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# First-principles study of calcium di-silicide under high pressure

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**Abstract.** Electronic states for two possible high-pressure phases (with the  $\text{ThSi}_2$  structure and with the  $\text{AlB}_2$  structure) of  $\text{CaSi}_2$  are determined by means of a local density approximation band-structure calculation. We confirm that these polymorphs can be regarded as doped  $\text{sp}^2$  networks of Si. However, a simple picture in terms of  $\pi$ -orbitals is not adequate for explaining the conduction bands, because (i) an s-like band, which is anti-bonding in  $\text{sp}^2$  connections but bonding between segments of the network, appears and (ii) there is  $\pi$ -d hybridization between Si and Ca.

## 1. Introduction

The topology of networks formed by covalently bonded atoms is a starting point for considering curious electronic states in group IV materials and their compounds. This is the case for silicides (silicon–metal compounds) in which we can find, e.g.,  $\text{sp}^2$ -like bond connections between silicon atoms. Typical examples are alkaline-earth and rare-earth silicides having the  $\text{AlB}_2$  structure (figure 1(a)) and the  $\text{ThSi}_2$  structure (figure 1(b)). The  $\text{AlB}_2$  structure may be regarded as an analogue for graphite intercalation compounds. On the other hand, the threefold-connected network found in  $\alpha$ - $\text{ThSi}_2$  may be regarded as a three-dimensional extension of the graphite structure [1–3].

To understand an electronic state of such a silicon network, however, we should exercise caution, for the following reasons.

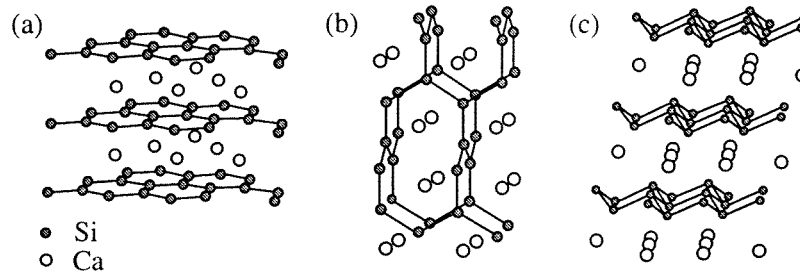
(i) Compared with carbon, silicon has rather expanded orbitals, so simple notions obtained from the Hückel-type approach might face some difficulties.

(ii) To stabilize  $\text{sp}^2$  networks, metallic ions seem to be necessary, which cause (1) ionicity in the material, (2) doping of electrons on the silicon network and (3) extra bondings between a cation and a silicon.

Thus we need a detailed study of the electronic states for these compounds, classified into the Zintl phases.

In a previous paper, we investigated the relative stability of the polymorphs by varying external pressure [4]. There, we showed that (i)  $\text{sp}^2$  structures are stabilized relative to the  $\text{CaSi}_2$  structure, having  $\text{sp}^3$  bondings at high pressure; (ii) the stability of the polymorphs and the structural phase diagram are determined by a volume effect in addition to an increase in the coordination number of Ca and (iii) the  $\text{AlB}_2$  structure is a possible candidate for being an unknown polymorph of  $\text{CaSi}_2$ .

In this paper, we perform an LDA band-structure calculation for these high-pressure polymorphs of  $\text{CaSi}_2$ . We will show that the lower  $\text{sp}^2$  band is well defined as expected.



**Figure 1.** (a) The hexagonal  $\text{AlB}_2$  structure, (b) the tetragonal  $\text{ThSi}_2$  structure and (c) the trigonal  $\text{CaSi}_2$  structure.

However, the conduction bands are rather different from the simple  $\pi$ -bands. Additional conduction bands to which electrons are doped from Ca appear.

## 2. The method

We utilize a so-called first-principles calculation using the LDA to obtain reliable information on the electronic state as well as the lattice structure of  $\text{CaSi}_2$ . The method is suitable for a Zintl-phase metal which has ionic character and exhibits covalent bondings simultaneously.

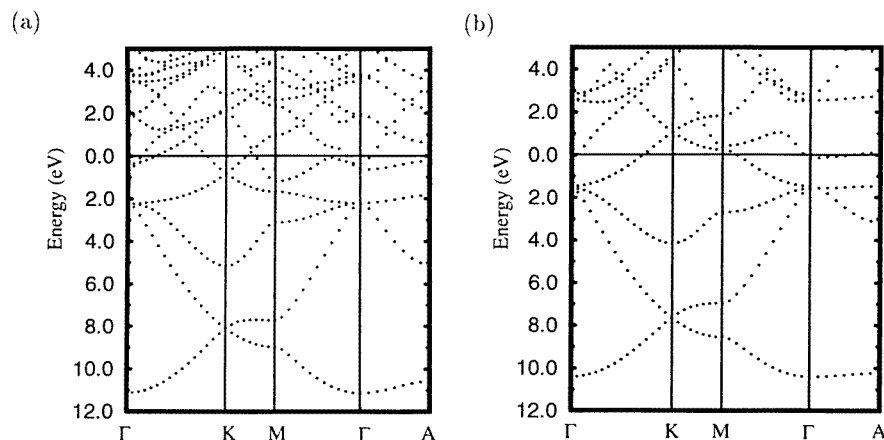
We utilize the pseudopotential method, in which the wavefunction and the electronic charge are expanded in plane waves. A self-consistent solution for the Kohn–Sham equation is obtained by an energy minimization using the conjugate-gradient method. The stress, as well as the force on the atoms, is calculated to perform the molecular dynamics study. Thus we can determine the enthalpy at a given pressure  $P_{\text{ext}}$ .

Details of the calculation have been given in a previous paper [4], so we only mention the important conditions which ensure reliability of the calculation. We use the Troullier–Martins soft pseudopotential with a Wigner-type exchange–correlation potential. An energy cut-off of 20 Ryd is sufficient for reproducing the lattice structure of  $\text{CaSi}_2$  to within a few per cent error from the experimental results. We use a  $k$ -point sampling restricted to an irreducible Brillouin zone, after confirming that the symmetry is conserved at each pressure using a uniform  $k$ -point sampling. The detailed band-structure calculation is done by fixing the charge density and the effective potential obtained in a self-consistent calculation with a few tens of  $k$ -points. The band structure obtained for trigonal  $\text{CaSi}_2$  agrees with that from an existing LDA calculation [5].

## 3. The electronic band structure for polymorphs of $\text{CaSi}_2$

We calculated band structures for (i) hex- $\text{CaSi}_2$  (the  $\text{AlB}_2$  structure) and (ii) tetra- $\text{CaSi}_2$  (the  $\text{ThSi}_2$  structure). We also look at band structures of pure Si networks obtained by removing Ca atoms from  $\text{CaSi}_2$  structures. Although the threefold-connected network is itself unstable, comparison between  $\text{CaSi}_2$  and a pure Si structure is a convenient way of identifying bands originating from the Si network. The characterization of the bands was done using (1) a projection operator projecting onto pseudo-wavefunctions and (2) direct observation of the wavefunctions.

We first discuss the band structure obtained for Si honeycomb planes (figure 2(b)). The lowest three bands have  $\sigma$ -character. The shape of the dispersion curves is similar to that

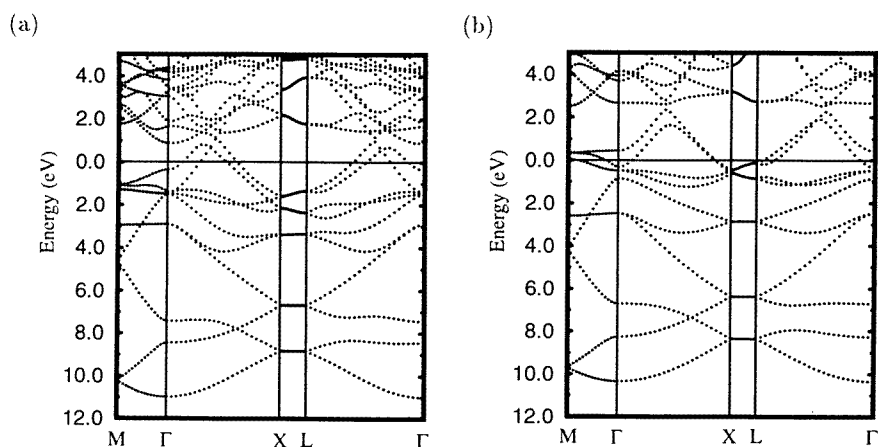


**Figure 2.** The electronic band structure for (a) hex-CaSi<sub>2</sub> and (b) graphitic silicon. The structure of planar silicon is obtained by removing Ca atoms from hex-CaSi<sub>2</sub>.

of graphite. At the  $\Gamma$  point, the  $\pi$ -band is close to the top of two  $\sigma$ -bands. We can also find degeneracy of  $\pi$ - and  $\pi^*$ -bands at the K point. However, there is another low-lying band close to these  $\pi$ -bands. The character of this extra band is s-like; it is an anti-bonding band in the Si planes. The reason for the relatively large stabilization for this s band is the character of the bonding between planes.

In hex-CaSi<sub>2</sub>, we can easily find corresponding bands not only for lower  $\sigma$ -bands but also for  $\pi$ -bands. Interestingly, a curious s band remains, retaining its main characteristics. The Fermi level just cuts the  $\pi$ -band and the s band. So, extra electrons coming from Ca ions also fill this s band. Another band appears due to the hybridization between the silicon  $\pi$ -orbitals and the Ca sd-hybridized orbitals at around the Fermi level.

Next, we proceed to the ThSi<sub>2</sub> structure. Let us look at the band structure of the 3D



**Figure 3.** The electronic band structure for (a) tetragonal CaSi<sub>2</sub> and (b) a threefold-connected silicon network. The structure of this three-dimensional silicon network is obtained by removing Ca atoms from tetra-CaSi<sub>2</sub>.

silicon network. Because the primitive unit cell contains four Si atoms, we see six bonding  $\sigma$ -bands. They are well separated from the upper bands throughout the whole BZ. Thus we can say that the frame of the network is constructed by  $sp^2$   $\sigma$ -bondings.

However, the upper conduction bands have a strange structure. At the  $\Gamma$  point, the seventh and eighth bands are one-dimensional  $\pi$ -bands. The reason for this is the following. This 3D network can be regarded as an assembly of polyacetylene-like zigzag chains of Si. Chains align in the  $x$ -direction on a plane perpendicular to the  $z$ -axis or in the  $y$ -direction on the next plane. Although these chains are coupled by vertical  $\sigma$ -bonds, a  $\pi$ -orbital on an atom cannot couple with another orbital on another chain connected by the vertical bond, because these two  $\pi$ -orbitals are orthogonal with each other.

The ninth and tenth bands are also interesting. We found that these bands consist of an  $s$ -like orbital on each Si atom. To be precise, the orbital is a back-bond state. Since such a state is usually not well described in the Hückel approach, the band structure obtained is different to that obtained from reference [1]. These curious bands are hybridized with  $\pi^*$ -bands, which come close to the  $\pi$ -bands at the X point.

In the band structure of tetra-CaSi<sub>2</sub>, we can again see that electrons doped from cations also fill the peculiar  $s$  bands. The existence of the extra bands, which are hybridized with  $\pi^*$ -bands, effectively makes the conduction bands narrower. The Fermi level is at the middle of these hybridized conduction bands. Several bands originating from orbitals on Ca ions seem to lie well above the Fermi energy in tetra-CaSi<sub>2</sub>. We should, however, note that such a rigid-band picture is not complete. The curves of the conduction bands are deformed by the hybridization between Si and Ca.

#### 4. Discussion

It is desirable to find a simple guiding principle governing the electronic states for these interesting materials with various Si networks. However, the present result suggests that the nature of the conduction bands is determined by the subtle geometrical configuration of the silicon atoms. This difficulty is partly due to the  $\pi$ -orbitals being larger than that for carbon. To achieve a complete understanding of silicide, we have to explore the details of the conduction bands, including back-bonds, to which electrons might be doped in silicides.

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