

Pseudopotential calculations on 3C-SiC

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Abstract

The pressure dependence of the direct and indirect band gaps and the electronic charge densities in cubic SiC are calculated by using an adjusted local pseudopotential method. The results for the pressure are in excellent agreement with the experimental values. The charge density results are discussed in terms of the ionicity of SiC.

Keywords: Silicon carbide; Pseudopotential calculations

1. Introduction

The physics of 3C-SiC is of interest, because of its potential use in solid-state devices owing to its high melting point, chemical inertness, and high hardness [1,2]. Silicon carbide occupies a somewhat special position among the numerous tetrahedrally bonded compound semiconductors of the $A^N B^{8-N}$ type. Although its eight bonding electrons are provided in equal numbers by the two constituents, the bonds cannot be symmetric – if only because of the difference in the size of the atoms. In contrast to the usual heteropolar semiconductors, the ionicity of SiC is believed to originate from the difference in the core sizes of C and Si. The core size difference results in an asymmetric electronic charge distribution about the midpoint of the bond. There are, however, some differences between SiC and other zinc blende compounds. We found it interesting to study SiC since its bonding properties exhibit some anomalies. According to the Phillips scale [3] it has a low ionicity (f_i) value, 0.177. However, according to the work of Christensen et al. [4], this is surprisingly small when the trends in ionicity are compared with those of the transverse effective charge, from which we would expect SiC to be considerably more ionic than is indicated by the value $f_i=0.177$. Several authors [5–7] show that a large fraction of the valence electrons are accumulated in the vicinity of the carbon atom, and the compound receives a large ionicity. The calculated ionicity value determined by Christensen et al. [4] is $f_i=0.395$, which is not so high as that predicted by Churcher et al. [5]. Their calculated pseudodensity suggests that SiC should have an ionicity

comparable to that of ZnS. Therefore, if we follow the Phillips value of $f_i<0.35$, SiC must first undergo a structural phase transition with pressure to a denser structure, which is the β -Sn metallic phase, whereas according to Christensen, for an ionicity value greater than 0.35 SiC will transform to rock salt phase at low pressure and β -Sn phase at very high pressure. However, some controversy still remains on this point, since according to the work of Chang and Cohen [7] the simple cubic structure for C and Si is metallic, and the rock salt phase of SiC might be expected to be metallic. This is consistent with the results of several authors [5–7], who have found that the effect of compression is to induce a substantial increase in the background charge density in the nonbonding areas, with a corresponding decrease in the peaks. They have ascribed this to increasing metallisation under pressure. However, it is difficult to understand from these results the observed increase in the transverse effective charge with pressure [8,9].

In this work we present an adjusted pseudopotential method for studying cubic SiC. The emphasis is on the description of the Si–C bond, which is the prerequisite for understanding the physical properties of SiC in any crystallographic modification.

2. Calculations

Let us define our empirical pseudopotential parameters (EPP) of a semiconductor as V_L . We determine the EPP parameters by the nonlinear least-squares

method, in which all the parameters are simultaneously optimized under a defined criterion of minimizing the root-mean-square (rms) deviation. The experimental electronic band structures at normal and elevated pressure are used.

Our nonlinear least-squares method requires that the rms deviation of the calculated level spacings (LS) from the experimental ones, defined by

$$\delta = \left[\sum_{i,j} [\Delta E^{(i,j)}]^2 / (m - N) \right]^{1/2} \quad (1)$$

should be minimum. Note that

$$\Delta E^{i,j} = E_{\text{exp}}^{(i,j)} - E_{\text{calc}}^{(i,j)}$$

where $E_{\text{exp}}^{(i,j)}$ and $E_{\text{calc}}^{(i,j)}$ are the observed and calculated LSs between the i th state at the wave vector $\mathbf{k} = \mathbf{k}_i$ and the j th at $\mathbf{k} = \mathbf{k}_j$, respectively, in the m chosen pairs (i,j) . N is the number of EPP parameters. The calculated energies obtained by solving the EPP secular equation depend nonlinearly on the EPP parameters. The starting values of the parameters are improved step by step by iterations until δ is minimized. Let us denote the parameters by P_u ($u = 1, 2, \dots, N$) and write them as $P_u(n+1) + \Delta P_u$, where $P_u(n)$ is the value at the n th iteration. These corrections ΔP_u are determined simultaneously by solving a system of linear equations

$$\sum_{u=1}^N \left[\sum_{i,j}^m (Q_u^i - Q_u^j)(Q_u^i - Q_u^j) \right] = \sum_{i,j}^m (E_{\text{exp}}^{(i,j)} - E_{\text{calc}}^{(i,j)}(n))(Q_u^i - Q_u^j) \quad (2)$$

$u' = (1, 2, \dots, N)$

where $E_{\text{calc}}^{(i,j)}(n)$ is the value at the n th iteration, Q_u is given by

$$Q_u^j = \sum_{q,q'} [C_q^i(\mathbf{k}_i)]^* (\partial H(\mathbf{k}_i) / \partial P_u)_{qq'} C_{q'}^j(\mathbf{k}_i) \quad (3)$$

$H(\mathbf{k}_i)$ is the pseudo-Hamiltonian matrix at $\mathbf{k} = \mathbf{k}_i$ in the plane-wave representation, and the i th pseudo wave function at $\mathbf{k} = \mathbf{k}_i$ is expanded as

$$\psi_{\mathbf{k}_i}^i(\mathbf{r}) = \sum_q C_q^i(\mathbf{k}_i) \exp[i(\mathbf{k}_i + \mathbf{q}_q)\mathbf{r}] \quad (4)$$

\mathbf{q}_q being the reciprocal lattice vector. Eq. (2) shows that all of the parameters are determined automatically in an interdependent way, among the parameters $V_L(\mathbf{k}_q^2)$. The same procedure is used for the determination of the pressure derivatives of the pseudo-potential form factors required when using the experimental values of Cardona [9,10].

3. Results

The energy band structure of cubic SiC calculated with our adjusted pseudopotential is shown in Fig. 1. There is an interesting similarity between the results

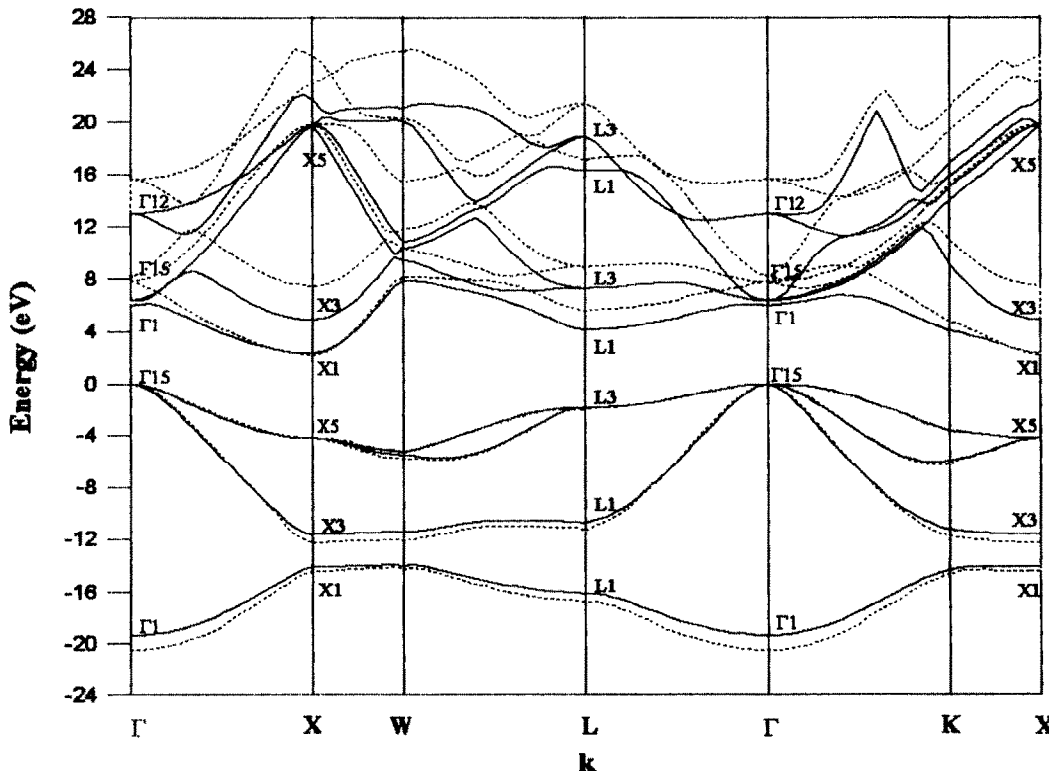


Fig. 1. The calculated energy band structure of SiC: (—) for normal pressure; (---) under 400 kbar.

Table 1

The calculated values of the different band gaps, and linear and quadratic pressure coefficients of important band gaps for SiC

Band gap	E_{nk} (eV)	dE_{nk}/dp (10^{-3} kbar $^{-1}$)	d^2E_{nk}/dp^2 (10^{-6} kbar $^{-1}$)
$\Gamma_{15}^v - \Gamma_1^c$	6.0 ^a , 6.0 ^b	5.50 ^a	-2.97 ^a
$\Gamma_{15}^v - X_1^c$	2.39 ^a , 2.39 ^b	-0.33 ^a	8.09 ^a
$\Gamma_{15}^v - L_1^c$	4.20 ^a , 4.2 ^b	3.95 ^a	-1.58 ^a

^aPresent work.

^bRefs. [9] and [10].

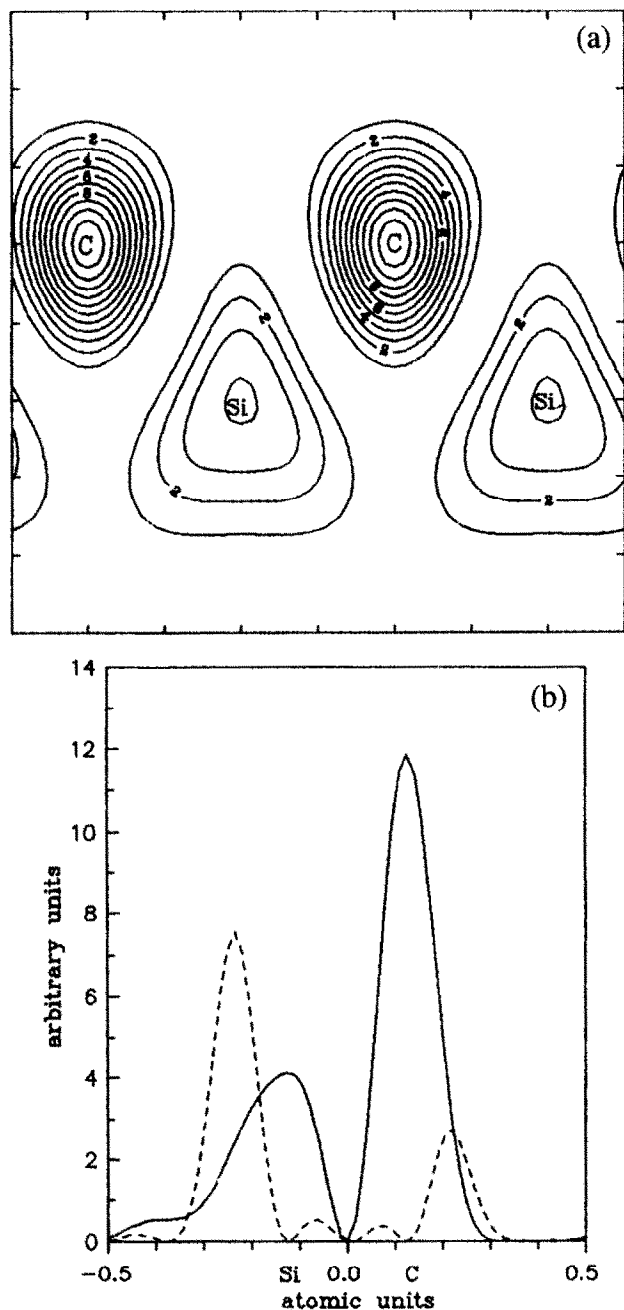


Fig. 2. The first conduction band charge densities at the Γ point in SiC: (a) in the (110) plane; (b) along the $\langle 111 \rangle$ direction ((—) normal pressure; (---) under 400 kbar).

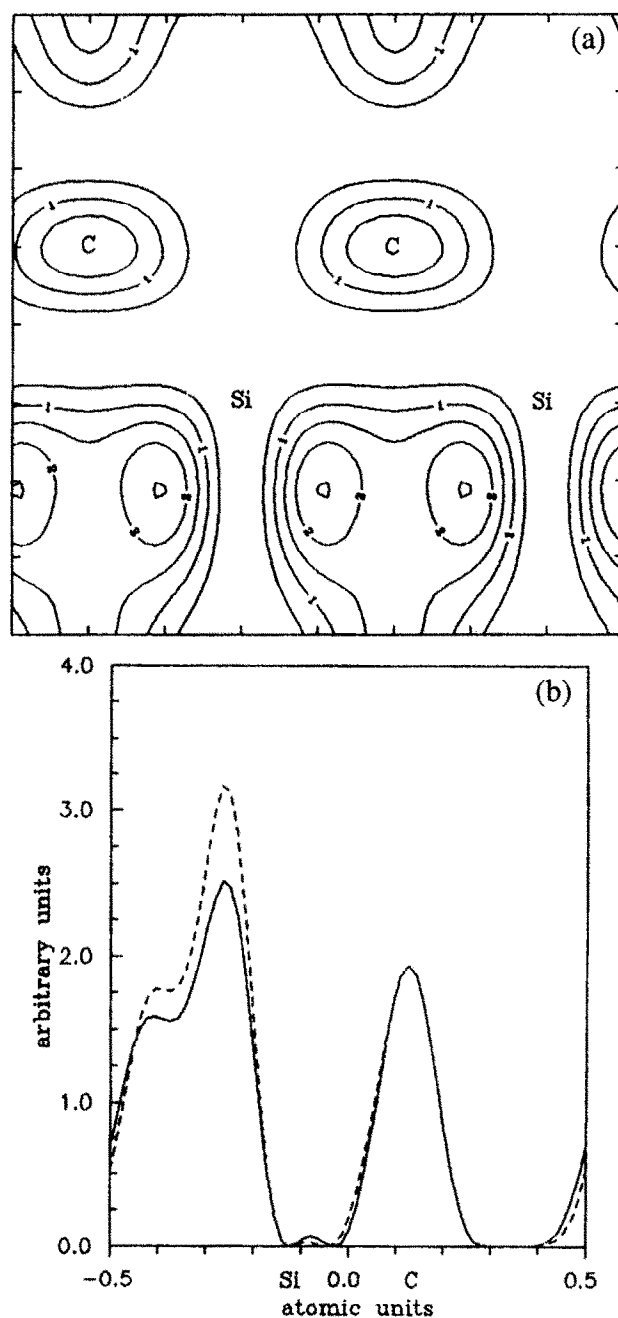


Fig. 3. The first conduction band charge densities at the X point in SiC: (a) in the (110) plane; (b) along the $\langle 111 \rangle$ direction ((—) normal pressure; (---) under 400 kbar).

shown here and our previously published energy band structure for diamond [11]. The band structure clearly shows the splittings of levels that arise from the loss of the symmetry operation of inversion through the bond center between two atoms in a cell upon going from two carbons per unit cell to a carbon and silicon atom. As a consequence, the valence band of SiC is separated into two parts by the lifting of degeneracies, e.g., at the X and W points.

The calculated bands of SiC are roughly 30% narrower (6.5 eV) than those obtained for diamond [11], yet

Table 2

The adjusted pseudopotential form factors (in Ry) for SiC at various pressures

P (kbar)	a (Å)	$v_s(3)$	$v_s(8)$	$v_s(11)$	$v_a(3)$	$v_a(4)$	$v_a(11)$
0	4.3500	−0.4280	0.1017	0.1108	0.0010	0.0800	0.0277
50	4.3173	−0.4005	0.0662	0.1509	0.0010	0.0812	0.0321
100	4.2874	−0.4016	0.0672	0.1616	0.0010	0.0823	0.0476
300	4.1882	−0.3947	0.0751	0.2585	0.0011	0.0921	0.1922
400	4.1475	−0.4093	0.0952	0.2233	0.0011	0.0880	0.1547
600	4.0783	−0.3825	0.0927	0.2633	0.0011	0.0910	0.1600

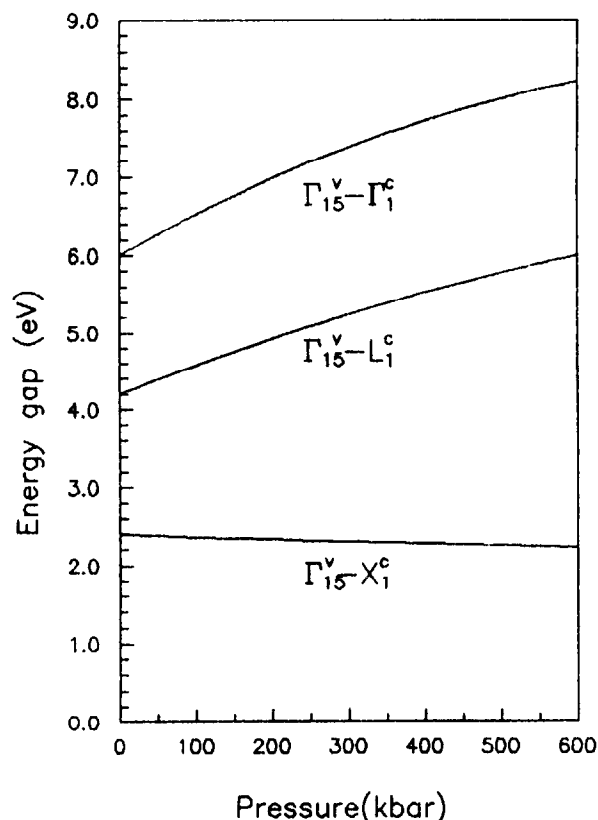


Fig. 4. The different band gaps vs. pressure.

wider than those presented for silicon by about 3.5 eV [12].

For purposes of comparison, we have tabulated the eigenvalues at high-symmetry k points in Table 1. Interestingly, our results are in excellent agreement with the known experimental transitions, [9,10]. We find the fundamental gap of SiC to be indirect from Γ_{15} to X_1^c .

The results for the pressure coefficients of the important direct as well as indirect band gaps are presented in Table 1 for SiC. The agreement of the calculated coefficients with experimental values is uniformly good for most of the gaps. The calculated pressure coefficients are generally within 1% or so of the experimental values, which we feel is within the experimental uncertainty.

Comparing previous high-pressure band-structure calculations with these calculations reveals that our calculated pressure coefficients agree with experimental data at least as well as those obtained from more complicated models. Our results are definitely in better agreement with experiment than those of Chang and Cohen [7] and Cheong et al. [13], which were the first high-pressure band-structure calculations for SiC. In light of the fact that in our calculations only the optical absorption data and normal-pressure pseudopotential parameters are used as input data, the good agreement obtained is rather gratifying. The fact that the pressure coefficients are accurately predicted in the present work would make our simple scheme useful for calculations of the pressure dependence of optical spectra.

The negative sign of the linear pressure coefficient of the Γ -X transition results in the pseudopotential calculation from a lowering of the X_1^c state and a raising of the Γ_8^c state upon a decrease in the volume (Fig. 1). The fact that dE/dp is also negative is due to the strong influence of the d levels, whose energy is well above that of the X minima of the conduction band. These levels repel the conduction band at X, forcing it downward in energy (relative to the minimum at Γ). However, this coefficient is small, and this may result from the fact that the X_1^c conduction band in C has a positive coefficient of $0.53 \text{ meV kbar}^{-1}$ [14]. Since the d state in C is absent in the low-lying valence states, the d-energy is much higher than that for Si [14]. Although the charge densities for the X_1^c conduction band in semiconductors are mostly d-like [8], the d-state contribution to the charge density at the X_1^c point is less for SiC and much less for C as compared with Si. Thus the X_1^c band in SiC decreases very slowly with pressure, while it increases in C. This fact is supported by the relatively small charge transfer from the first conduction band at the Γ point to that at the X point (Figs. 2 and 3).

The energies of the direct and indirect band gaps as a function of pressure, obtained from these calculations for SiC, are plotted in Fig. 4.

A particular aim of this work is to discuss qualitatively the ionicity of SiC. One of the successes of the dielectric theory, derived by Phillips and Van Vechten [3], was

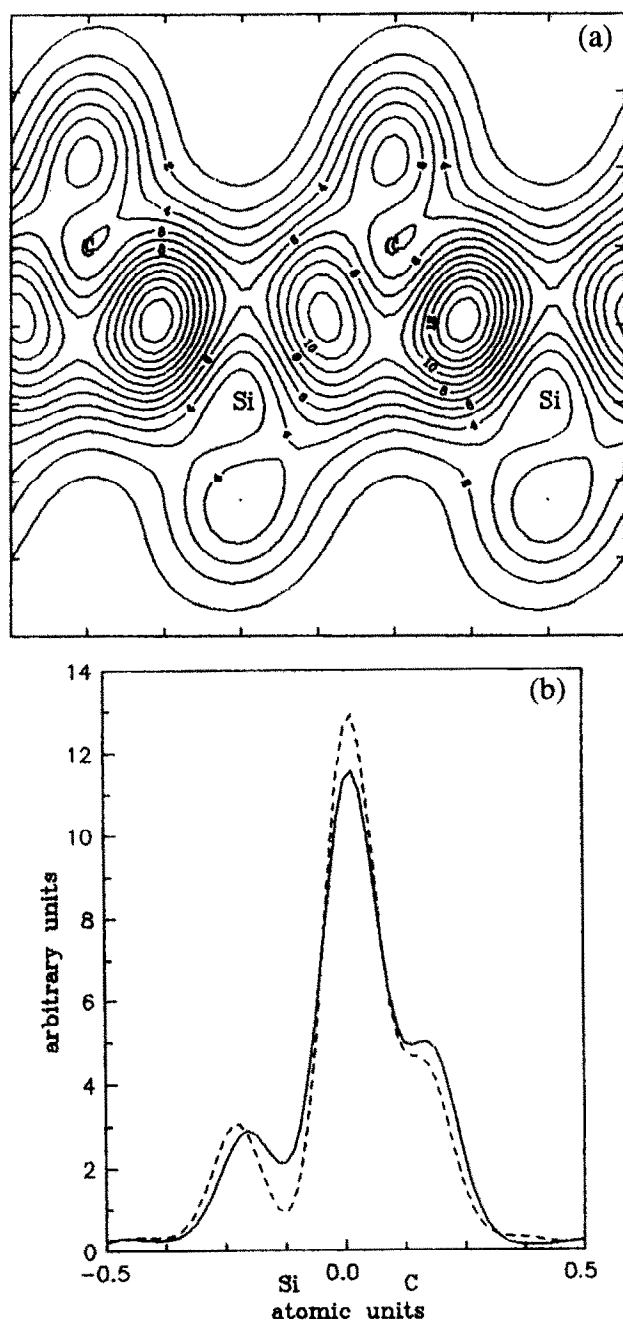


Fig. 5. The total valence charge densities calculated using the special two-point scheme of Chadi and Cohen [20] in SiC: (a) in the (110) plane; (b) along the $\langle 111 \rangle$ direction ((—) normal pressure; (---) under 400 kbar).

Table 3
The transverse effective charge and its variation with the lattice constant, as calculated for SiC

e^*_T	$\partial e^*_T /\partial \ln a_0$
2.79 ^a , 2.697 ^b , 1.69 ^b	-10.3 ^a , -5.4 ^c , 2.97 ^b

^aPresent work.

^bRef. [16].

^cRef. [18].

that it made it possible to ascribe, in a systematic manner, an ionicity value f_i to each compound, and that a specific critical value $f_i^c = 0.786$ provided a complete separation between $N_c = 4$ and $N_c = 6$ structures. Of particular interest has also been the volume dependence of the transverse effective charge e^*_T , which can be related to the dependence of the ionicity of the chemical bond on the bond length [15,16]. In all cases, with the exception of SiC, $|e^*_T|$ and thus the ionicity have been found to decrease with decreasing bond length. For SiC the opposite occurs. In fact, a semiquantitative interpretation of these results by means of a pseudopotential band structure of e^*_T has been made. The theoretical calculation of e^*_T is based on the pseudopotential expression [17]

$$e^*_T = -\Delta Z + (2/N) \sum_{\mathbf{G}} \sum_n \sum_{n'} \sum_{\mathbf{k}} \frac{(\langle n, \mathbf{k} | p_x | n', \mathbf{k} \rangle \langle n', \mathbf{k} | e^{i\mathbf{G} \cdot \mathbf{r}} | n, \mathbf{k} \rangle) / (E_{n\mathbf{k}} - E_{n'\mathbf{k}})^2}{\times G_x [i v_s(\mathbf{G}) \sin \mathbf{G} \cdot \mathbf{t} - v_a(\mathbf{G}) \cos \mathbf{G} \cdot \mathbf{t}]} \quad (5)$$

This expression follows from the calculation of the macroscopic dipole moment, which is induced by a small ionic displacement at zero macroscopic electric field. Eq. (5) is derived in the framework of linear-response theory, with the Hartree approximation and the method of long waves. The single-particle Bloch states $|n, \mathbf{k}\rangle$ and the energies $E_{n\mathbf{k}}$ of the electrons are calculated within our pseudopotential framework. ΔZ is one half the difference in core charges between the anion and the cation ($\Delta Z = 0, 1$ and 2 for IV-IV, III-V and II-VI compounds, respectively), N denotes the number of unit cells, the \mathbf{G} s are reciprocal lattice vectors, \mathbf{p} is the momentum operator, and $\mathbf{t} = (a/8)(1, 1, 1)$. The first term in Eq. (5) arises from the bare core charges. $v_s(\mathbf{G})$ and $v_a(\mathbf{G})$ are the symmetric and antisymmetric pseudopotential form factors (see Table 2). The results of our calculations are summarized in Table 3. The theoretical values of e^*_T and its pressure derivative agree well with the experimental values. However, the empirical rule of Vogl [17] cannot be applied in the case of SiC, since it gives erroneous values.

Since e^*_T is a measure of ionicity, one concludes that this ionicity increases with pressure in SiC, which is consistent with the work of Cardona and co-workers [9]. This anomalous sign of the derivative of $|e^*_T|$ with respect to the bond length results from the strong difference in the pseudopotentials of C and Si for small wave vectors, which in turn is related to the lack of p electrons in the core of the carbon atoms.

According to the Phillips scale SiC has a low ionicity, with $f_i = 0.177$. This is surprisingly small when the trends in ionicity are compared with those of the transverse charge [4,19], from which we would expect SiC to be considerably more ionic than indicated by the value of

$f_i=0.177$. Indeed, the charge density calculation, illustrated in Fig. 5, shows that a large fraction of the valence electrons are accumulated in the vicinity of the carbon atom. This charge flow is possible because C has no p states in the core, i.e., there are no orthogonality requirements that would prevent the valence p states from accumulating near the nucleus. Thus the electrons easily flow from Si to C, and the compound obtains a large ionicity. A similar conclusion was reached by other authors [5–7]. According to this charge density topology, SiC would be more ionic than is often assumed. This topology is rather similar to those obtained for GaAs and GaSb [12], which have an ionicity factor of greater than 0.3. In addition, this assumption is supported by the charge densities of the conduction bands at the Γ and X points (Figs. 2 and 3), which are highly similar to those obtained for III-V compound semiconductors.

The effect of pressure on the charge densities is shown in Figs. 2, 3 and 5 (dashed lines). For the valence charge density, the most pronounced effect is the substantial increase in the background of the charge density on the peaks, with a corresponding decrease in the atom sites, which is the opposite of the results obtained by other authors [5–7]. We would describe this as increasing ionicity under pressure (the ratio of the peak heights around the C atom in the bonding and antibonding region is roughly altered, indicating a radical change in the degree of covalency). These results are consistent with the observed increases in the transverse effective charge with pressure.

Since the ionicity itself is a direct measure of the ionic interaction energy, a larger ionicity value tends to stabilize the crystal structure with a high coordination number (6), and zinc-blende-type crystals transform under pressure to the rock salt structure. As a consequence of the large ionicity value of SiC ($f_i > 0.3$) and positive df_i/dp , SiC would then be expected to have an unusually strong tendency to transform to the rock salt structure. This fact is supported by total energy calculations [4].

4. Conclusions

We may conclude that the calculated high-pressure electronic band structure of SiC, using the adjusted pseudopotential form factors, gives pressure coefficients much closer to experimental values than those obtained from more complicated models. This makes our simple scheme useful for calculations of the pressure dependence of optical spectra for other semiconductors. On the other hand, the calculations showed that SiC presents a rather large ionicity, and SiC would then be expected to have an unusually strong tendency to transform to the rock salt structure.

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