

Effect of Pressure on the Band Structure of SiC

تأثير الضغط على التركيب الحزمي لكاربيد السليكون

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Abstract

Numerical simulation based on large unit cell within intermediate neglect of differential overlap method (LUC-INDO) method is applied to study bulk modulus, hybridization state, band gap, high symmetry points, conduction and valence bandwidths, and valence charge density of cubic SiC under pressure. The calculated properties are, in general, in good agreement with theoretical and available experimental values except the indirect band gap. The increase of pressure is predicted to cause; an increase of the cohesive energy, a linear increase of the indirect band gap with a pressure, a linear increase of the valence bandwidth, a decrease of the conduction bandwidth, and a slight decrease of the electronic occupation probability for the s-orbital and p-orbital of silicon with a slight increase of this probability for the s-orbital and p-orbital of carbon.

الخلاصة

محاكاة عددية تستند على طريقة خلية الوحدة الكبيرة ضمن إطار الإهمال المتوسط للتداخل التفاضلي (LUC-INDO) طبقت لدراسة معالم المرونة الحجمي و حالة التهجين وفجوة الطاقة والنقاط عالية التناظر و عرض حزم تي التوصيل والتكافؤ و كثافة شحنة التكافؤ لكاربيد السليكون ذي الشبكية المكعبة تحت تأثير الضغط. الخواص المحسوبة بصورة عامة كانت متوافقة بشكل جيء مع القيم النظرية و العملية المتوفرة باستثناء فجوة الطاقة غير المباشرة. يتوقع أن تؤدي الزيادة في الضغط إلى زيادة في طاقة الترابط و زيادة خطية في فجوة الطاقة غير المباشرة مع الضغط. و زيادة خطية في عرض حزمة التكافؤ ونقصان في عرض حزمة التوصيل ونقصان طفيف في احتمالية الإشغال الالكترونية للمدارات s و p للسليكون بصاحبها زيادة طفيفة في هذه الاحتمالية للمدارات s و p للكاربون.

Introduction

Silicon carbide (SiC) is a wide-gap semiconductor with an indirect band gap with intriguing properties. It possesses a number of unique properties, hardness, chemical inertness, low diffusion rates of dopants and host atoms, electrical and thermal properties, which make it a potential candidate for semiconducting device application [1]. For example, blue light emitting diodes, high-power, high frequency devices and sensors working in harsh environments are only the first steps in the application of SiC as an advanced material. Consequently, SiC is now in the focus of detailed experimental and theoretical investigations [2]. In the last few years, the electronic properties of some SiC polytypes have been calculated; further studies went deep into the elastic, the optical, the thermomechanical properties, and the high-pressure behaviour.

Under normal conditions SiC has differing structures depending on how they are ordered, SiC may adopt a large variety of semiconducting polytypic forms which are all very close in energy [3]. They consist of different stackings of hexagonal Si-C bilayers, the most common of which are 3C (zinc-blende structure, the stable form), 6H, 4H, and 2H, (wurtzite structure) [4]. The structural stability of SiC at high pressure has been the object of number of experimental studies as well as theoretical ones [5], the zinc-blende (ZB) phase is known to transform to the $\beta 1$ or rock salt phase (NaCl) at about 100 GPa [6], but theoretically this transformation is taken at much smaller pressures (~66 GPa) [7]. Experimental progress in the study of SiC has been obstructed for many years by the difficulty of growing homogeneous single crystal, partly because of large number of SiC polytypes. Recent developments on the bulk crystal growth [8] and control of polytypism, in epitaxially grown layers, have yielded high quality single crystals, making possible the systematic experimental study of this material.

In this paper, we present detailed information on the band structure, bulk modulus, cohesive energy, hybridization of state, and valence charge density of cubic zinc-blende silicon carbide (3C-

SiC) under pressure, calculated using the self-consistent large unit cell within intermediate neglect of differential overlap method (LUC-INDO) in the linear combination of atomic orbital (LCAO) approximation [9]. This method, has gained wide acceptance in calculations of the electronic structure of crystals.

2. Method of Calculation

We use large unit cell in the intermediate neglect of differential overlap (LUC-INDO) [9] to obtain a self-consistent solution for the valence electrons in bulk phases of SiC, at various lattice constants. In a first step, we calculate the lattice constant. The iteration process was repeated until the calculated total energy of crystal converged to less than 1 meV. A total of seven iteration was necessary to achieve self-consistency.

In this work, we choose the large unit cell (LUC) of eight atoms with zinc-blende (ZB) structure. The calculations are carried by forming a cube of a side 3a where a is the lattice constant of the Bravais lattice. The number of Bravais lattices in this cube is 27 lattices. The interaction of the atoms in the central Bravais with the surrounding atoms up to the fourth neighbors is included. These calculations require the determination of wave functions and positions of 864 electrons and 216 nuclei. We choose zinc-blende phase since it has fewer atoms per unit cell, and is therefore computationally easier to treat. In the calculations, the Si atom has been chosen to be at the origin and the C atom at the position (1/4, 1/4, 1/4) in units of the lattice constant.

3. Results and discussion

3.1. Choice of parameters

The number of parameters in the LUC–INDO method is four. These are the orbital exponent ζ , the bonding parameter β , the electronegativity of s-orbital (E_s), and the electronegativity of p-orbital (E_p). The value of the orbital exponent determines the change distribution of electrons around the nucleus or in the solid. These parameters are varied firstly to give nearly the exact value of the equilibrium lattice constant, cohesive energy, indirect band gap and valence bandwidths. The remaining of the output data of the programs is a result of the theory, which is used in the present work. We found that the investigated properties were sensitive to the aforementioned parameters. The optimum values of these parameters used for SiC in the present work are listed in table 1.

Table 1. Parameters sets of 3C-SiC used in this work.

| Parameter | Si | C |
|-----------------------------|-------|-------|
| ζ (a.u) ⁻¹ | 1.657 | 1.872 |
| β (eV) | -5.52 | -9.83 |
| E_s (eV) | 7.58 | 5.69 |
| E_p (eV) | 4.72 | 4.24 |

3.2. The electronic and structural properties

Figure 1 displays the total energy versus lattice parameter of SiC, obtained using the same set of parameters. The curves are fitted to the Murnaghan's equation of state [10]:

$$E_{tot}(V) = E_{tot}(V_0) + \frac{B_0 V}{B'_0} \left[\frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{B_0 V_0}{B'_0 - 1} \tag{1}$$

Where V_0 is the equilibrium volume at zero pressure, E_{tot} is the total energy, B_0 the bulk modulus, and B'_0 its derivative.

From equation 1, we obtain the equilibrium lattice parameter a_0 , the bulk modulus B , and its derivative B'_0 . The result of structural and electronic properties of 3C-SiC are given in table 2, along

with the experimental measurements and other results. We notice that the lattice constant and the cohesive energy for 3C-SiC are in excellent agreement with experimental results. For example, the calculated lattice constant and bulk modulus are 4.3592Å and 216 GPa, respectively, its excellent agreement with the corresponding experimental values of 4.3596 Å and 225 GPa, respectively (see Table 2).

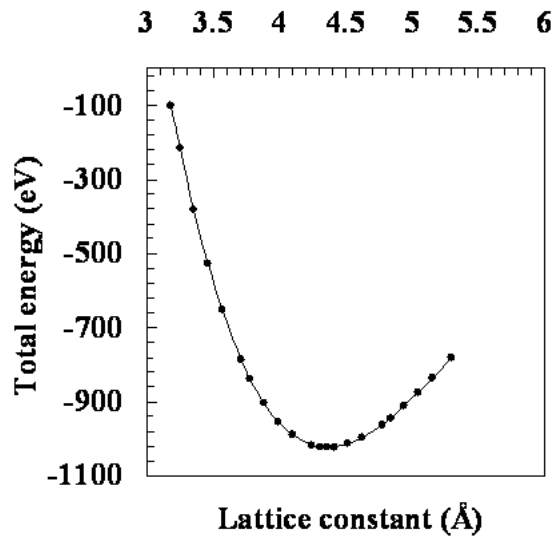


Figure 1. Total energy as a function of lattice constant for 3C-SiC.

Table 2. Structural and electronic properties of 3C-SiC at zero pressure determined by LUC-INDO compared with previous theoretical and experiments works.

| Property | Present work | Other results | Experimental |
|---------------------------|--------------|--|--------------------|
| Lattice constant (Å) | 4.3592 | 4.376 [11] | 4.3596 [12] |
| Cohesive energy (eV/atom) | - 6.3398 | - 6.18 [13] | -6.34 [14] |
| Conduction bandwidth (eV) | 13.4785 | ---- | ---- |
| Valence bandwidth (eV) | 17.664 | ---- | (15.44,16.85)[15] |
| Indirect band gap (eV) | 2.8315 | 2.59 [16] | 2.39 [17] |
| Hybridization state | Si C | $s^{0.9776} p^{3.588}$ $s^{0.759} p^{2.6758}$ | ---- |
| Bulk modulus (GPa) | 216 | 213 [11] | 224 [18], 225 [19] |
| B'_0 | 4.14 | 3.93 [11] | 4.0 [20] |

Based on the total energy results, we obtained the cohesive energy (E_{coh}) per atom as follows:

$$-E_{coh} = E_{tot} / 8 - E_{free} - E_0 \tag{2}$$

Where E_{tot} is the total energy, E_{free} is the free atom sp shell energy, and E_0 is the zero–point vibration energy. In this work $E_{free} = 125.582$ eV, and this value is taken from ionization potential of SiC, so $E_0 = 0.233$ eV, is calculated by the formula $E_0 = (9/8)k_B\Theta_D$ (per atom) with Θ_D being the Debye temperature which is equal to 1200 K [21]. The cohesive energy value of the present work is in good agreement with experimental results as we seen in table 2.

The minimum gap is indirect for SiC with conduction-band minimum (CBM) occurring at X point. The indirect band gap, valence and conduction bandwidth are listed in table 2 and the differences between LUC-INDO and experimental result of indirect band gap, and valence bandwidth are relatively small, where the band gap values is higher than experimental values this is, mainly, a consequence of two approximations made in this calculation. First, the core structure was ignored, through some

compensation results from using semiempirical parameters. Second, using minimal basis set atomic orbitals (without considering any excited levels). However, the INDO method predicts a one - electron eigenvalues band gap that is too large and conduction bands that is much narrower than the band model values. The valence and conduction states X_1 of the zinc-blende (ZB) lattice, which have degeneracy two split into the nondegenerate state X_1 and X_3 when the antisymmetric potential is introduced. This splitting produces a gap in the valence band of the ZB type compounds. The splitting X_1 - X_3 seems to decrease with increasing atomic number of elements of the compound.

Hybridization state show an increasing s-state occupation and p-state occupation with the increasing atomic number of the compound where the occupation of s and p orbital of silicon is larger than of that for carbon. This reflects the weakening of the directional character of these bonds represented by the sp^3 hybridized orbitals with increasing the atomic number.

3.3 The band structure and energy eigenvalues

The energy eigenvalues for 3C-SiC crystal are calculated at various high symmetry points of the Brillouin zone as we see in table 3. For folding reasons the electronic structure is only studied at Γ and X points of the FCC Brillouin zone. The most important band states are considered. They are the valence bands Γ_{1v} , Γ_{15v} , X_{1v} , and X_{5v} . In the case of the conduction bands we consider the states X_{1c} , X_{5c} , Γ_{15c} , and Γ_{1c} . Selected energy eigenvalues at various high symmetry points of the BZ are listed in table 3, along with the results of the GW method [22], and the DFT-LDA method [16]. Table 3 also includes experimental and theoretical values for comparison with present work. Which illustrate a good agreement with the present calculation, also the results of LUC-INDO with experimental data is almost equivalent values good agreement.

Table 3. Eigenvalues (in electron volts) at Γ and X high-symmetry points of Brillouin zone. In the first column are results from the present LUC-INDO method, in the second from the DFT method (Ref.16), in the third from the GW method (Ref.22), and in the fourth experimental data.

| Symmetry point | LUC-INDO | DFT [16] | GW [22] | Experimental |
|----------------|----------|----------|----------|-----------------------|
| Γ_{1v} | -17.664 | -15.51 | -16.54 | ---- |
| Γ_{15v} | 0.0 | 0.0 | 0.0 | 0.0 |
| Γ_{1c} | 6.546 | 6.77 | 7.24 | 7.4 [23] |
| Γ_{15c} | 9.904 | 8.77 | 8.35 | 7.75 [17], 9±0.2 [24] |
| X_{1v} | -10.209 | -10.50 | -11.46 | ---- |
| X_{5v} | -4.4344 | -3.24 | -3.65 | -3.6 [17], -3.4[23] |
| X_{1c} | 2.8315 | 2.59 | 2.18 | 2.39 [17] |
| X_{4c} | 16.31 | 14.17 | 15.91 | ---- |

For a more detailed comparison, we presented in table 4 the calculated values of direct gaps in 3C-SiC and the experimental results, which are in good agreement.

Table 4. Direct gaps in (electron volts) for 3C -SiC, calculated within the LUC-INDO method, compared with other results.

| Symmetry point | This work | Theory [25] | Theory [23] | Experimental |
|-------------------------------|-----------|-------------|-------------|--------------|
| $\Gamma_{1c} - \Gamma_{15v}$ | 6.546 | 7.58 | 7.40 | 7.4 [24] |
| $\Gamma_{15c} - \Gamma_{15v}$ | 9.904 | 8.81 | 8.27 | 9.0 [24] |
| $X_{1c} - X_{5v}$ | 7.2659 | 6.07 | 5.8 | 6.0 [26] |

The electronic charge density for each direction in the crystal can be calculated in this work from the density matrix. Figure 2 shows the charge density along the line joining two IV-IV elements in (100), (110), (200), and (400) directions.

In the ZB structure, the lack of inversion symmetry may cause splitting of this spin degeneracy; only along (100) directions all states remain degenerate, while along the (110) directions the spin degeneracy is removed [24]. We noticed that the silicon ions are larger than the carbon ions and the charge accumulated along the distance between the atoms.

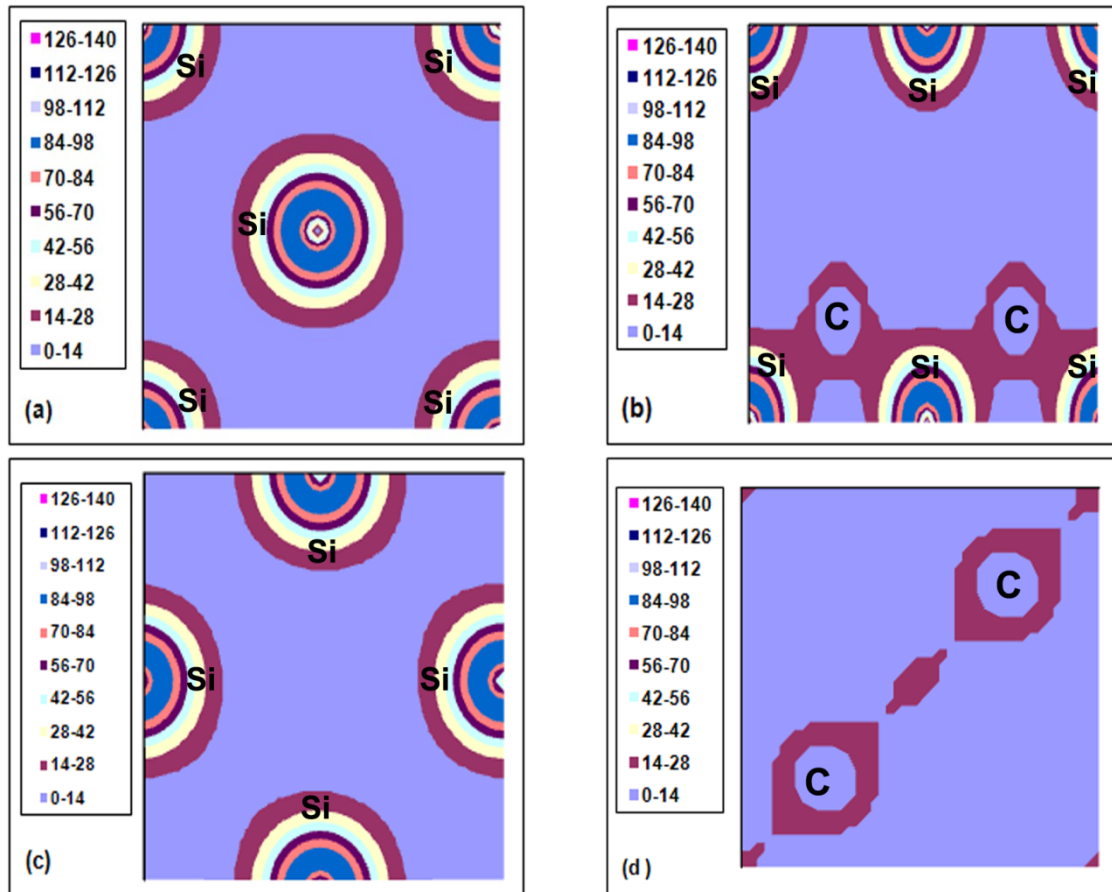


Figure 2. The valance charge density for SiC at zero pressure in the planes (a) (100), (b) (110), (c) (200), and (d) (400).

4. Effect of pressure on the 3C-SiC properties

The effect of pressure on the electronic structure and other properties can be calculated from the present theory and computational procedure. By the use of our calculated values of the bulk modulus, its derivative B'_0 , and the volume change (V) with applied pressure was calculated using the equation [28]:

$$P = \frac{B_0}{B'_0} \left[\left(\frac{V_0}{V} \right)^{B_0} - 1 \right] \tag{3}$$

Where P is pressure. We applied a pressure up to 95 GPa, because this structure transforms to another phase, rock salt (NaCl), when pressure exceeds nearly 100 GPa [6]. The calculated lattice constant as a function of pressure is shown in figure 3a. The relation between bulk modulus and the pressure can be written as follow [29]:

$$B = -V \left(\frac{dP}{dV} \right)_T = B_0 + B'_0 P \tag{4}$$

The pressure dependence of the bulk modulus is illustrated in figure 3b, and the relation between the cohesive energy and the pressure is shown in figure 3c. It is shown from figure 3c that the increase of pressure causes a decrease of the absolute value of the cohesive energy.

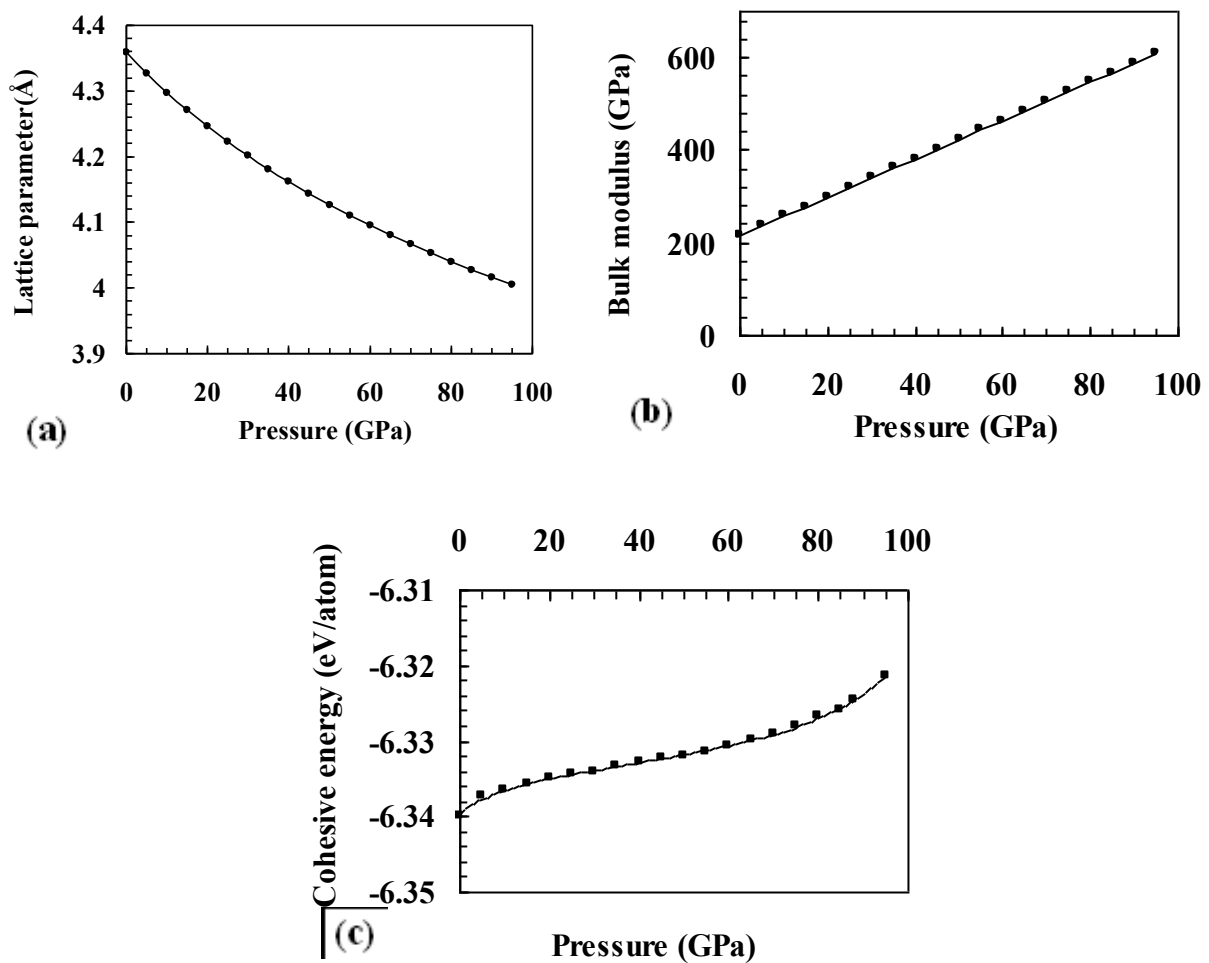


Figure 3. The effect of pressure on (a) the lattice constant, (b) bulk modulus, and (c) cohesive energy of 3C-SiC.

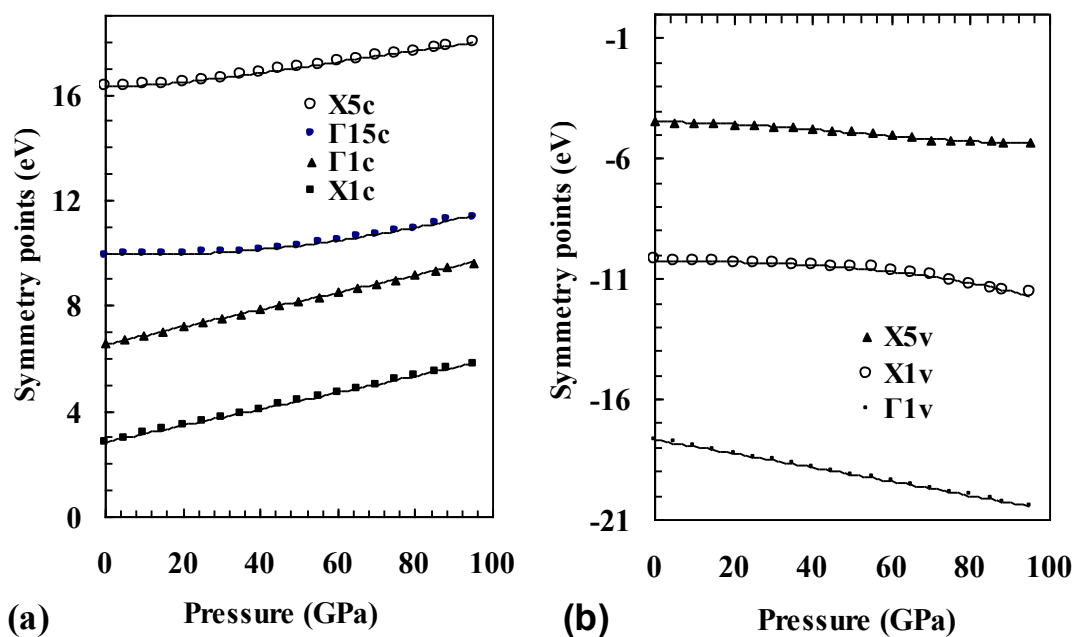


Figure 4. The effect of pressure on the high symmetry points in (a) conduction band (X_{5c} , Γ_{15c} , Γ_{1c} , X_{1c}), and (b) valence band (X_{5v} , X_{1v} , Γ_{1v}).

From the above figure, we predict eigenvalues at conduction band ($X_{5c}, \Gamma_{15c}, \Gamma_{1c}, X_{1c}$) are increase with pressure, whereas eigenvalues at valence band ($X_{5v}, X_{1v}, \Gamma_{1v}$) are decrease, so, the decrease of X_{5v}, X_{1v} with pressure is very small.

The predicted effect of pressure on the indirect band gap, valence bandwidth, and conduction bandwidth is illustrated in figure 5, the indirect band gap and the valence bandwidth increase with the increase of pressure, while the conduction bandwidth decrease with the increase of pressure. In the present work, the pressure derivative of the indirect band gap is computed to be 31.2 meV/GPa, for the valence bandwidth and conduction bandwidth our calculation give pressure derivative 29 meV/GPa for the valence bandwidth, and - 30.7 meV/GPa conduction bandwidth.

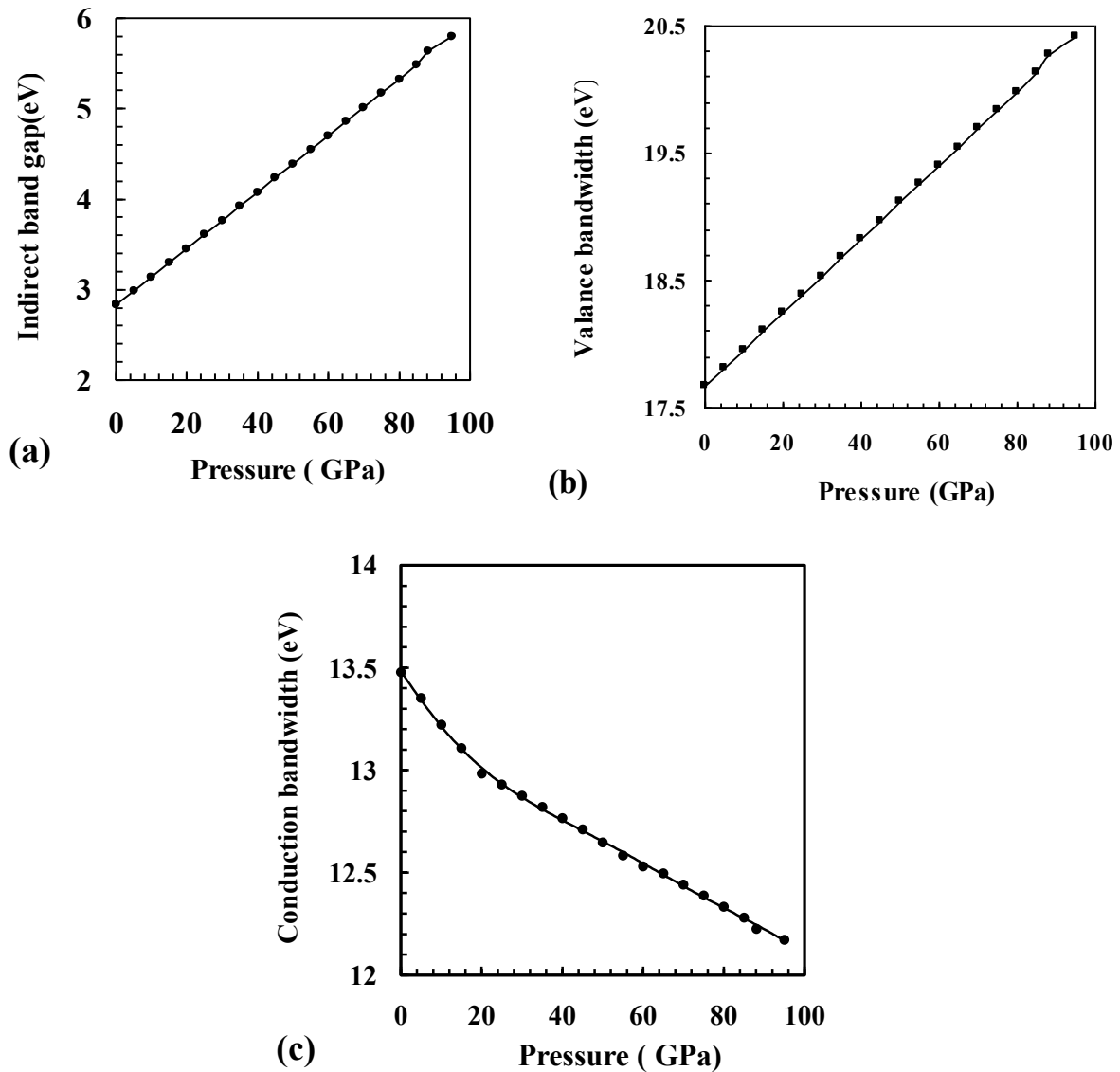


Figure 5. Effect of pressure on (a) indirect band gap, (b) the valence bandwidth, and (c) conduction bandwidth.

It has been noted that the direct gaps of 3C-SiC varies with the increase of pressure. This increase is shown in figure 6. The pressure derivative of the direct band gap at the Γ and X points is between (29-43) meV/GPa. In general this result is in good agreement with the plane wave pseudopotential (PWPP) calculation of Kim *et al.* [30], and the calculation of Christensen and Gorezyca [31] using LMTO, where these references support increase of band gap with increase of pressure, but the direct gap does not shows a linear dependence as in the previous calculation.

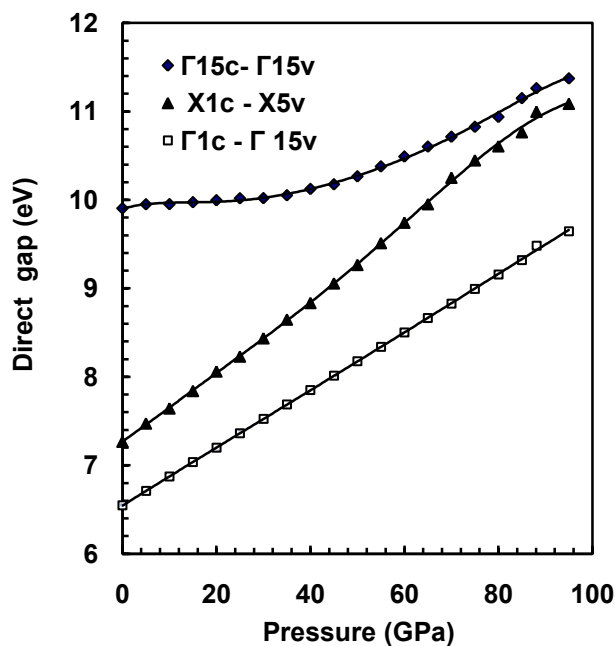


Figure 6. The effect of pressure on direct gaps for 3C –SiC, calculated within the LUC-INDO method.

We found that the s and p states occupation for Si decrease with the increase of pressure, whereas the s and p states occupation for C increase in this case. The s and p states occupation for Si and C with pressure are shown in figure 7, the increase of pressure causes an increase of the probability of electron transition from s-orbital and p-orbital of Si to s-orbital and p-orbital of carbon, this phenomenon is known and leads to phase transition due to the change of electronic distribution such as s-d transition in alkali metals [32].

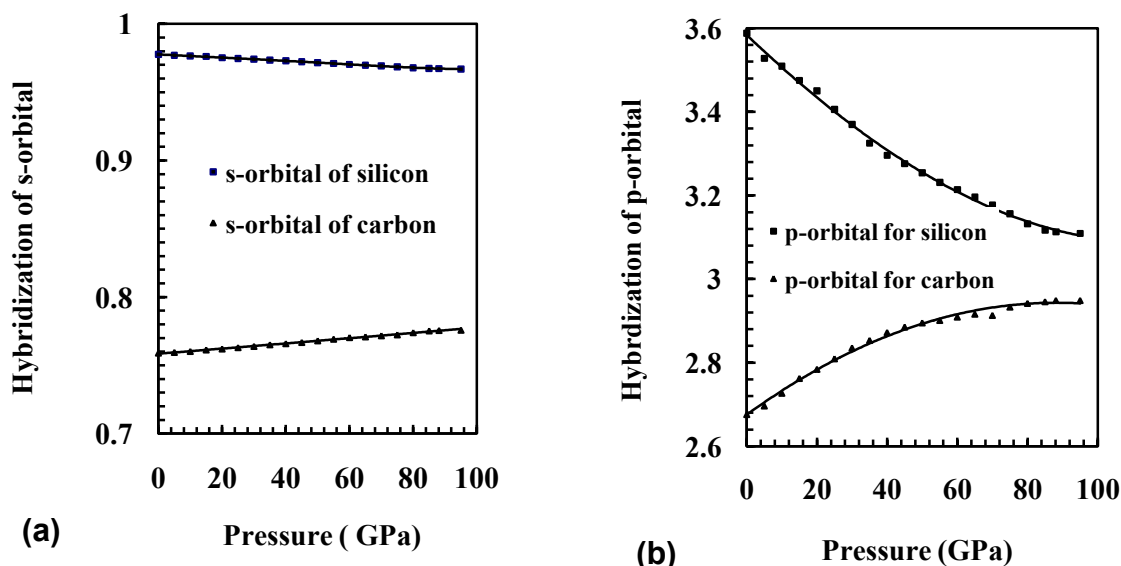


Figure 7. Effect of pressure on the hybridization of (a) s- state and (b) p- state.

The valance charge densities in the planes (100), (110), (200), and (400) at (95GPa) are shown in figure 8. It be noted that the increase of pressure causes, in general, an increase of valance charge density around the nuclei and a decrease of this density at the intermediate distance between the nuclei, and this can see in figure 8 comparing this figure with figure 2.

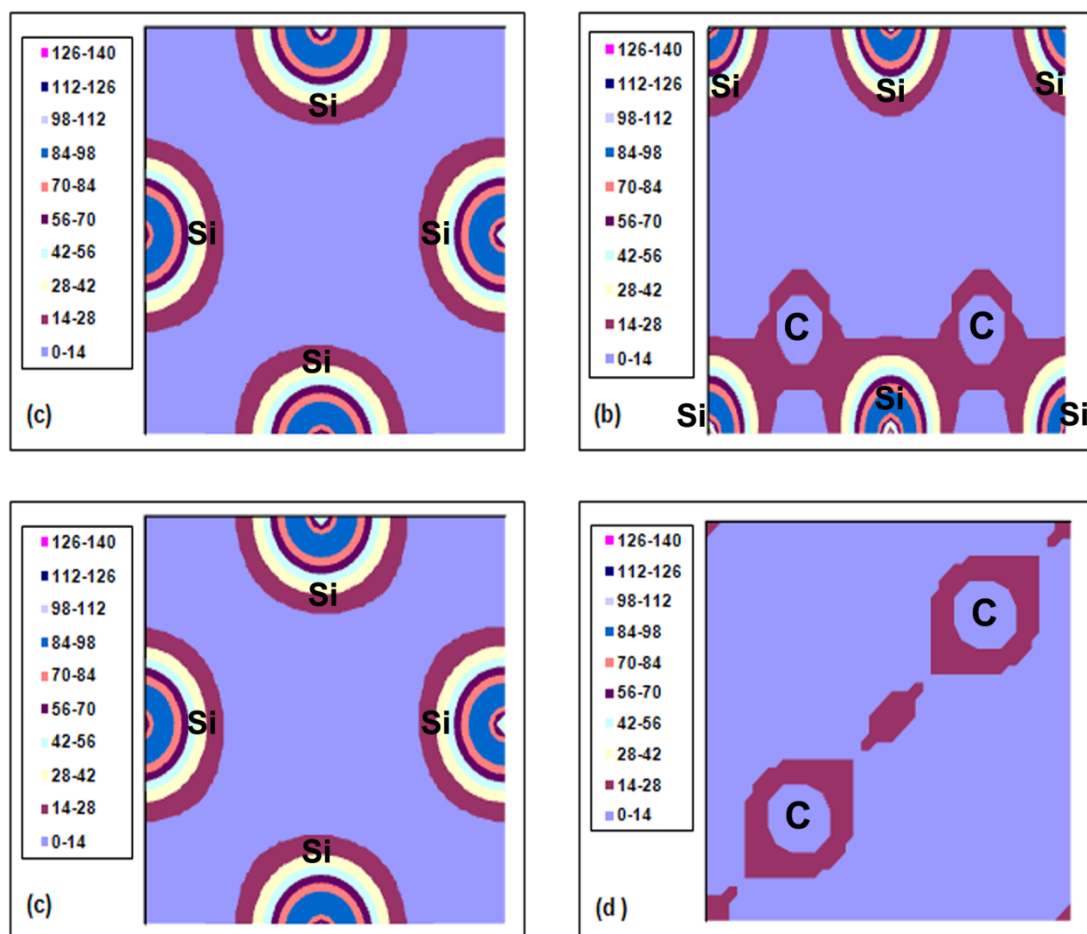


Figure 8. Valance charge density of 3C-SiC under effect of pressure (95 GPa) in the planes (a) (100), (b) (110), (c) (200), and (d) (400).

5. Conclusions

We have performed calculation for the electronic, structural properties, and the effect of pressure on these properties. For the evaluation of the electronic properties, the LUC-INDO method was used. It is found that the equilibrium lattice constant and cohesive energy is in excellent agreement. The indirect band gap and valence bandwidth are greater than the experimental results. The results on high symmetry point are in reasonable agreement with experimental results. It is found that bulk modulus, the direct and indirect band gap, valence bandwidth, and the s and p states occupation for C increase with increasing the pressure, whereas lattice constant, the conduction bandwidth, the s and p states occupation for Si decrease. It be noted that the increase of pressure causes, in general, an increase of valance charge density around the nuclei and a decrease of this density at the intermediate distance between the nuclei.

It is concluded that the (LUC-INDO) method gives good results when choosing optimum empirical parameter sets and it has a reliable prediction for the effect of pressure.

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