatures at the same pressure. When temperature T increases, the curve of V/V_0–P becomes steeper, indicating that the WSi_2 alloy is compressed much more easily with increasing temperature.

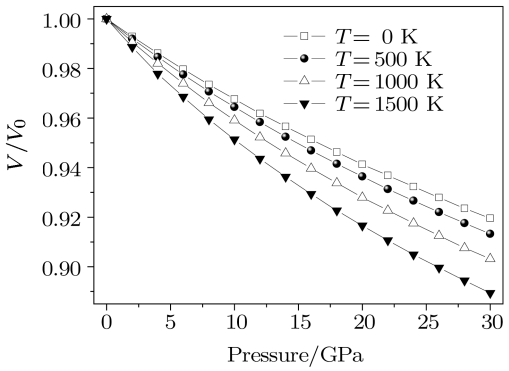


Fig.1. Variations of the relative volume V/V_0 with pressure for different temperatures.

Using the quasi-harmonic Debye model, the relationship of the bulk modulus B as a function of temperature T can be obtained, as shown in Fig.2. The calculated bulk modulus B is 241.5 GPa at 0 K and 229.8 GPa at 300 K, which is in agreement with the value obtained by Nakamura *et al* (= 222.4 GPa at room temperature).[24] From Fig.2, we can see that when $T < 100$ K, B is nearly a constant. We conclude that the lattice parameters a and c nearly keep constant and the variation of cell volume is very small in the temperature interval 0–100 K. When $T > 100$ K, the decrease of bulk modulus with temperature is more drastic, which indicates that the cell volume changes rapidly. The bulk modulus B drops by more than 45% between 0 and 1600 K, which indicates that the hardness of WSi_2 decreases with increasing temperature. However, it is found that the effect of tem-

perature on WSi_2 is very moderate as the bulk modulus is still above 130 GPa at 1600 K. By fitting the $B-T$ data points to the third-order polynomial, we obtain

$$B = 244.3067 - 4.61 \times 10^{-2}T - 1.60497 \times 10^{-5}T^2 + 1.74183 \times 10^{-9}T^3, \quad \text{for} \quad T < 1600\ K. \tag{4}$$

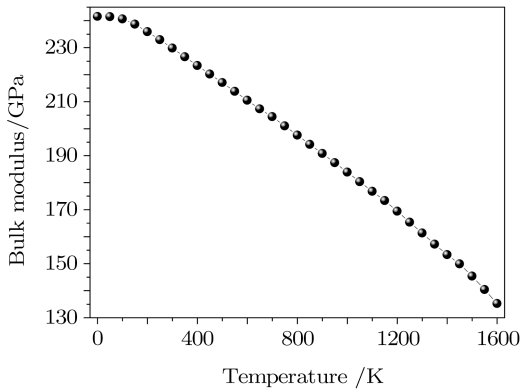


Fig.2. Bulk modulus B as a function of temperature T up to 1600 K at zero pressure.

3.2. Thermal properties

The calculated relationships between heat capacity at constant volume C_v and temperature are plotted in Fig.3. It is found that the heat capacities C_v under different pressures displays roughly a similar behavior for the whole temperature range. The temperature dependence of C_v, follows the Debye law. At low temperature $C_v \sim T^3$ and tends to zero when the temperature vanishes. The heat capacity C_v is strongly dependent on both temperature T and pressure P when $T < 400$ K. This is due to the anharmonic effect of the Debye approximations used here. However, when $T > 400$ K, the anharmonic effect is suppressed. The heat capacity C_v at sufficient high temperatures does not depend much on temperature and tends to approach 75 J/mol·K (Dulong–Petit's rule: $C_v(T) \sim 3R$ for mono-atomic solids). Unfortunately, to our knowledge there is no experimental data for comparison with our calculated result. Hence our work is a first attempt in this direction.

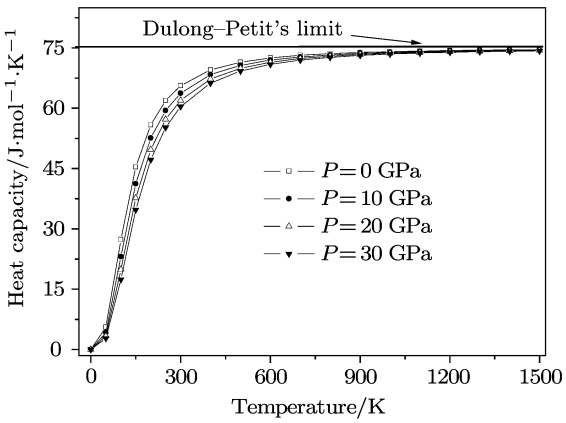


Fig.3. Variations with temperature of the heat capacity C_v.

Table 1. The heat capacity C_P (J·mol^{-1}·K^{-1}) at different temperatures and pressures.

T/K	Ref.[25]	$P = 0$ GPa	$P = 10$ GPa	$P = 20$ GPa	$P = 30$ GPa
0	0	0	0	0	0
50	7.49	5.57	4.21	3.34	2.76
100	29.09	27.47	23.15	19.92	17.41
150	45.49	45.87	41.51	37.89	34.92
200	56.82	56.85	53.28	50.20	47.57
250	64.11	63.47	60.55	58.03	55.85
300	69.58	67.73	65.24	63.14	61.32
400	74.08	72.87	70.79	69.15	67.75
500	75.74	76.03	74.01	72.52	71.33
600	76.64	78.40	76.24	74.75	73.61
700	77.49	80.43	77.99	76.42	75.26
800	78.42	81.33	79.53	77.80	76.57
900	79.31	82.24	80.96	79.02	77.68
1000	80.20	84.22	82.35	80.14	78.68
1100	81.09	86.34	83.74	81.25	79.62
1200	81.98	88.65	85.15	82.34	80.50
1300	—	91.30	86.66	83.44	81.40
1400	—	93.35	88.24	84.56	82.29
1500	—	96.94	89.92	85.72	83.20
1600	—	101.59	91.71	86.90	84.12
1700	—	107.78	93.64	88.18	85.07
1800	—	115.95	95.81	89.52	86.05

Another vibrational property is the isobaric heat capacity C_P. In Table 1, one can notice that the calculated results under zero pressure are in excellent agreement with the experimental data in the temperature interval 0–1200 K. It can be seen from Table 1 that as pressure increases, the isobaric heat capacity C_P decreases at a given temperature. As pressure increases, the increase of C_P with temperature becomes smaller. The effects of pressure on C_P are not as significant as the effects of temperature on C_P.

Then, the thermal expansion coefficients are determined in the temperature interval 0–2000 K.

In Fig.4(a), the relationships between thermal expansion α and temperature under different pressures are clearly seen. For the WSi_2 crystal, there is no phase transition in the temperature and pressure interval as shown in Fig.4.[26] Our calculated value for α equals 1.913×10^{-5}/K at 300 K, which is in agreement with the value obtained by Chaix–Pluchery *et al*[27] ($\alpha = 1.87 \times 10^{-5}$/K at 298 K). The calculated value for α is in relatively good agreement with the linear thermal expansion $\alpha_{\rm L}$ obtained by Lahav *et al*[28] ($\alpha_{\rm L} = 7.199 \times 10^{-6}$/K at 300 K) and Touloukian *et al*[29] ($\alpha_{\rm L} = 7.2 \times 10^{-6}$/K at 273 K) for the WSi_2 thin film ($\alpha \approx 3\alpha_{\rm L}$.[27]). Additionally, the measurements of α are done using polycrystalline samples having defects and porosity. In our case, however, all calculations are related to perfect crystal. As the thermal expansion coefficient has anharmonic behavior, one could not expect linear variations with temperature and pressure. As can be seen, below 400 K, the thermal expansion coefficient, as expected, rises sharply with temperature. As the pressure increases, the increase of α with temperature becomes smaller. At zero pressure, the thermal expansion α of WSi_2 exhibits a parabolic behavior at high temperature while the high pressure α values show an almost linear dependence with the temperature T. It is important to notice that the neglect of intrinsic anharmonicity in the quasi-harmonic approximation leads to an overestimation of thermal expansion at high temperatures and low pressures. In Fig.4(b), we can find that for a given temperature, α decreases dramatically with increasing pressure. When the pressure is above 30 GPa, the thermal expansion α at 2000 K is just a little larger than that of 700 K, which means that the temperature dependence of α is very weak at high temperatures and pressures.

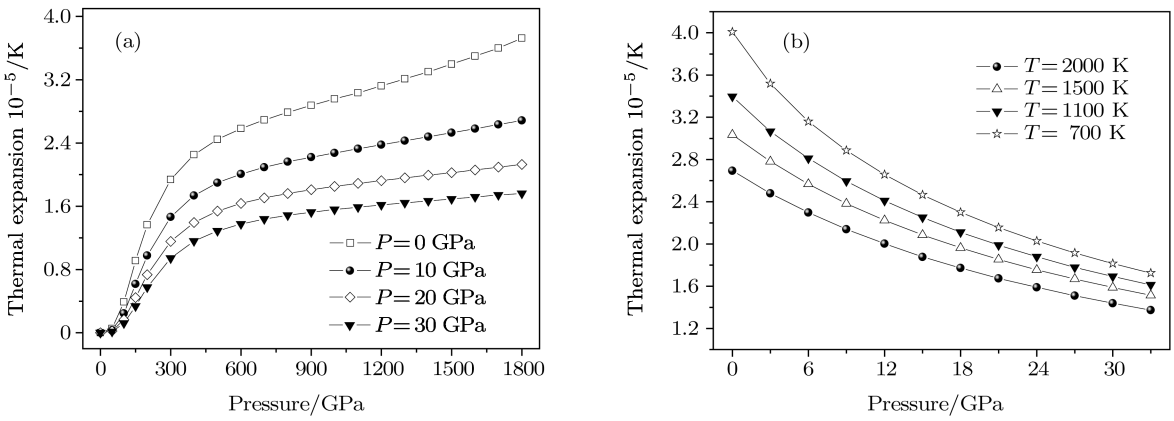


Fig.4. Variations of the volume thermal expansion coefficient with temperature (a) and variations of the volume thermal expansion coefficient with pressure (b).

Finally, the temperature and pressure dependences of the Debye temperature are plotted in Fig.5. Our calculated Debye temperature $\Theta_{\rm D}$ equals 603.3 K at 300 K, which is in agreement with the values obtained by Nakamura *et al*[24] ($\Theta_{\rm D}$ = 625 K at room temperature) and Krontiras *et al*[30] ($\Theta_{\rm D}$ = 580 K at room temperature). It is shown that the Debye temperature $\Theta_{\rm D}$ decreases with pressure. Compared with Fig.2, one can see that the increase of compressibility leads to the decrease of Debye temperature. In Fig.5(b), we note that the Debye temperature $\Theta_{\rm D}$ decreases exponentially with T at high temperatures. As the pressure increases, the decrease of $\Theta_{\rm D}$ with temperature becomes smaller. At a given temperature, $\Theta_{\rm D}$ increases with increasing pressure. These results are in agreement with the results of Debye theory, which applies to many kinds of materials.

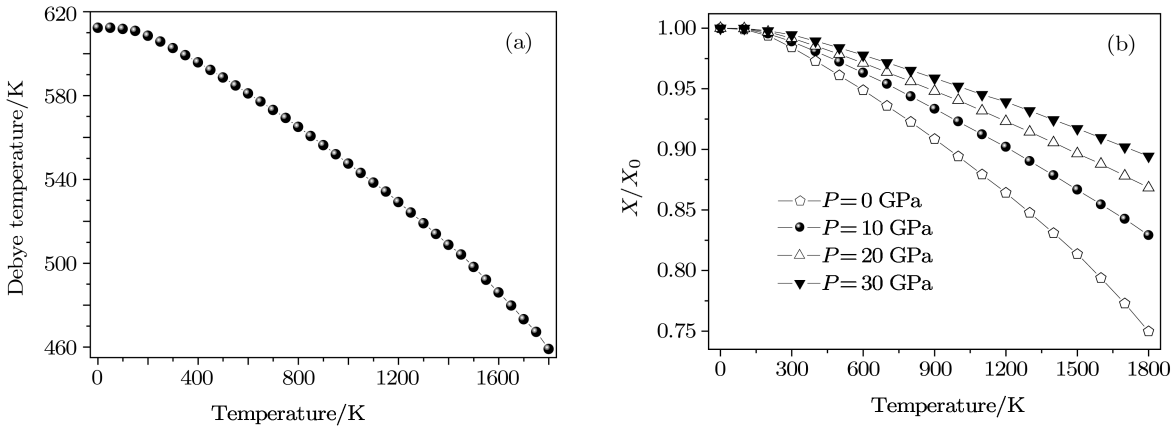


Fig.5. Debye temperature versus temperature for WSi_2 at zero pressure (a) and variations of the Debye temperature with temperature T under different pressures, where X and X_0 are the Debye temperature at any temperature T and zero temperature T_0 under pressures of 0, 10, 20 and 30 GPa, respectively (b).

4. Conclusion

The quasi-harmonic Debye model and the plane-wave pseudopotential method using the generalized gradient approximation within the density functional theory are applied to the study of the bulk modulus, heat capacity, Debye temperature and thermal expansion coefficient of the WSi_2 crystal. We have analysed the bulk modulus of WSi_2 up to 1600 K. The major trend shows that the WSi_2 crystal becomes more compressible when the temperature T rises. The thermal properties of WSi_2 are predicted using the quasi-harmonic Debye model. Significant differences in properties are observed at high temperatures and pressures. Calculations of the thermal properties are performed with the experimental data. Such consistence indicates that first-principles simulation combined with the quasi-harmonic Debye model can reasonably describe the high-temperature and high-pressure behavior of the WSi_2 crystal.

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