Electronic properties of MoSi$_2$

Mani Shugani$^a$,*, Mahendra Aynyas$^b$, S P Sanyal$^c$ & M Rajagopalan$^d$

$^a$Department of Physics, Sadhu Vaswani College, Bairagarh, Bhopal (M P) 462 030, India
$^b$Department of Physics, C S A Govt P G College, Sehore (M P) 466 001, India
$^c$Department of Physics, Barkatullah University, Bhopal (M P) 462 026, India
$^d$Crystal Growth Center, Anna University, Chennai 600 025, India

*E-mail: shugani.mani@gmail.com

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The electronic structure and ground state properties of MoSi$_2$ have been studied using first principles density functional theory (DFT). The full potential linearized augmented plane wave (FP-LAPW) method within the generalized gradient approximation (GGA) and local spin density approximation (LSDA) for exchange correlation have been used for calculation of total energy. The ground state properties such as equilibrium lattice constants ($a_0$, $c_0$), bulk modulus ($B$), its pressure derivative ($B'/g$), are computed. Apart from the density of states ($N(E_F)$), specific heat coefficient ($\gamma$) are also estimated and compared with the experimental data. The density of states at the Fermi level ($N(E_F)$) is 0.25 states/eV for MoSi$_2$. The band structure and density of states around the Fermi level suggest that this compound is semi-metal in nature. The calculated parameters are found to be in overall good agreement with the experimental data.

Keywords: Density functional theory, Band structure, Density of states, Lattice constant, Bulk Modulus, Specific heat

1 Introduction

Transition-metal silicides (TMS) are the compounds which constitute a diverse class of materials. Due to low resistivity and stability over a wide range of temperature, TMS are useful in operating different electronic systems.$^{12}$ The low electrical resistance of these silicides in combination with higher thermal stability, electron-migration resistance and excellent diffusion-barrier characteristics are crucial for microelectronic applications.$^3$ Increasing activities in the research and development of transition-metal silicides, ensure that they will enter in other fields as well. The disilicides of vanadium, niobium and tantalum are iso-electronic. They crystallize in the same hexagonal structure (type C40 space group with P6$_2$22). The elastic properties of XSi$_2$ (X=V, Nb, Ta, Cr and W) have been reported by Chu et al.$^4$. The structural properties of the group-VI refractory disilicides RSi$_2$ (R= Cr, Mo and W) have been calculated using the linear augmented-plane wave (LAPW) method in the local density approximation (LDA) by Mattheiss.$^5$ Jarrige et al.$^6$ have investigated electronic structure of transition metal silicides both experimentally and theoretically. They suggested that the chemical bonding in silicides is mainly due to the extension of the metal ‘d’ wave function and local structure. Alouani et al.$^7$ have calculated the elastic constants and structural properties of Mo and MoSi$_2$ by using the linear muffin tin orbital (LMTO) method in the atomic sphere approximation (ASA). Lasjaunias et al.$^8$ have reported specific heat measurement of MoSi$_2$. The phase stability, electronic structure and mechanical properties of MoSi$_2$ have been explained by Qiao et al.$^9$, using first principles density functional theory. They focused mainly on bonding characteristics and confirmed that the Si-Si interactions play a central role in the hardness and ductility of MoSi$_2$ materials. The electronic structure of Mo-Si alloys have been investigated by Pankhurst et al.$^{10}$ using valence-band X-ray photoelectron spectroscopy (VBXPS) and density-functional theory. The differences between the VBXPS spectra for MoSi$_2$, Mo$_5$Si$_3$ and Mo$_3$Si are explained in terms of various hybridization involving Si-$p$ and Mo-$d$ states.

Molybdenum disilicide is a material for structural applications at high temperature and known for its technological usefulness. It is at the borderline of ceramic intermetallic compound thus both ceramic and metal processing methods are used to develop the material. The unit cell can be thought of as consisting in three squashed cubic pseudo-cells stacked in the $c$ direction, each pseudo-cell containing an atom at its body center.$^{11}$ The MoSi$_2$ crystallizes in tetragonal
The ground state and electronic properties of tetragonal MoSi$_2$ have been investigated and compared. We have calculated the value of density of states and specific heat coefficient theoretically for the first time by using WIEN2K, an FP-LAPW method.

2 Method of Calculation

The calculations have been performed in the framework of density functional theory (DFT). The full potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2K code has been used. The exchange and correlation effects were treated using the generalized gradient approximation (GGA) in the scheme of Perdew et al., Wu and Cohen, for local spin density approximation (LSDA) calculation. In order to achieve convergence, we expand the basis function up to $R_{MT}K_{max} = 7$ where $R_{MT}$ is the smallest atomic radius in the unit cell and $K_{max}$ gives the magnitude of the largest $k$ vector in the plane wave expansion. The maximum value for partial waves inside the atomic sphere is $l_{max} = 10$ while the charge density is Fourier expanded up to $G_{max} = 12$. The self-consistent calculations are converged when the total energy of the system is stable within $10^{-4}$ Ry. A dense mesh of 1000 $k$ points and the tetrahedral method have been employed for the Brillouin zone integration. The total energies are fitted to Birch equation of state.

3 Results and Discussion

The ground state properties have been determined by minimizing the energy with respect to volume for B$_1$ phase using the first principles FP-LAPW method. The plot of total energy with respect to volume is shown in Fig. 1. These energy values have been fitted to the Birch equation of state to obtain the ground state properties such as equilibrium lattice constants ($a_0$ and $c_0$), bulk modulus ($B$) and its pressure derivative ($B'$) at minimum equilibrium volume $V_0$, which is found to be 40.791 Å$^3$ for tetragonal MoSi$_2$ and corresponding lattice parameters are $a_0=3.212$ Å and $c_0=7.862$ Å within PBE-GGA approximation. Similarly, the equilibrium volumes are 40.012 Å$^3$, 39.208 Å$^3$ and the corresponding lattice parameter values are $a_0=3.191$ Å, $c_0=7.812$ Å and $a_0=3.170$ Å, $c_0=7.759$ Å for WC-GGA and LSDA approximations, respectively, and compared with the experimental and theoretical values in Table 1. The deviation of lattice constants from experimental data has an effect on the total energy. It is observed that our calculated lattice parameters of MoSi$_2$ when compared with the experimental values are underestimated when the electronic exchange and correlation effects are described in the LSDA. While in PBE-GGA approximation these are very close to the experimental values, only 0.1% deviation from the experimental values indicating that our input parameters are moderate. We have studied MoSi$_2$ using PBE-GGA, WC-GGA and LSDA approximations and found that the total energy is minimum in PBE-GGA approximation. Therefore, the structure is stable in this approximation. The

![](image)

Fig. 1 — Variation of total energy with volume of MoSi$_2$

<table>
<thead>
<tr>
<th>Work</th>
<th>Lattice constants</th>
<th>$B$ (GPa)</th>
<th>$B'$ (State/eV)</th>
<th>$\gamma = C_v/T$ (mJ/mol K$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work (PBE-GGA)</td>
<td>3.212 7.862</td>
<td>212.4</td>
<td>3.0</td>
<td>0.26</td>
</tr>
<tr>
<td>Present work (WC-GGA)</td>
<td>3.191 7.812</td>
<td>218.0</td>
<td>3.9</td>
<td>0.25</td>
</tr>
<tr>
<td>Present work (LSDA)</td>
<td>3.170 7.759</td>
<td>228.6</td>
<td>4.0</td>
<td>0.26</td>
</tr>
<tr>
<td>Experimental data</td>
<td>3.206$^a$ 7.847$^a$</td>
<td>210$^a$</td>
<td>-</td>
<td>0.24$^b$</td>
</tr>
<tr>
<td>Other theory</td>
<td>3.186$^c$ 7.800$^c$</td>
<td>222$^c$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Ref. [9],$^b$ Ref. [8],$^c$ Ref. [7].
Fig. 2 — Band structure of MoSi₂

Fig. 3 — Partial density of states of MoSi₂

calculated bulk modulus of MoSi₂ within PBE-GGA agrees well with the experimental value\(^9\). The calculated values of ground state properties are presented in Table 1 together with the available experimental and theoretical data.

The electronic band structure (BS) of tetragonal MoSi₂ is shown in Fig. 2. The lowest lying bands are mainly due to Si-\(s\) like states. The bands lying just above this and below the Fermi level, are mainly due to strong hybridization of Mo-\(d\) and Si-\(p\) like states and also small mixing of Mo-\(p\) like states. The top of the valence band is found at \(\Gamma\)-point, while the bottom of the conduction band is situated at the H-point, and there is an indirect small overlapping between these two points. It shows semi-metallic behaviour because it has negative indirect band gap, and has very low DOS at the Fermi level. The overall DOS profile is found to be the same as those previously reported\(^7\).

In order to understand individual contribution of various electronic states of MoSi₂, we have plotted the partial density of states in Fig. 3. The lowest lying bands around \(-13.4\) eV are due to \('s'\) like states of Si. While the energy range for these states is 11.5–12.5 eV in literature\(^9,18\). The major contribution to the peaks on either side of Fermi level is due to Mo-\(d\) derived character. These higher peaks observed at around \(-2.5\) eV, while it is approximately \(-2\) eV obtained by Alouani \textit{et al}.\(^7\). The larger peaks in upper valence band is mainly due to Mo-\(d\) and Si-\(p\) states within \(-5\) eV of the Fermi level, the Si \('s'\) and \('p'\) derived bands extend to \(-12\) eV below Fermi level. The larger peaks in the conduction band is due to hybridization of Mo-\(d\) and Si-\(p\), and small amount of Si-\(s\) like states.

We found a number of density of states (DOS) at the Fermi level, \(N(E_F)\) is 0.26 states/eV for tetragonal MoSi₂ within PBE-GGA and LSDA approximation. This value is slightly greater than the experimental value. While the value of \(N(E_F)\) is 0.25 states/eV calculated by using WC-GGA agrees well with the experimental value\(^8\). The calculated value of specific heat coefficient is compared with the available experimental result\(^8\), which shows good agreement.

4 Conclusions

In the present study, we have investigated the electronic properties of the MoSi₂ and found it semi-metallic due to indirect small overlapping of bands and very low density of states at Fermi level. The equilibrium lattice constants, bulk modulus, density of states, and specific heat evaluated using PBE-GGA approximation are found to be in good agreement with the previously reported.

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References

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