First-principles calculations of structural and electronic properties of SrSi$_2$ under pressure.

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Abstract: *The structural and electronic properties of SrSi$_2$ under pressure were investigated by using the planewave ultrasoft pseudopotential technique which is based on the first-principles Density Functional Theory (DEF) with Generalized Gradient Approximation (GGA). The pressure dependence of the lattice parameters is smooth. As the pressure increases the lattice parameters decrease exponentially. The electronic structures of SrSi$_2$ show that the top of the valence band is determined by Si 3p states, the bottom of the conduction band is determined by Sr 3d states. It is observed that at ambient pressure no bands cross the Fermi level, which suggests that the system is non metallic. On the other hand the effect of pressure on the electronic properties of SrSi$_2$ indicates that with the increase of pressure, SrSi$_2$, being a narrow-gap semiconductor at ambient pressure, transforms a metal at around 20 GPa.*

Keywords: *SrSi$_2$; Ab initio calculations; Structural properties; Electronic band structure*

I. Introduction

Silicon is a primary material in modern solid-state electronics and semiconducting silicides which are composed of non- or less toxic and naturally abundant elements from earth's crust have attracted considerable attention because of their practical applications in photoelectric and thermoelectric [1-3] devices, such as light-emitting diode and in the field of optoelectronic devices. Thermoelectric materials are capable of converting waste heat into electricity [4]. It is very important for developing alternative energy technologies in the reduction in our dependence on fossil fuels [5] to utilize the technology of energy conversion. The effectiveness of a material for thermoelectric applications is determined by the dimensionless figure of merit, $ZT=S^2\sigma T/k$, where S is the Seebeck co-efficient, σ the electrical conductivity, k the thermal conductivity and T the absolute temperature [6]. Photoelectric devices give an electrical signal in response to visible, infrared, or ultraviolet radiation. They are often used in systems which sense objects or encoded data by a change in transmitted or reflected light. Photoelectric devices which generate a voltage can be used as solar cells to produce useful electric power. The operation of photoelectric devices is based on any of the several photoelectric effects in which the absorption of light quanta liberates electrons in or from the absorbing material. Photoconductive devices are photoelectric devices which utilize the photo-induced change in electrical conductivity to provide an electrical signal. Narrow gap semiconductors are semiconducting materials with a band gap that is comparatively small compared to silicon. They are used as infrared detectors or thermoelectric. Among alkaline-earth metals disilicides, very recently SrSi$_2$ was reported to be a narrow-gap semiconductor with a band gap of 0.035 eV estimated by the Hall coefficient measurements ranging from 10 to 300 K and the electrical resistivity measurements ranging from 2 to 760 K [7]. On the other hand, band structure calculations [8-12] indicated the presence of a semi metallic character. Furthermore, it has been reported to b a metal [13-14]. Also the variation of lattice parameters with pressure and the behavior of electronic band structures of SrSi$_2$ under pressure have not studied. Therefore, electrical properties of SrSi$_2$ are still unclear, further investigation is necessary to clarify its electrical properties. Based on the above, in this work, structural and electronic properties of SrSi$_2$ at different pressures have been investigated by using the first-principles density function calculations in order to reveal a complete understanding of the basically physical properties and the results are analyzed in detail.

The rest of the paper is organized as follows: in Sec. 2, description of the method of calculation is given; Sec. 3 contains our results and discussion, involving structural and electronic properties for SrSi$_2$ composition under pressure. Finally, the conclusion is given in Sec.4.

II. Computational methods

All the calculations are performed using the first-principle pseudopotential method in the framework of density functional theory (DFT) with generalized gradient approximation as implemented in the CASTEP code [15]. All the calculating properties for SrSi$_2$ (P4$_3$32), we used 8x8x8 Monkhorst-pack [16] grid, a plane wave basis set cut-off energy of 350 eV and default the Perdew-Burker-Ernzerhof and generalized gradient approximation (GGA) density function (DF). In CASTEP code, we have used the ultrasoft pseudopotential for Sr and Si. As the name suggests, ultrasoft pseudopotential attain much smoother (softer) pseudo-wavefunctions so use considerably fewer plane waves for calculations of the same accuracy. The kinetic energy cutoff controls

number of plane waves at given k-point. This is the single parameter which can have an enormous effect on the quality of the calculation. Basically, the calculation is better converged due to the higher energy cut-off. For all first-principles calculations, we must pay attention to two convergence issues, i.e. one is the energy cut-off, which is the cut-off for wave-function expansion and the other is number of k- points, which measures how well our discrete grid has approximated the continuous integral.

III. Results and discussion

3.1. Pressure effects on structural and electronic properties of SrSi$_2$

At atmospheric pressure and room temperature, SrSi$_2$ crystallizes in the cubic structure with space group P4$_3$32. The corresponding number of group is 212[17] and three atoms in one unit cell. Figure1 shows the perspective views of the SrSi$_2$ structure. It contains four Sr atoms and eight Si atoms, each Si atom is surrounded by three Si atoms and seven Sr atoms, and each Sr atom is surrounded by fourteen Si atoms and six Sr atoms. Fig.1 shows the schematic representation of the unit cell of SrSi$_2$ and some neighbor atoms in cell. The nearest-neighbor <Si-Si> distances are 2.402 Å, and <Si-Sr> distances are 3.252 Å, which are excellent agreement with the experimental value of 2.39 Å and 3.25 Å respectively [18-19].
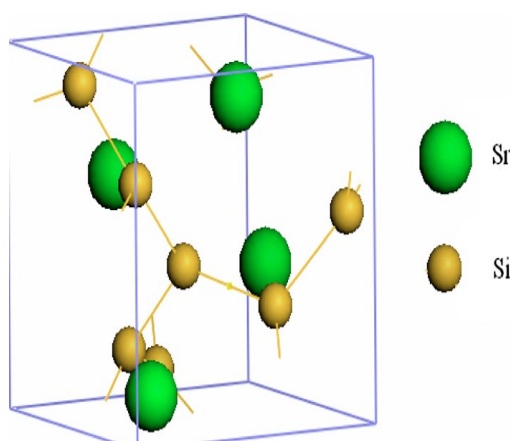

Fig.1. Structures of cubic SrSi$_2$.

The total energy is minimized by the geometry optimization of the specified system at zero pressure using CASTEP code with generalized gradient approximation (GGA). After geometry optimization, the lattice parameters of SrSi$_2$ are obtained at different pressure. The unit cell volume (V) of SrSi$_2$ (P4$_3$32) are then plotted as a function of pressure (P) as shown in Fig. 2.1. From pressure versus volume graph, we observed that the volume decreases with increasing pressure. The calculated values of energy, E for this structure as a function of volume (V) and Pressure (P) are shown in Figs. 2.2 and 2.3 respectively. We also observed that the energy increases with increasing pressure. The pressure dependence of the lattice parameters and the normalized lattice parameters of this compound are plotted in Fig. 2.4 and Fig. 2.5. From Figs. 2.4 and 2.5, it can be seen that lattice parameters decrease systematically with pressure. The variation of the lattice parameters with pressure clearly shows the anisotropy in bonding of the compound. The optimized lattice parameters and volume of SrSi$_2$ at zero pressure are shown in Table 1 (CASTEP code). These results are in good agreement with the available theoretical and experimental data [17-19].

Table 1: Calculated and experimental structural parameters of cubic SrSi$_2$

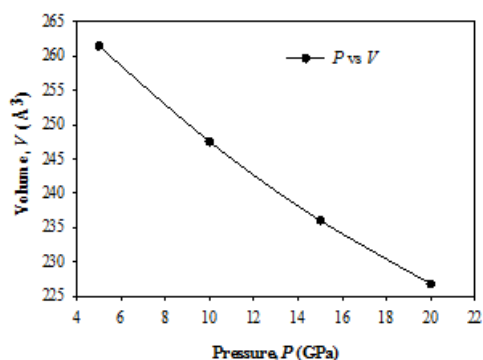| Compound	Pressure (GPa)	a (Å)	V (Å^3)	Ref.
SrSi$_2$		6.545[a]	279.10[b]	[a,b]Expt.[17]
	0	6.563	282.69	
	5	6.394	261.43	
	10	6.279	247.55	
	15	6.181	236.081	
	20	6.098	226.836	

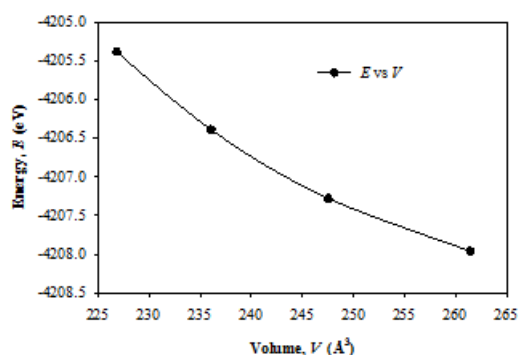**Fig.2.1:** Pressure dependence of the unit cell volume of SrSi₂.

Fig.2.2: The calculated values of energy, *E* for SiSi₂ as a function of volume, *V*.
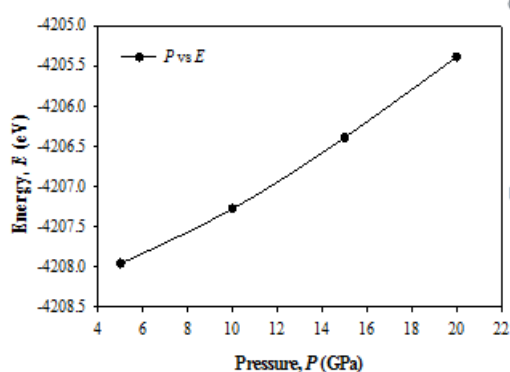

Fig. 2.3: The calculated values of energy, *E* for SrSi₂ as a function of pressure, *P*.
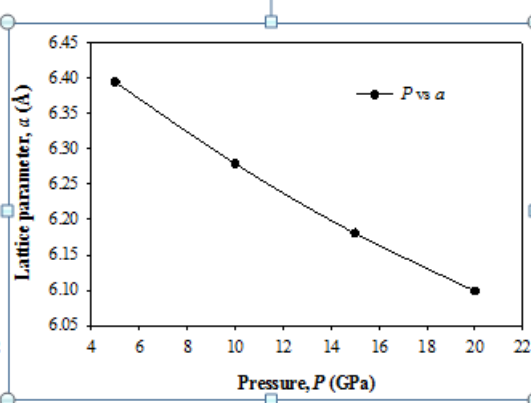

Fig.2.4: The calculated values of lattice parameter, *a* for SrSi₂ as a function of pressure, *P*.
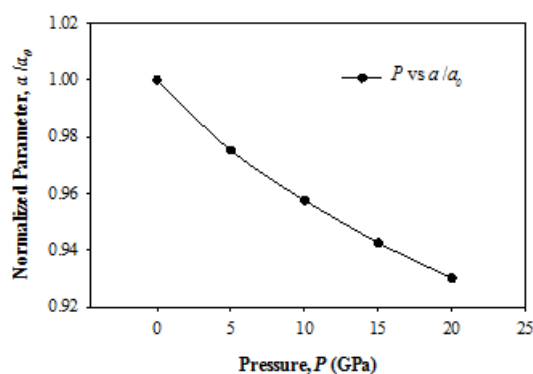

Fig. 2.5: The calculated values of normalized lattice parameter, a/a_0 for SrSi₂ as a function of pressure, P.

3.2. Electronic Properties

The electronic band structure is the spectrum of the energy eigen values of a periodic system. The band structure diagram contains information about both the bonding interactions. However, the ability to understand the band structure diagram allows one to extract valuable information about a material: electronic conductivity, optical properties and stability of compound toward oxidation or reduction. In this way knowledge of the electronic band structure provides predictive insight and understanding of certain very important physical properties of solids. The calculated energy band structures at different pressures with the geometrically optimized structure for SrSi₂ along high symmetry directions in the Brillouin Zone (BZ) is shown in Fig.3. The total density of states (TDOS) and the partial density of states (PDOS) are also plotted in Fig.4. For SrSi₂, the top of the valence band (VB) is mainly composed of Si 3p state. The bottom of conduction band (CB) is dominated by Sr 3d state. At the same time, it is obvious that there is a strong hybridization between the Si 3s and the 3p states (Fig.4), which facilitates the formation of covalently bonded three-dimensional Si anionic network in the crystal. The result is consistent with the previous study [11, 12] .The Fermi level E_F is located in the narrow dip of the DOS curve, the band structure of SrSi₂ shows that top of the valence band is located between G and R. The energy minimum of the lowest conduction band is located between G and M (Fig. 3). So

SrSi$_2$ presents an indirect narrow gap semiconductor, which is an excellent agreement with experimental determination by Emai et al [20, 21]. The energy gap 0.059 eV is little higher than the observed value of 0.035 [22] and 0.0437 [23]. This is because of the fact that we make use of the GGA to the exchange- correlation part of the potential which overestimates the band gap value in most semiconductor and insulators. The effect of different pressures on the band structure of SrSi$_2$ has been examined in the present study as shown in Fig. 3. The results of pressure effect indicate that the band gap of SrSi$_2$ is decreases with pressure. At pressures 5, 10 and 15 GPa the values of the band gap are 0.057. 0.024 and 0.005 eV respectively as shown in Fig.3; which indicate that SrSi$_2$ is a indirect narrow-gap semiconductor. But at pressure 20 GPa, we observe that valence band and conduction band are overlapped and there is no band gap. As a result, SrSi$_2$ would demonstrate as a metal or semimetal.
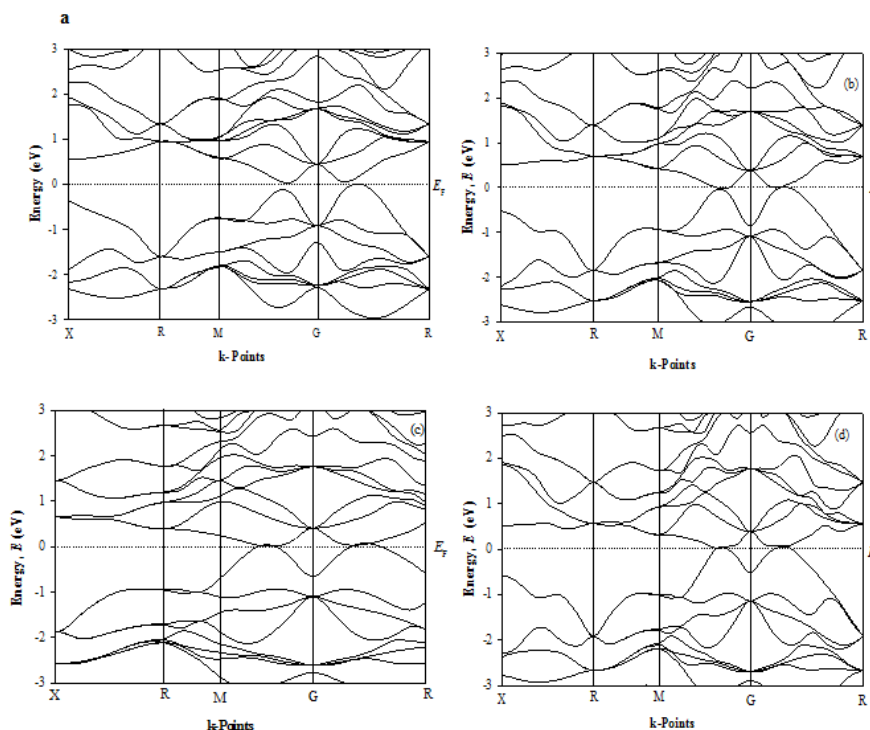

Fig. 3: Electronic band structures for SrSi$_2$ at (a) P=5 GPa, (b) P=10 GPa, (c) P=15GPa and (d) P= 20 GPa.

In solid-state and condensed matter physics, the density of states (DOS) of a system describes the number of states per interval of energy at each energy level that are available to be occupied. A high DOS at a specific energy level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that energy level. The total density of states is written as a sum over atomic contributions. The density of states is calculated by using the following expression

$$n(\epsilon) = 2 \sum_{n,k} \delta\left(\epsilon - \epsilon_n^k\right) = (2/V_{BZ}) \sum_n \int \delta\left(\epsilon - \epsilon_n^k\right) dk$$

and the number of electron in the unit cell is given by

$$\int_{-\infty}^{\epsilon_F} n(\epsilon)\, d(\epsilon)$$

The total and partial electronic densities of states of SrSi$_2$ at different pressures are illustrated in Fig.4 where the vertical line indicates the Fermi level E$_F$. The partial contributions of s, p and d orbitals at E$_F$ of Sr and Si are displayed. In Fig. 4 the conduction band above the Fermi level is mostly derived from the Sr states. Note that, the most remarkable feature of the DOS for this compound is a narrow intense peak in the vicinity of the Fermi level. The calculated values of partial and DOS at the Fermi level show that dominating contributions are due to Sr d states, where as the contribution of the states of Si is much less. The partial contributions of s, p and d orbitals at E$_F$ of Sr and Si are also displayed. The total and partial densities of states of SrSi$_2$ at different pressures (P= 5, 10, 15 and 20 GPa) are plotted in Fig. 4. Further the variation of the total densities of states of SrSi$_2$ as a function of pressure is shown in Fig. 5. It is observed that the total density of states (DOS) decreases with the increase in pressures. The total and partial densities of states of SrSi$_2$ are given in Table 2.

Table 2: Total and partial DOS of SrSi$_2$

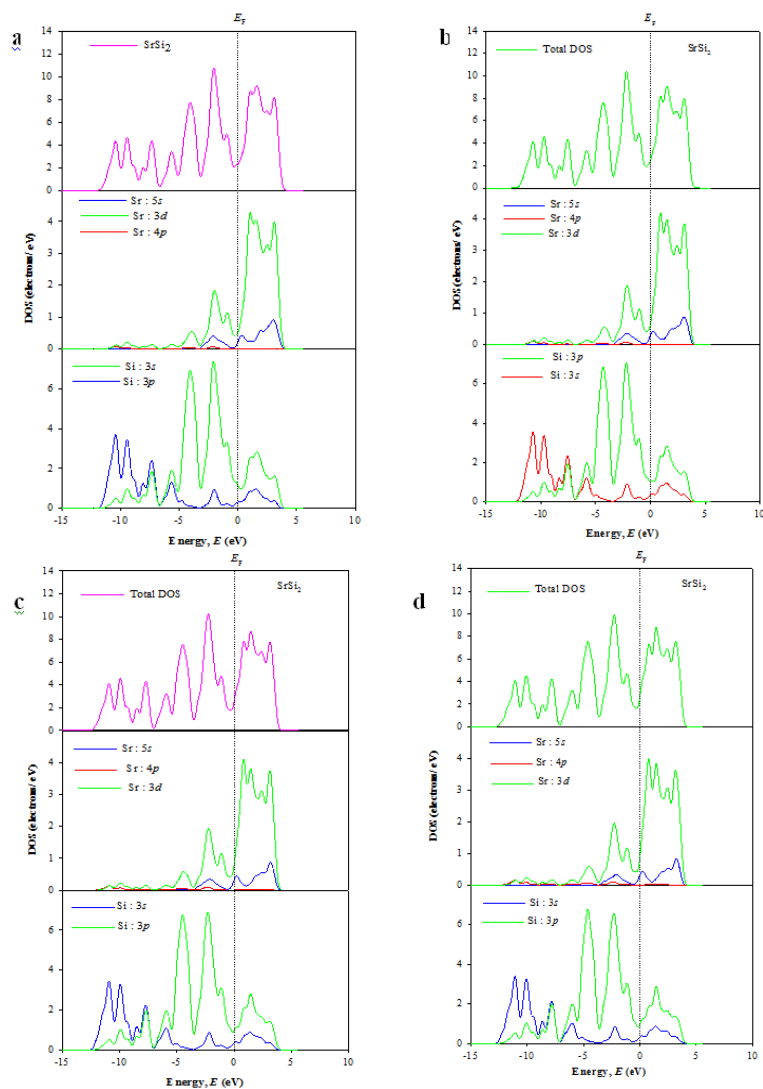| Compound	pressure (GPa)	Partial densities of states (PDOS) (electrons/ eV)					Total DOS (electrons/ eV)
		Sr- s	Sr- p	Sr- d	Si- s	Si- p	
SrSi$_2$	0	0.311	0.000	0.499	0.242	1.472	2.526
	5	0.199	0.000	0.489	0.287	1.153	2.335
	10	0.249	0.000	0.633	0.336	1.001	2.302
	15	0.332	0.000	0.791	0.316	0.950	2.301
	20	0.310	0.000	0.770	0.301	0.901	2.282

Fig. 4: Total and partial densities of states of SrSi$_2$ at (a) 5 (GPa), (b) 10 (GPa), (c) 15(GPa) and (d) 20 (GPa) pressures.
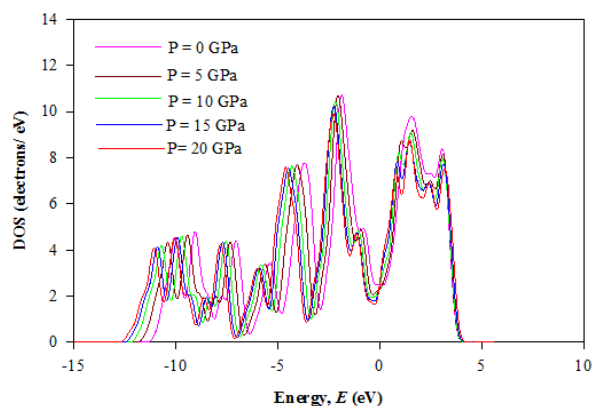
Fig. 5: The variation of total densities of states of SrSi$_2$ at different pressures.

IV. Conclusion

Employing the pseudopotential planewave (PP-PW) approach based on density functional theory (DFT), with generalized gradient approximation (GGA), we have studied the structural and electronic properties of SrSi$_2$ under pressure. Our structural parameters of SrSi$_2$ are in good agreement with the experimental data. The pressure dependence of the lattice parameters is smooth. As the pressure increases the lattice parameters decrease exponentially. The electronic structures show that the top of the VB is determined by Si 3p states, the bottom of the CB is determined by Sr 3d states, and at the ambient pressure the band structure presents an indirect narrow-gap semiconductor with energy gap of 0.059 eV, which is in excellent agreement with experimental determination. The analysis of pressure effect on the band structure of SrSi$_2$ indicates that with the increase of pressure, SrSi$_2$, a narrow-gap semiconductor at ambient pressure, transforms to a metal at around 20 GPa.

Acknowledgments

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