

Theoretical study of second and third order elastic constants of β -SiC

N. Lebga^{1,2*}, K. Bouamama², P. Djemia³ and S. Mourad Chérif³

¹Mohamed Elbachir Elibrahimi University, 34000 El-Annaseur, Bordj Bou-Arreidj Algeria

²Optoelectronics and composant Laboratoire, Ferhat Abbas University, 19000 Sétif, Algeria

³LPMTM, UPR CNRS 9001, Paris-Nord University, 93430 Villetaneuse, France

* Corresponding author: Tel./Fax: +213663815340 ; E-mail address: noudjoud.lebga@univ-bba.dz

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Abstract

First principles calculations of the second and third order elastic constants of the cubic silicon carbide β -SiC have been accomplished using the density functional theory within the local density approximation and the pseudopotential plane-wave method with the Hartwigsen Goedecker Hutter scheme. The second order elastic constants C_{ij} compared fairly well with those previously measured by one of us using the Brillouin light scattering technique (P. Djemia) [1]. The ab-initio calculations include parameters pressure dependence determinations in relation with the structural transformation from a zinc Blende to a rocksalt structure. The transition pressure at which arises elastic instabilities is found to be $P_t = 113$ GPa. Also, we investigate the effects of anharmonicity by calculating the third order elastic constants C_{ijk} . The experimental values are still unknown and comparisons with our calculations are suitable in the future.

Keywords: Silicon carbide; elastic constants, pressure effects, Density Functional Theory (DFT).

1. Introduction

It is well known that there are a large number of polytypes for the SiC crystal whose properties are different for each polytype. Over the last decade, there has been growing interest in the only polytype with a cubic structure 3C-SiC (β -SiC) as a MEMS material. Unlike 6H-SiC, the 3C polytype can be epitaxially grown on single-crystal silicon substrates. At CWRU, the first successful depositions of spatially uniform, single-crystal, 3C-SiC films on 4-inch (100) silicon wafers were made possible. Some of its structural and mechanical properties have been investigated by various techniques [1,3] and will provide us some comparisons with our ab-initio calculations.

In this work, we do first-principle calculations of the second order and third order elastic constants for the silicon carbide zinc blende polytype β -SiC. We compare our numerical results with our experimental available ones [1] and we give prediction for third order elastic constants and pressure dependence of second order elastic constants until the structural transformation from a zinc Blende to a rocksalt structure takes place.

The paper is organized as follows: the computational method is described in section 2. In sections 3 and 4 the results of the calculations of structural and elastic properties are respectively presented and compared with available experimental and theoretical data. In section 5 and 6 the results of the calculations with hydrostatic pressure and of the third order elastic constants are respectively presented. A conclusion is given in section 7.

2. Computational Method

The calculations were performed within the local density approximation LDA to the density-functional theory DFT [4,5], using the pseudopotential plan-wave method as implemented in the ABINIT code [6]. We have used the Teter and Pade parameterization [7] for LDA. Only the outermost electrons of each atom were explicitly considered in the calculation. The effect of the inner electrons and the nucleus (the frozen core) was described within a pseudopotential scheme. We used the Hartwigsen-Goedecker-Hutter scheme [8] to generate the norm-conserving nonlocal pseudopotentials, which results in highly transferable and optimally smooth pseudopotentials. A plane-wave basis set was used to solve the Kohn-Sham equations in the pseudopotential implementation of the DFT-LDA.

The Brillouin zone integrations were replaced by discrete summations over a special set of k-points using the standard k-point technique of Monkhorst and Pack [9] where the k-point mesh used is (8 X 8 X 8). The plane –wave energy cutoff to expand the wave functions is set to be 90 Hartree (1 Hartree = 27.211396 eV).

3. Structural Properties

The minimization of the total energy with respect to the unit cell volume allows us to obtain the equilibrium structural properties of β -SiC. The equilibrium lattice parameter and the bulk modulus can be determined by fitting the total energies calculated at several lattice constants to the Murnaghan's equation of state [10]:

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

$$B = V \frac{\partial^2 E}{\partial V^2} = \frac{4}{9a} \frac{\partial^2 E}{\partial a^2} \quad (2)$$

where, at zero pressure, B_0 is the bulk modulus, V_0 is the unit-cell volume, $E(V_0)$ energy at the cell volume and $B'_0 = \partial B / \partial P$. Note that another method to compute the equilibrium lattice parameter is the structural optimization using the Broyden-Fletcher-Goldfarb-Shanno minimization (BFGS) [11].

In Table 1, we show the lattice parameter a_0 along with the values of B_0 and B'_0 ; experimental [1,12] and previous theoretical calculations [13,14] are also displayed. We observed that the values of the lattice parameter calculated from the BFGS tool are in good agreement with the ones obtained from

the fits to Murnaghan's equation of the total energies. Moreover, a_0 of SiC agrees quite well with experimental [12] and theoretical [13,14] values.

Table 1. Lattice constant, bulk modulus, elastic constants and their derivative and phase transformation pressure for β -SiC in comparison with experimental [1,12] and other theoretical [13,14] values.

^a fit to Murnaghan's equation, ^b BFGS and ^c from $B = (C_{11} + 2 C_{12})/3$.

	Our data	Expt	Calc.
a (Å)	4.3355 ^a 4.331 ^b	4.3596 [12]	4.3397 [13] 4.36[14]
B ₀ (Gpa)	218 ^a 228 ^c	225 [12] 219 [1]	218 [13] 210 ^a , 216 ^c [14]
B ₀ '	3.599		3.71 [14]

4. Elastic Properties

In a cubic lattice, three independent elastic constants C_{11} , C_{12} and C_{44} are determined by employing suitable lattice distortions. Following the work of Nielsen and Martin [15], we determine these constants. C_{11} and C_{12} can be found from the stress-strain relation with the application of an ε_1 strain. This strain scales the x dimensions by $(1+\varepsilon_1)$ while maintaining constant the y and z dimensions. For small strain the harmonic approximation defines the relations :

$$C_{11} = \frac{\sigma_1}{\varepsilon_1} \quad (3)$$

$$C_{12} = \frac{\sigma_2}{\varepsilon_1} \quad (4)$$

Where σ_i with ($i = 1,2$) represent the stress.

From the following stress-strain relation [15], one can obtain the elastic constant C_{44} .

$$\sigma_4 = \left[C_{44}^0 - \Omega^{-1} \Phi \left(\frac{\xi a_0}{4} \right)^2 \right] \varepsilon_4 = C_{44} \varepsilon_4 \quad (5)$$

In Eq. (5), C_{44}^0 denotes the elastic constant in absence of internal displacements u , Ω is the volume of the unstrained unit cell, Φ is the force constant and ξ is the internal strain parameter. We can determine C_{44} and ξ with two independent calculations: setting $\varepsilon_4=0$ and a small relative displacement u then with small ε_4 and $u=0$; details about this method can be found in ref. [15]. The calculations were performed with $\varepsilon_1 = \pm 0.004$ in the direction (100) to determine C_{11} and C_{12} and with $\varepsilon_4 = \pm 0.004$ and $u = \pm 0.002\sqrt{3}a_0$ in the direction (111) to find C_{44} , ξ and the optical Γ -phonon frequency ω_Γ . Φ is the constant force that raise from our results of phonon frequencies and is equal to

$$\Phi = \mu \omega_\Gamma^2 \quad (6)$$

Where μ is the reduced mass.

In Table 2, we show the elastics constants calculated compared with experimental [1,12,16] and previous theoretical calculations [13,14]. The second order elastic constants C_{ij} compared fairly well with those previously measured by one of us using the Brillouin light scattering technique (P. Djemia) [1].

For cubic systems, the bulk modulus B can be expressed as a linear combination of the two elastic constants C_{11} and C_{12} :

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (7)$$

The bulk modulus B obtained from Eq. (7) is in reasonable agreement with the values computed by total energy fitting to Murnaghan's equation (1) found earlier (see table 1).

Table 2. Elastic constants and their derivative and phase transformation pressure for β -SiC in comparison with experimental [12,1,16] and other theoretical [13,14] values.

	Our data	Expt	Calc.
C_{11}	402.3 (LDA)	390 [12] 395±12 [1]	385 [13] 384 [14]
C_{12}	141.1 (LDA)	142 [12] 132±9 [1]	135 [13] 132 [14]
$(C_{11}-C_{12})/2$	130.5 (LDA)	136±8 [1]	
C_{44}	253.4 (LDA)	256 [12] 236±7 [1]	257 [13] 241[[14]
$(C_{11}+C_{12}+2C_{44})/2$	525.1 (LDA)	504±15 [1]	
ξ	0.413		0.41 [13]
dC_{11}/dp	3.12		3.49 [13]
dC_{12}/dp	3.4		4.06 [13]
dC_{44}/dp	1.32		1.58 [13]
dC_{44}^0/dp	2.75		3.65 [13]
P_i (Gpa)	113.5	100 [16]	65 [14]
V_T/V_0	0.748	0.757 [16]	0.817 [14]

5. Pressure Effect On Elastic Properties

We have calculated the three elastic coefficients C_{11} , C_{12} and C_{44} of β -SiC from the stress-strain relations up to 100 Gpa to study the elastic instability. Both C_{11} and C_{12} increase monotonously with increasing pressure values with a linearly variation for pressure less than 80 GPa, as is shown in fig. 1. On other hand, the variation of C_{44} with the pressure is non-linear one (see figure 1). Analytical relations for the pressure dependence of these elastic constants are given by the quadratic fit below.

$$C_{11} = 408.4 + 3.44p - 0.00365p^2 \quad (8-a)$$

$$C_{12} = 143.8 + 3.57p - 0.00196p^2 \quad (8-b)$$

$$C_{44} = 260.71 + 1.321p - 0.0052p^2 \quad (8-c)$$

For a cubic crystal under pressure p , the generalized elastic stability criteria [17,18] are:

$$K = \frac{1}{3}(C_{11} + 2C_{12} + p) > 0 \quad (9-a)$$

$$G' = C_{44} - p > 0 \quad (9-b)$$

$$G = \frac{1}{2}(C_{11} - C_{12} - 2p) > 0 \quad (9-c)$$

For zero pressure, we find the well-known Born elastic stability criteria [19].

When pressure is applied, SiC transform from zinc-blend phase into rocksalt. We find that G decreases gradually with pressure and vanishes at about 113 GPa and G' decreases also to zero but at higher pressure, as it is shown in fig. 2. Therefore, the phase transition occurs for β -SiC at the much higher pressure at which G becomes zero ($P_i=113$ GPa). The zinc-blend structure becomes unstable at a volume reduction $V_T/V_0 \approx 0.748$. Where V_0 is the volume at equilibrium and V_T the volume at phase transition.

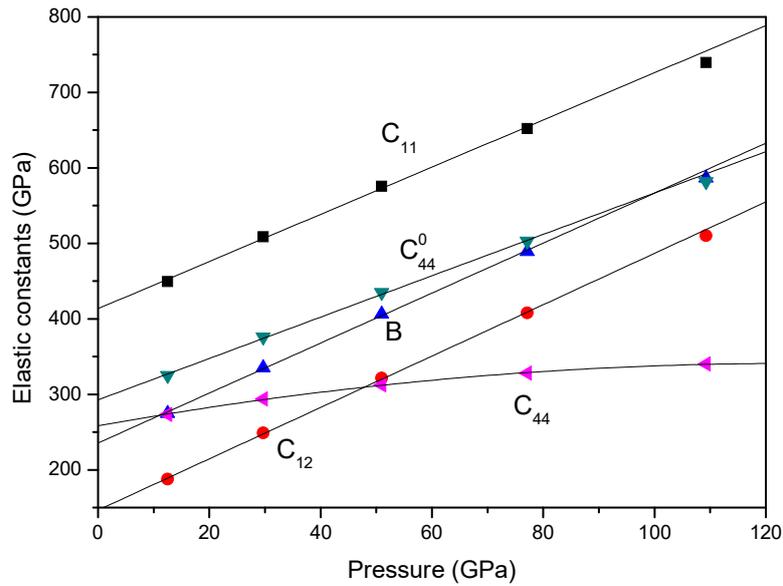


Figure 1. Pressure dependence of the elastic constants for β -SiC. ■ our data, — fit.

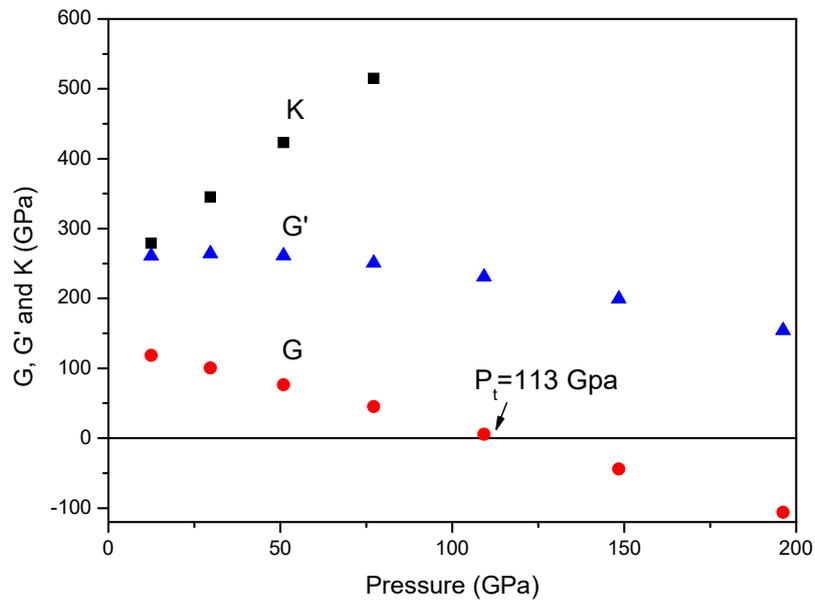


Figure 2. The pressure variation of G , G' and K for β -SiC.

6. Third Order Elastic Constants

Higher-order elastic constants provide an efficient measure of many aspects of lattice anharmonicity. In particular, the third order elastic constants are useful in the calculations of many mechanical and thermal properties related to the anharmonic nature of the lattice potential energy. In addition the third

order elastic constants would be expected to provide useful new information on the nature of cohesive properties and inter atomic forces, so why this constants have received an enormous attention for many materials.

Lattice dynamical models used to model anharmonic properties typically use large numbers of fitting parameters. In contrast, ab-initio methods are inherently free from fitting parameters, thus they usually increase physical insight.

In this part second and third order elastic constants are calculated from the energy variation by applying a strain to the equilibrium lattice configuration. The change in total internal energy per unit of undistorted volume V_0 in response to an applied stress is given by:

$$\frac{\Delta E}{V_0} = \frac{1}{2} C_{ij} e_i e_j + \frac{1}{6} C_{ijk} e_i e_j e_k + \dots \quad (10)$$

Where ΔE is the energy increment by the strain vector $e(e_1, e_2, e_3, e_4, e_5, e_6)$ and C_{ij} , C_{ijk} are the matrix of second and third order elastic constants respectively.

For cubic materials, in addition to the three independent C_{ij} , symmetry dictate six independent C_{ijk} ($C_{111}, C_{112}, C_{123}, C_{144}, C_{166}, C_{456}$). This constants were computed using six distortion type labeled I, II, III, IV, V and VI using six component strain notation, distortion I-VI respectively correspond to: uniform dilatation ($e_1 = e_2 = e_3, e_4 = e_5 = e_6 = 0$); both of [100] and [010] strain ($e_1 = e_2, e_3 = e_4 = e_5 = e_6 = 0$); distortion at inverse eight ($e_1 = e_2 = -e_3, e_4 = e_5 = e_6 = 0$), here the phrase constant height refers to constant height of the f.c.c. unit cell ; uniform distortion along [111] ($e_1 = e_2 = e_3 = e_4 = e_5 = e_6$); [111] shear strain ($e_1 = e_2 = e_3 = 0, e_4 = e_5 = e_6$) and finally ($e_1 = e_4, e_2 = e_3 = e_5 = e_6 = 0$) strain.

For the six distortions employed in this study, strain component relate as scalar multiples, adding subscript D to denote the type of distortion while using the above definition of strains I-VI yields the following relationship:

$$\frac{\Delta E_D}{V_0} = \frac{1}{2} k_D e_1^2 + \frac{1}{6} g_D e_1^3 \quad (11)$$

where:

$$k_I = 3C_{11} + 6C_{12} \quad (12-a)$$

$$k_{II} = 2C_{11} + 2C_{12} \quad (12-b)$$

$$k_{III} = 3C_{11} - 2C_{12} \quad (12-c)$$

$$k_{IV} = 3C_{11} + 6C_{12} + 3C_{44} \quad (12-d)$$

$$k_V = 3C_{44} \quad (12-e)$$

$$k_{VI} = C_{11} + C_{44} \quad (12-f)$$

$$g_I = 3C_{111} + 18C_{112} + 6C_{123} \quad (13-a)$$

$$g_{II} = 2C_{111} + 6C_{112} \quad (13-b)$$

$$g_{III} = C_{111} + 6C_{112} - 6C_{123} \quad (13-c)$$

$$g_{IV} = 3C_{111} + 18C_{112} + 6C_{123} + 9C_{144} + 18C_{166} + 6C_{456} \quad (13-d)$$

$$g_V = 6C_{456} \quad (13-e)$$

$$g_{VI} = C_{111} + 3C_{144} \quad (13-f)$$

$k_i, g_i (i = I, II, \dots, VI)$ are second order force constants and third order force constants respectively.

As is seen from equations (12-a) to (13-f) it is possible to derive the three C_{ij} and the six C_{ijk} from calculation using the sets of strains chosen.

In the present work, 50 sets of $\frac{\Delta E}{V_0}$ for each distortion are obtained from PW-PP calculation by

varying the appropriate strains from about -0.5 to about +0.3. The second and third order elastic constants are then obtained from a cubic polynomial fitting of energy strains relation. We have included the following points : all points for distortion type I, II, III;IV for strain type V, $-0.002 \leq e_1 \leq 0.5$; and for strain type VI, $-0.1 \leq e_1 \leq 0.1$. The calculated k_i and g_i are fitted simultaneously and listed in table II with the corresponding third order elastic constants for the β -SiC. The combination of C_{ij} derived from the second order terms are also given in table 3.

Third order elastic constants calculated using the Keating model by Davydov [20] are shown in Table 3. Other second order elastic constants ($C_{11} = 410.5$ GPa, $C_{12} = 164$ GPa, $C_{44} = 194$ GPa) [21] larger than ours were used for his calculations that may explained the large discrepancy between his results and our calculation of C_{ijk} .

Table 3. Calculated second and third-order force constants and the third order elastic constants in units of GPa of β -SiC.

^a calculated using Eqs (12-a)-(12-f) and the C_{ij} calculated previously.

^b calculated using Eqs (12-a)-(12-f) and the measured C_{ij} reported in table I.

^c From Davydov [20] using Keating model and other C_{ij} [21] as input parameters.

	This study		Measured values
K_I	1950.54	2053.5 ^a	1977±20 ^b
K_{II}	1041.66	1086.8 ^a	1054±20 ^b
K_{III}	915.28	924.7 ^a	921±20 ^b
K_{IV}	2748.78	2813.7 ^a	2685±28 ^b
K_V	813.58	760.2 ^a	708±21 ^b
K_{VI}	661.16	655.7 ^a	631±19 ^b
g_I	-17051.17		
g_{II}	-6345		
g_{III}	-6514.92		
g_{IV}	-44391.48		
g_V	-3159.72		
g_{VI}	-1268		
C_{111}	+453.5	-1680 ^c	
C_{112}	-906.33	-1026 ^c	
C_{123}	+255.08	-371 ^c	
C_{144}	-573.83	3 ^c	
C_{166}	-1056.46	-621 ^c	
C_{456}	-526.62	-69.5 ^c	

Because of the lack in experimental and theoretical value of third order elastic properties of β -SiC, no satisfactory comparison has been made, so why we have calculated the non-linear elastic properties of diamond which are known in order to check the consistency of our calculations. The calculated second and third order force constants are reported in table 4 and show good agreement with known calculated or measured values.

TABLE 4. Calculated second and third-order force constants and in units of GPa of the diamond.

^a calculated using Eqs. (12-a)-(12-f) and the measured C_{ij} reported in ref [22].

^b calculated using Eqs. (12-a)-(12-f) and the C_{ij} reported in ref. [23]

^c calculated using Eqs. (12-a)-(12-f) and the C_{ij} reported in ref [24].

^d calculated using Eqs. (13-a)-(13-f) and the C_{ijk} reported in ref. [23]

	This study	Measured values	ref. [23]	ref. [24]
K_I	4052	3993 ^a	3912 ^b	3897 ^c
K_{II}	2418	2412 ^a	2354 ^b	2342 ^c
K_{III}	2975	2993 ^a	2896 ^b	2873 ^c
K_{IV}	5763	5730 ^a	5562 ^b	5499 ^c
K_V	1740	1737 ^a	1650 ^b	1602 ^c
K_{VI}	1648.24	1660 ^a	1600 ^b	1577 ^c
g_I	-32982,66		-33300 ^d	-54309
g_{II}	-14905,56		-17400 ^d	
g_{III}	-12016,56		-11100 ^d	
g_{IV}	-86882,52		-87900 ^d	
g_V	-6201,18		-7800 ^d	
g_{VI}	-3578.7		-6300 ^d	

The six second order force constants of diamond calculated using Eq. (12-a) to (12-f) and measured C_{ij} agree well with our results to within 2 %, also our six third order force constants are in good agreement with the one calculated using Eq. (13-a) to (13-f) and the ab-initio C_{ijk} reported in ref [23].

The procedure applied in the case of diamond has been employed for the β -SiC, but in view of the limited experimental and theoretical value no valuable comparison has been made and we suggest that the C_{ij} and C_{ijk} in table II are predictions to be verified by future experiments.

7. Summary And Conclusions

We have performed high pressure ab-initio calculations of the elastic properties for the zinc blende polytype of silicon carbide β -SiC. the results obtained of the elastic constants (C_{11} , C_{12} , and C_{44}), are in good agreement with the available experimental and theoretical data reported in the literature.

The pressure at which the transition from zinc-blende to Rocksalt structure should arise is found to be 113 GPa and is associated to the elastic instability $(C_{11} - C_{12} - 2p) = 0$. Our results predict the pressure dependence of the three independent elastic constants (C_{11} , C_{12} , C_{44}) for β -SiC that still have not been experimentally derived.

Also, we investigate the effects of anharmonicity by calculating the third order elastic constants C_{ijk} . Because of the lack in experimental and theoretical value of third order elastic properties no comparison has been made. Then, further experiments are suitable.

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