



Ab-initio determination of thermodynamic properties of CoSi₂



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ABSTRACT

Cobalt disilicide (CoSi₂) is an interesting and promising metallic material with numerous applications in silicon microelectronics. In this article, various thermodynamic properties of CoSi₂ are studied using first-principles density-functional theory. In particular, Gruneisen parameter, thermal expansion coefficients, Debye temperature and temperature dependent heat capacities are determined using quasiharmonic approximation. The Gruneisen parameter dispersion curves are obtained from the variation of phonon frequencies with volume. The frequencies of zone center phonon modes are calculated to be 348.2 cm⁻¹ (IR active) and 347.1 cm⁻¹ (Raman active). The calculated linear thermal expansion coefficient ($\sim 9.1 \times 10^{-6}/\text{K}$) and Debye temperature (~ 547 K) are found to be in good agreement with reported experimental values. Further, the thermodynamic Gruneisen parameter is calculated to be 1.66. The presented results are expected to generate further interest in experimental investigations of thermal properties of CoSi₂.

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1. Introduction

Transition metal silicides are of great importance not only because of their diverse technological applications but also from fundamental scientific point of view [1–10]. They are excellent materials for applications as ohmic contacts, Schottky barrier contacts, diffusion barriers, gate electrodes and local interconnects in complimentary metal–oxide–semiconductor (CMOS) devices [1–4]. In fact, silicides have played an important role in the development of silicon based microelectronics. Semiconducting silicides are now being considered for applications in silicon-based optoelectronics (IR detectors and LEDs), photovoltaics and as thermoelectric materials [11]. In addition to technological applications, silicides also exhibit many fascinating properties such as kondo lattice behavior, quantum critical phase transition, and non-Fermi liquid behavior [12,13]. Some silicides and their alloys also display diverse magnetic behavior and phases such as helical magnetic ordering, and Skyrmion magnetic phases [14–16]. Over past three decades, silicides of titanium, cobalt, and nickel have been used in integrated silicon microelectronics. Among the transition metal silicides, CoSi₂ is particularly interesting because it is one of the few silicides which can be grown epitaxially on single-crystalline Si(111) substrate [17,18]. Further, CoSi₂ has relatively low resistivity than other silicides such as NiSi₂ making it even more attractive for technological applications. The fabricated single-crystal

CoSi₂/Si(111) interfaces generally show a B-type orientation with interface structure varying according to the preparation [17,18].

Although CoSi₂ have been investigated experimentally due to its technological importance, relatively few theoretical studies of it have been reported. In particular, no theoretical work on its thermodynamic properties has been reported to best of our knowledge. In this article, we present theoretical investigation of various thermodynamic properties and parameters of CoSi₂ within the framework of first principles density-functional theory.

In particular we calculate (1) volume dependence of phonon spectrum, (2) Gruneisen parameter dispersion, (3) linear and volume expansion coefficients, (4) thermal expansion, (5) temperature dependent heat capacities at constant volume and pressure (6) bulk modulus and its temperature dependence and (7) Debye temperature.

The rest of the paper is organized as follows. Theoretical details and computational methodology are described in Sections 2 and 3 respectively. The results and discussions are presented in Section 4. Finally, the concluding remarks are given in Section 5.

2. Theoretical details

In quasiharmonic approximation the Helmholtz free energy $F(V, T)$ at volume V and temperature, T , is given by [19]

$$F(V, T) = E(V) + F_{\text{vib}}(V, T) \\ = E(V) + k_B T \sum_{\vec{q}} \sum_n \ln \left\{ 2 \sinh \left(\frac{\hbar v_n(\vec{q}, V)}{2k_B T} \right) \right\} \quad (1)$$

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where $E(V)$ is static contribution to internal energy at temperature equal to 0 K, F_{vib} is vibrational contribution to free energy, $v_n(\vec{q}, V)$ is the frequency of n 'th phonon mode at the wave vector \vec{q} in the Brillouin zone of the crystal with volume V (per cell), h is the Planck's constant, and k_B is the Boltzman's constant respectively. The equilibrium state of a given crystal is determined by the condition that the variation of Helmholtz free energy ($F(V, T)$) with respect to all possible internal degrees of freedom, at a given temperature, T , and volume, V , is at minimum. In this study, the static energy $E(V)$ is obtained from standard *ab-initio* DFT calculations. It should be noted that the anharmonic contributions to the Free energy are approximately accounted through the volume dependence of phonon frequencies and through deviation of $E(V)$ from the quadratic behavior. Further the contribution of electronic excitations to the Free energy is neglected since the temperatures considered here are well below the electronic energy scale.

The mode Gruneisen parameter $\gamma_n(\vec{q})$ corresponding to n 'th mode and wave vector \vec{q} in the Brillouin zone is given by [20]

$$\gamma_n(\vec{q}) = -\frac{\partial v_n(\vec{q})}{\partial V} \frac{V}{v_n(\vec{q})} \quad (2)$$

The linear thermal expansion coefficient α is given by [20]

$$\alpha = \frac{1}{l(T=298\text{ K})} \left(\frac{\partial l}{\partial T} \right)_p \quad (3)$$

Similarly, the volume thermal expansion coefficient β is defined as

$$\beta = \frac{1}{V(T=298\text{ K})} \left(\frac{\partial V}{\partial T} \right)_p \quad (4)$$

where $a(T=298\text{ K})$ and $V(T=298\text{ K})$ are lattice constant and volume of the unit cell at temperature $T=298\text{ K}$. The temperature dependence of the bulk modulus, $B(T)$, is related to second derivative of the Free energy and is given by

$$B(T) = V \left(\frac{\partial^2 F}{\partial V^2} \right) = V \frac{\partial^2 E}{\partial V^2} + V \left(\frac{\partial F_{vib}(v, T)}{\partial V^2} \right)_T \quad (5)$$

In case of crystals with isotropic or cubic symmetry, the linear expansion is independent of direction and related to volume expansion as $\beta = 3\alpha$.

The heat capacity at the constant volume, C_V , is given by

$$\begin{aligned} C_V &= T \left(\frac{\partial S}{\partial T} \right)_V = \sum_{\vec{q}} \sum_n C_{V,n}(\vec{q}) \\ &= k_B \sum_{\vec{q}} \sum_n \left(\frac{h v_n(\vec{q})}{2 k_B T} \right)^2 \frac{1}{\sin h^2(h v_j(\vec{q})/2 k_B T)} \end{aligned} \quad (6)$$

The thermodynamic Gruneisen parameter γ is calculated from the weighted average of mode Gruneisen parameter $\gamma_n(\vec{q})$ and is given by

$$\gamma = \frac{\sum_n \sum_{\vec{q}} \gamma_n(\vec{q}) C_{V,n}(\vec{q})}{\sum_n \sum_{\vec{q}} C_{V,n}(\vec{q})} \quad (7)$$

The heat capacity at the constant pressure, C_p , is given by

$$C_p = C_V + \alpha_V^2(T) B V T \quad (8)$$

The thermal expansion, ε , is described by

$$\varepsilon = \frac{a(T) - a(T=298\text{ K})}{a(T=298\text{ K})} \quad (9)$$

where $a(T)$ and $a(T=298\text{ K})$ are the equilibrium lattice constants at temperature T and 298 K, respectively. The phonon frequencies as a function of temperature can be obtained approximately through

their volume dependence and can be expressed in terms of linear thermal expansion (ε) and thermodynamic Gruneisen parameter (γ)

$$\frac{v(T) - v(T=298\text{ K})}{v(T=298\text{ K})} \cong 3\gamma\varepsilon \quad (10)$$

The Debye temperature can be calculated using average sound velocity [21] and is given by

$$\theta_D = \frac{h}{k_B} \left(\frac{3}{4\pi V_a} \right)^{1/3} v_m \quad (11)$$

where V_a and v_m are atomic volume and sound velocity respectively. The longitudinal velocity, v_l , and transverse velocity, v_t , in the polycrystalline material is calculated using polycrystalline shear (G) and bulk (B) moduli:

$$v_l = \left(\frac{G}{\rho} \right)^{1/2} \quad \text{and} \quad v_t = \left(\frac{3B + 4G}{3\rho} \right)^{1/2} \quad (12)$$

Finally, the average sound velocity in polycrystalline materials is calculated using v_l and v_t as follows

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_l^3} + \frac{1}{v_t^3} \right) \right]^{-1/3} \quad (13)$$

The polycrystalline shear (G) and bulk (B) moduli are obtained using single crystal elastic constants [22].

3. Computational methodology

Density-functional calculations (DFT) [23] are performed using the ultrasoft pseudopotentials (USPP) [24] as implemented in the PWscf package [25]. The Perdew–Zunger (PZ) parameterization of the local density approximation for exchange and correlation is employed. The kohn–sham wavefunctions are expanded using a standard plane wave basis set with a kinetic energy cutoff of 40 Ry. The Brillouin zone sampling is done using a $16 \times 16 \times 16$ Monkhorst–Pack k -point mesh. The structures are relaxed until the largest force becomes less than 10^{-3} eV/Å and the calculations are converged to 10^{-7} eV/cell. To determine phonon frequencies in the Brillouin zone, we use DFT-Linear response with iterative Green's function approach of density-functional perturbation theory as implemented in PWscf package [25].

4. Results and discussions

CoSi₂ crystallizes in the primitive fcc structure in CaF₂-type lattice with space group $Fm\bar{3}m$. There is one Co and two Si atoms at (0,0,0), (1/4,1/4,1/4) and (3/4,3/4,3/4) positions in the unit cell. The lattice constant of CoSi₂ is calculated to be 5.28 Å and is in good agreement with the experimental value of 5.36 Å. In Fig. 1a the total density of states of CoSi₂ are shown, and in Fig. 1b and c, we show the partial density of states projected onto Co and Si atoms, respectively. The states below the Fermi energy in CoSi₂ are derived primarily from the 3d orbitals of Co. Further, Co 3d orbitals are delocalized and extend throughout the entire valence band. Also, the density of states at the Fermi level in CoSi₂ is significantly smaller than those in pure bulk Co, suggesting that CoSi₂ is a poor metal. It is also clear that the Fermi level in CoSi₂ misses the high density region of 3d states primarily due to low volume density of d -orbitals in the CoSi₂ as compared to that in bulk Co. Fig. 2 shows the charge density contours on CoSi₂ (1 $\bar{1}$ 0) plane. As can be seen in Fig. 2, relatively strong three-center, Co–Si–Co, covalent bonds are formed between Co and Si atoms due to hybridization between these atoms.

Next the phonon modes of CoSi₂ in the Brillouin zone of the fcc lattice are calculated. The zone-center phonon modes of CoSi₂

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