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First-Principles Calculations of Elastic and Thermal Properties of Molybdenum Disilicide *

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The first-principles plane-wave pseudopotential method using the generalized gradient approximation within the framework of density functional theory is applied to anaylse the equilibrium lattice parameters, six independent elastic constants, bulk moduli, thermal expansions and heat capacities of $MoSi_2$. 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, thermodynamic properties and vibrational effects. The calculated zero pressure elastic constants are in overall good agreement with the experimental data. The calculated heat capacities and the thermal expansions agree well with the observed values under ambient conditions and those calculated by others. The results show that the temperature has hardly any effect under high pressure.

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Molybdenum disilicide ($MoSi_2$) is an attractive material for structural applications at high temperature, due to its many desirable properties, such as high melting point, moderate density, excellent high-temperature oxidation resistance, strong plastic anisotropy and pertinent electrical resistance.[1,2] These features, combined with good thermal and electrical conductivities, have led to the application of $MoSi_2$ as a high-temperature heating material. On the other hand, it is well recognized that $MoSi_2$ is an attractive wear resistant material for applications at high temperature corrosive environments because of its high hardness and elastic modulus.[3] In recent years, there have been increasing activities in research of materials based on $MoSi_2$ for high-temperature applications, especially in the aerospace industry.[4,5] There have been many scientific investigations for the $MoSi_2$ alloy.[6,7] However, there have been few works reported on the elastic and thermodynamic properties.

A study of the elastic properties for materials is well motivated by, for example, the understanding one gains about the chemical bonds and the cohesion of material. From the elastic constants, one can obtain valuable information about the bonding characteristic between adjacent atomic planes, and about the anisotropic character of the bonding and structural stability. Because these effects are related to elastic properties, there are good reasons to calculate the elastic properties of the $MoSi_2$ alloy. In this Letter, we report the results of calculations based on the density functional theory for $MoSi_2$.

Molybdenum disilicide crystallizes in the body-centered $C11_b$ structure (space group $I4/mmm$). The Mo atom occupies the $2a(0,0,0)$ Wyckoff site; the Si atom occupies the $4e(0,0,1/3+\Delta)$ site, where Δ is the internal structural parameter ($\Delta = 0.0019$).[8] Firstly, we make a first-principles total energy electronic structure calculation. In our calculation, we adopt the plane-wave pseudopotential method (CASTEP code).[9] The generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE)[10] is used for the exchange-correlation energy functional. Initial convergence test guided the choice of 500 eV for the plane-wave cutoff energy. The $13 \times 13 \times 6$ Monkhorst-Pack grids of k-points are adopted for sampling the Brillouin zone.[11] The total energy is converged to 5.0×10^{-7} eV/atom and the force components on each atom are relaxed to less than 5×10^{-3} eV/Å.

Then, the quasi-harmonic Debye model[12] is applied to calculate the equation of states (EOS) and the thermodynamic properties which are constructed from the Helmholtz free energy at the temperature below melting point in the quasi-harmonic approximation. The energy-volume ($E - V$) curve can be obtained by fitting the calculated $E - V$ data points to the universal Birch–Murnaghan EOS,[13] in which the pressure-volume relationship can be expanded as

$$P = 3B_0 f_E (1+2f_E)^{\frac{5}{2}} \Big[1 + \frac{3}{2}(B'-4)f_E + \frac{3}{2}\Big(B_0 B'' + (B'-4)(B'-3) + \frac{35}{9}\Big) f_E^2\Big], \quad (1)$$

where $f_E = [(V_0/V)^{2/3} - 1]/2$, B and B' are hydrostatic bulk modulus and first order pressure derivative of the bulk modulus, B'' is given by[13]

$$B'' = -\frac{1}{B_0}\Big[(3-B')(4-B') + \frac{35}{9}\Big]. \quad (2)$$

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In this model, the non-equilibrium Gibbs function $G^*(V;P,T)$ takes the form[14]

$$G^*(V;P,T) = E(V) + pV + A_{\rm Vib}(V;T), \quad (3)$$

where $E(V)$ is the total energy per unit cell; the second term pV corresponds to the constant hydrostatic pressure condition. The third term $A_{\rm vib}$ is the vibrational Helmholtz free energy, which can be written using the Debye model of the phonon density of states as[14]

$$A_{\rm vib}(\theta_D;T) = nk_BT\Big[\frac{9}{8}\frac{\theta_D}{T} + 3\ln(1-e^{-\theta_D/T}) - D(\theta_D/T)\Big]. \quad (4)$$

The bulk modulus B, the expansion coefficient α, the heat capacity C_v, and the Grüneisen parameter γ are defined as[15]

$$B_T(P,T) = V\left(\frac{\partial^2 G^*(V;P,T)}{\partial V^2}\right), \quad (5)$$

$$\alpha = \frac{\gamma C_v}{B_S V - \gamma^2 T C_v}, \quad (6)$$

$$C_v = 3nk_B\left[4D(\theta_D/T) - \frac{3\theta_D/T}{e^{\theta_D/T}-1}\right],$$
$$C_P = C_v(1+\alpha\gamma T), \quad (7)$$

$$\gamma = -\frac{d\ln\theta_D(V)}{d\ln V}, \quad (8)$$

where

$$D(z) = \frac{3}{z^3}\int_0^z \frac{x^3}{e^x-1}dx, \quad z = \frac{\theta_D}{T}, \quad (9)$$

The Debye temperature θ_D is given as

$$\theta_D = \frac{h}{2\pi}(6\pi^2V^{1/2}n)^{1/3}f(\sigma)\sqrt{\frac{B_S}{k_B^2M}}. \quad (10)$$

In these equations, V, M, n, Bs, $D(z)$ and k_B are the unit cell volume, the mass, the number of atoms per unit cell, the adiabatic bulk modulus, the Debye integral, and the Boltzmann constant; $f(\sigma)$ is a scaling function that depends on Poisson's ratio σ ($\sigma = 0.151$ [16] for $MoSi_2$). In this method, the phononic contributions and anharmonic effects are also considered. A detailed description of this procedure can be found in Ref. [12] and references therein.

In order to compute the elastic stiffness constants C_{ij}, we apply the CASTEP package. It is well known that there are six independent components of elastic constants for the tetragonal C11$_b$ lattice, i.e. C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66}. The zero temperature bulk modulus B_0 are given by[17]

$$B_0 = \frac{(C_{11}+C_{12})C_{33} - 2C_{13}^2}{C_{11}+C_{12}+2C_{33}-4C_{13}}. \quad (11)$$

The calculated lattice constants, elastic constants and bulk modulus of $MoSi_2$ are presented in Table 1.

In Table 1, it is clear that the agreement between our calculated ground state properties, the experimental data and the other theoretical results, is good. The relative errors for the lattice parameters are less than 0.8%, which are within the general accuracy of density functional theory using GGA. The maximum relative error for the elastic constants C_{ij} is only 3%, which is slightly larger than that of lattice constants. Comparison with experimental data indicates the validity of our computational scheme. Due to the symmetry of its crystal structure, the C_{12} value of $MoSi_2$ reflects the velocities of longitudinal and transverse waves in the [110] direction, the C_{44} value reflects the velocities in the [001] and [100] directions. The Cauchy relationships for the elastic constants $C_{13} = C_{44}$ and $C_{12} = C_{66}$ [20] do not hold true in the $MoSi_2$ alloy having tetragonal structure, which means that all of the forces between Mo–Mo, Mo–Si and Si–Si atoms are non-central. On the one hand, the ratio C_{33}/C_{11} is 1.266, which indicates that the ratio of the distance between atoms in the [100] direction to an average distance between atoms in the [001] direction is approximately 1.266 (due to the fact that the elastic constants are closely related to potential energies between atoms). The chemical bond -Si–Mo–Si- along [001] direction is much stronger than the chemical bonds -Mo–Mo- and -Si–Si- along the [100] and [010] directions due to $C_{33} > C_{11}$. Deformation is easier in directions normal to the c-axis than along the c-axis. On the other hand, it is clear that $MoSi_2$ is elastically stable in the tetragonal C11b lattice since $C_{11} > C_{12}$ and all the following quantities are positive: $C_{11}+C_{33}-2C_{13}$, $2C_{11}+C_{33}+2C_{12}+4C_{13}$, C_{11}, C_{33}, C_{44} and C_{66}. The large values of bulk moduli may reflect the fact that the melting point of molybdenum disilicide is high.

Table 1. Lattice constants, elastic constants C_{ij} (GPa) and bulk modulus B_0(GPa) of $MoSi_2$ at 0 K.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B_0	Method	a(Å)	c(Å)
Present work	406.4	111.5	91.8	514.7	202.1	193.7	211.6	PW-PP	3.1849	7.7918
Annealed $MoSi_2$ [16]^a	417.0	104.2	83.8	514.5	204.2	193.6	209.1	FLAPW[6]	3.1772	7.7731
As-grown $MoSi_2$ [16]^a	410.3	125.8	–	520.2	203.0	192.5	–	Expt.[8]	3.2021	7.8509
Ref. [2]^a	404.0	115.0	88.0	505.0	203.0	195.0	209.5	Expt.[18]	3.2021	7.8519
Experiment[19]^b	410.0	114.9	87.5	514.0	206.5	199.6	211.6	Expt.[19]	3.2020	7.8520

^{a}Elastic constants of $MoSi_2$ at room temperature. ^{b}Elastic constants of $MoSi_2$ at $T = 0$ K.

Through the quasi-harmonic Debye model, the relationships of the bulk modulus B as a function of temperature T are calculated and plotted in Figs. 1 and 2. The calculated bulk modulus B is 209.9 GPa at 0 K, which is in excellent agreement with the values obtained by Nakamura *et al.*[16] (209.1 GPa), Tanaka *et al.*[19] (211.6 GPa) and Dietzsch *et al.*[2] (209.5 GPa). The value obtained by the quasi-harmonic Debye model is in agreement with the result of CASTEP code ($B = 211.6$ GPa). From Fig. 1, we can see that when $T < 100$ K, B is nearly a constant, and this results in very little change in unit cell volume. When $T > 100$ K, the bulk modulus B decreases dramatically with the increment of temperature T, which indicates that the cell volume changes rapidly. It is the rapid volume variation that makes the bulk modulus B rapidly decreases. For the $MoSi_2$ alloy the B value drops by more than 40% between 0 and 1100 K, which indicates that $MoSi_2$ can not stay a hard material at high temperature. By fitting the $B - T$ data points to third-order polynomial, we obtain the following relationship

$$B = 211.33245 - 2.138 \times 10^{-2}T - 8.50359 \times 10^{-5}T^2 + 2.78642 \times 10^{-8}T^3, \quad \text{for } T < 1100\,\text{K}. \tag{12}$$

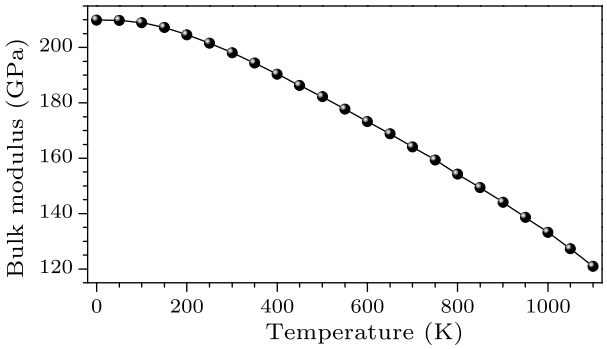


Fig. 1. Bulk modulus B as a function of temperature T up to 1100 K at $P = 0$ GPa.

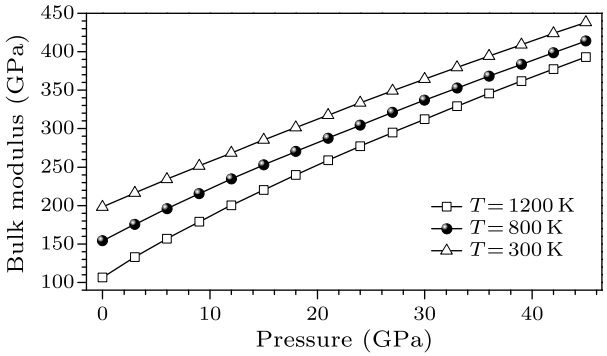


Fig. 2. Relationships between bulk modulus B as a function of pressure at temperatures $T = 300$, 800, 1200 K.

In Fig. 2, it is clear that the bulk modulus B increases with pressure at a given temperature and decreases with temperature at a given pressure. The relationships between bulk modulus and pressure are nearly linear at temperatures $T = 300$, 800, 1200 K, respectively. It shows the fact that the effect of increasing pressure on $MoSi_2$ is the same as that of decreasing temperature on this material. However, there is no experimental data for comparison with our calculated results of bulk modulus at high temperature. Therefore, the obtained results cover this lack of data for $MoSi_2$.

From the quasi-harmonic Debye model, we can determine the heat capacity at constant pressure C_P and the thermal expansion coefficient α of $MoSi_2$ at simultaneous high temperature and high pressure conditions, shown in Figs. 3 and 4.

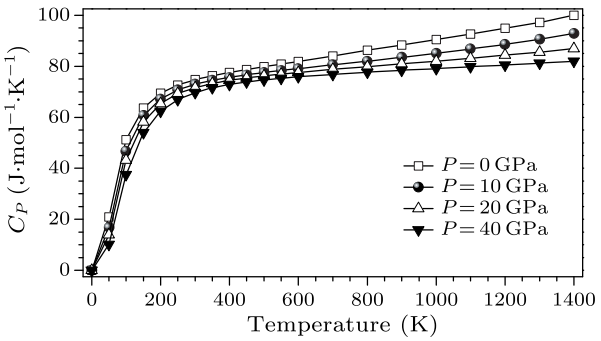


Fig. 3. Variation of the heat capacity C_P with temperature under different pressures.

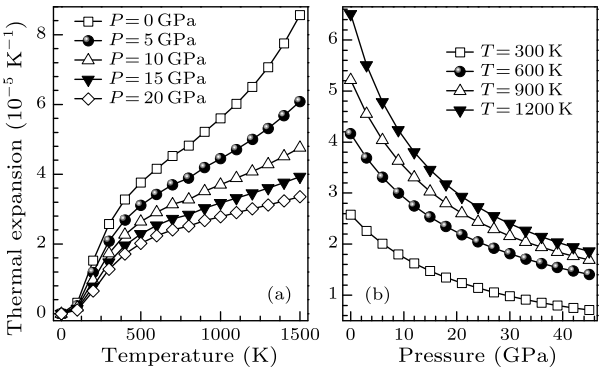


Fig. 4. Variations of the thermal expansion α versus temperature (a) and variations of α versus pressure (b).

The computed heat capacity C_P against temperature curves, shown in Fig. 3, are smooth and without anomalies. As the heat capacity C_P has anharmonic behavior, one could not expect completely linear variation with pressure or temperature. After a sharp increase, up to about 300 K, the behaviors of the $MoSi_2$ alloy under different pressures are similar between 400 and 1400 K. It is clear that when $T < 400$ K, the heat capacity increases with temperature at a given pressure and decreases with pressure at a given temperature. The heat capacity C_P is strongly dependent on both temperature and pressure. When $T > 400$ K, C_P shows a nearly linear dependence with the temperature under a given pressure. These results show the fact that the interactions among ions in $MoSi_2$ have big effects on

heat capacity C_P especially at low temperatures. The calculated zero pressure heat capacities equal to 74.82 J·mol^{-1}K^{-1} (T = 300 K), 78.74 J·mol^{-1}K^{-1} (T = 450 K) and 81.29 J·mol^{-1}K^{-1} (T = 600 K), which are in excellent agreement with the experimental values 75.02 J·mol^{-1}K^{-1} (T = 300 K), 77.22 J·mol^{-1}K^{-1} (T = 450 K) and 79.21 J·mol^{-1}K^{-1} (T = 600 K) determined by the standard differential scanning calorimeter.[21] Under zero pressure, there is an overall topological resemblance of the present heat capacities and those calculated by Bose *et al.*[21]

In Fig. 4(a), the relationships between thermal expansion α and temperature under different pressures are clearly seen. We can find that the variation of α with T is similar to that of C_P. Nevertheless, the effects of pressure on α are more significant than the effects of pressure on C_P. The thermal expansion α increases with T^3 at low temperatures and gradually approaches a linear increase at high temperatures, and then the increasing trend becomes gentler. As the pressure increases, the increase of α with temperature becomes smaller. At zero pressure, the thermal expansion α of $MoSi_2$ exhibits a parabolic behavior at high temperature while the high pressure α values show an almost linear dependences on temperature T, this is an indication of the inadequacy of the quasi-harmonic approximation at high temperatures and low pressures.

In Fig. 4(b), we can find that for a given temperature, α decreases dramatically with increasing pressure. The higher the temperature is, the faster the thermal expansion decreases. When the pressure is above 40 GPa, the thermal expansion α at 1200 K is slightly larger than that of 600 K, which means that the temperature dependence of α is very weak at high temperature and pressure. Our calculated $\alpha = 2.575 \times 10^{-5}$/K at 300 K, which is in agreement with the values obtained by Chu *et al.* ($\alpha = 2.58 \times 10^{-5}$/K at 298 K)[22] and Zhao *et al.* ($\alpha = 2.56 \times 10^{-5}$/K at 298 K).[23] However, the calculated values may be inaccurate at high temperatures and low pressures for the following reasons: (1) the use of the quasi-harmonic approximation may not be justified at temperatures near the melting point; (2) the experimentally measured $MoSi_2$ alloy contains porosities and defects. In our case, all calculations are related to prefect crystal.

In summary, the quasi-harmonic Debye model formalism with the plane-wave pseudopotential method using the generalized gradient approximation within the framework of density functional theory are applied to the study of the lattice parameters, elastic constants, bulk moduli, thermal expansions, and heat capacities of $MoSi_2$ alloy having $C11_b$ structure. We have analyzed the bulk modulus of $MoSi_2$ up to 1100 K. The major trend shows that a crystal becomes more compressible when temperature is applied. The temperature and pressure dependences of thermal expansions and heat capacities are also successfully obtained. Significant changes in properties are observed above 300 K. Our calculated results are in excellent agreement with the available experimental data. The approach presented here is a promising alternative for the determination of several properties in structures that are difficult or costly to obtain from experiments.

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