Pressure-dependent properties of SiC polytypes

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We present a first-principles study on the pressure-dependent properties of cubic and hexagonal polytypes of silicon carbide (SiC). Our calculations have been performed within density-functional perturbation theory, using the plane-wave pseudopotential approach. The stability of several high-pressure SiC phases is discussed in terms of the ionicity and metallicity of the Si–C bonds. Furthermore, we investigate pressure dependence of the zone-center frequencies, of the Born effective charges, and of the static and high-frequency dielectric constants for 3C, 2H, and 4H polytypes of SiC. Whereas the structural and electronic properties of the cubic and hexagonal polytypes are very similar, remarkable pressure-induced differences are found for the dynamical and dielectric properties. The unusual behavior of the transverse effective charge recently observed experimentally for 6H SiC is discussed. [S0163-1829(96)02119-4]

I. INTRODUCTION

The recent growing scientific and technological interest on silicon carbide (SiC) arises from its salient physical properties, in particular its mechanical, chemical, and thermal stability.¹ The scientific interest in SiC is driven by the existence of a variety of different polytypes, and its peculiar structural, lattice-dynamical, and electronic properties. SiC is the only IV-IV compound that forms stable long-range ordered structures: About 200 crystallographic modifications have been reported so far.² The polytypism originates from differences in the stacking sequence of Si-C bilayers along the [111] or [0001] direction, giving rise to cubic (*C*), hexagonal (*H*), or rhombohedral (*R*) arrangements of *n* double layers within a unit cell. The most common polytypes are 3 *C* (zinc blende), 6*H*, 4*H*, and 2*H* (wurtzite).

The technological interest in SiC is driven by its outstanding mechanical and electronic properties, such as the high melting point, the high thermal conductivity, and the large bulk modulus, as well as the large band gap and the low dielectric constant, which make it usfull for electronic and optical device applications. Microelectronic devices made of SiC can be used in high-power, high-speed, hightemperature, high-frequency, and even hard-radiation applications.³ The most favorable polytype for device applications is still in debate.

Experimental high-pressure studies have been carried out almost exclusively on 3*C* SiC. In particular, the Raman modes have been studied up to 0.4 Mbar.^{4,5} Meanwhile, there are also ultrahigh pressure studies for the zinc-blende 3*C* and for the hexagonal 6*H* polytypes of SiC.^{6,7} The 3*C* SiC undergoes a phase transition to a rocksalt-type structure at about 1.0 Mbar. On the other hand, the 6*H* polytype of SiC remains stable up to the highest pressures studied experimentally with an indication of a phase transition above 0.9 Mbar. The 6*H* SiC semiconductor becomes transparent to visible light at high pressures, and an anticipated metallic phase has not been observed yet.⁷ Both polytypes exhibit a remarkable and practically identical volume reduction under applied external hydrostatic pressure.⁶ Contrary to this volume dependence, the pressure-dependent dynamical and dielectric properties of the 3C and 6H polytypes seem to be rather different.^{4,7} The LO(Γ)-TO(Γ) splitting of the strong Raman-active modes of 6H SiC shows a saturation behavior at ultrahigh pressures. The Born effective charge of 6H SiC is found to decrease at high pressures, after increasing at lower pressures and reaching a maximum value at about 0.4 Mbar.⁷ For 3C SiC, the data of Ref. 4 exhibit a nearly linear increase of the effective charge with increasing hydrostatic pressure in the low-pressure region. Up to now, theoretical studies of pressure-dependent properties of SiC are restricted to the band gaps and to the transverse optical frequency at the zone center for 3C SiC.^{8,9}

In this paper, we present a first-principles study of the pressure-dependent properties of cubic 3C and hexagonal 2H and 4H phases of SiC. In all SiC polytypes, the chemical bonds between the silicon and carbon atoms are practically identical. Therefore, it is an interesting problem to find out how the stacking order of the Si-C bilayers influences the different physical properties of SiC polytypes. We investigate the occurrence of semimetallic and metallic highpressure phases of SiC. The stability of these phases is discussed in terms of bonding properties, such as ionicity and metallicity, and is used for an explanation of the phase transition found experimentally. Furthermore, we calculate the pressure dependence of the structural, lattice-dynamical, and dielectric properties of 2H and 4H SiC. The results for these hexagonal phases of SiC are compared with the corresponding ones of 3C SiC. In particular, we study the pressure dependence of the tensor of the Born effective charges, of the tensor of the high-frequency dielectric constant, and of the zone-center phonon frequencies. We also discuss the influence of the symmetrically inequivalent Si and C atoms in 2H and 4H polytypes on the macroscopic properties.

TABLE I. Comparison of the theoretical equilibrium lattice constant *a* and *c* (a.u.), bulk modulus B_0 (Mbar), its pressure derivative B'_0 , Poisson ratio μ for the uniaxial stress along the *c* axis, and linear compressibilities β_{\parallel} and β_{\perp} (Mbar⁻¹) of 3*C*, 2*H*, and 4*H* SiC with the available experimental data.

		а	с	B_0	B_0'	μ	$oldsymbol{eta}_{\parallel}$	$oldsymbol{eta}_{ot}$
3 <i>C</i>	Theory Expt.	8.207 8.238ª		2.236 2.27 ^b	3.77 3.57 ^b	1.0000	0.1518	0.1518
2 <i>H</i>	Theory Expt.	5.792 5.818 ^c	9.522 9.547°	2.250 2.23 ^d	3.78	0.9882	0.1457	0.1474
4 <i>H</i>	Theory Expt.	5.798 5.807 ^e	18.994 18.995 ^e	2.243	3.72	0.9963	0.1481	0.1486

^aReference 28.

^bReference 5.

^cReference 20.

^dReference 57.

^eReference 21.

II. COMPUTATIONAL DETAILS

Our calculations are performed within the framework of the density-functional theory (DFT) and the local-density approximation (LDA), using the plane-wave pseudopotential method. The analytical forms of the exchange-correlation energy and potential are taken from Ref. 10. We have generated soft norm-conserving pseudopotentials, using the scheme proposed by Troullier and Martins,¹¹ paying particular attention to the choice of the reference configuration for the atomic d states. The sums over electronic eigenstates in the Brillouin zone (BZ) have been performed, using 12 (6) Chadi-Cohen special points (SP) in the irreducible wedge of the BZ of the hexagonal 2H (4H) phase of SiC.¹² Furthermore, 10 SP are used for the semiconducting zinc-blende structure, 24 SP for the semimetallic hexagonal nickel arsenide and antinickel arsenide, and 44 SP for the semimetallic rocksalt structure. For an accurate description of the Fermi energy of the metallic cesium chloride phase 56 SP have been used.

In order to determine the volume dependence of the static total energies, we use the Vinet equation of state.¹³ The pressure-dependent lattice-dynamical and dielectric properties of the different SiC polytypes are determined within the framework of the self-consistent density-functional perturbation theory (DFPT).^{14–16} DFPT allows the calculation of the high-frequency dielectric tensor and of the Born effective charge tensor for each atom in the unit cell. This approach is also used to determine the harmonic force constants. The dimension of the plane-wave basis set at a given q point in the first BZ is fixed through the condition $\frac{1}{2}(\mathbf{q}+\mathbf{G})^2 \leq E_{\text{cut}}$, where **G** is a reciprocal-lattice vector and E_{cut} is the kineticenergy cutoff. For the calculation of the dynamical and dielectric (static) properties at the equilibrium volume, a value of 40 (48) Ry for $E_{\rm cut}$ is used to ensure convergence of the calculated phonon frequencies to within 2 cm^{-1} . To guarantee consistent results for the different physical properties at varying crystal volumes, the number of the plane waves per atom has been fixed. Further computational details have been already presented elsewhere.15,17

III. RESULTS

A. Structural properties

The equation of state (EOS) of a solid (*p*-*V* relation) plays an important role in condensed-matter physics and geophysics. Many analytical and semiempirical relations have been proposed to describe the EOS. The best-known EOS for solids was suggested by Murnaghan,¹⁸ and it is based on the empirical fact that the isothermal bulk modulus depends almost linearly upon pressure. Nowadays the Birch¹⁹ and the universal Vinet¹³ EOS, which are more accurate than the Murnaghan EOS, are mostly used in solid-state physics. In addition to the mere volume dependence of the EOS for cubic 3*C* SiC, the EOS of the hexagonal *nH* modifications of SiC depends also on the form of the unit cell (the ratio c/a of the lattice constants) and on the *n*/2 structural parameters, which fix the positions of the atoms within the unit cell.

The equilibrium structural parameters of the 2H and 4Hphases of SiC are obtained by minimizing the static total energy, with respect to the lattice constants a and c, and in case of 2H structure, with respect to the structural parameter u. The $P6_3mc$ space symmetry of these phases was fixed. We have performed the calculations in two steps. For a given unit cell volume $V = \sqrt{3}a^2c/2$, the static total energy was minimized with respect to c/a and u. This procedure was repeated for several other volumes. The theoretical equilibrium volume, V_0 , the isothermal bulk modulus at zero pressure, B_0 , and its pressure derivative, B'_0 , have been then determined by fitting the total energy as a function of volume to the Vinet EOS. In Table I, we compare the calculated equilibrium structural and elastic properties of zinc-blende 3C and hexagonal 2H and 4H SiC with the available experimental results. The theoretical lattice constants and bulk moduli are in excellent agreement, being within 2% of the room-temperature experimental data.^{20,21} To the best of our knowledge, no experimental data are available for B_0 and B'_0 of 4H SiC.

In addition, we determined the Poisson ratio $\mu = \partial \ln a / \partial \ln c$ for uniaxial stress applied along the *c* axis and the linear compressibilities parallel, $\beta_{\parallel} = -\partial \ln c / \partial p$, and



FIG. 1. Zigzag chain structure of silicon and carbon atoms in the $(11\overline{2}0)$ plane of 3C (a), 2H (b), and 4H SiC (c). The different ($\overline{1}100$) planes within the hexagonal unit cell are denoted by A, B, and C. The hexagonal (h) and cubic (c) bonding character of the bilayers is also indicated.

perpendicular, $\beta_{\perp} = -\partial \ln a/\partial p$, to the *c* axis. The rather small anisotropy of the 2H (4H) phase of SiC is described by $\mu = 0.988$ (0.996) and $\beta_{\perp} / \beta_{\parallel} = 1.012$ (1.003), both being very close to 1.0. Because of the predominantly covalent character of all SiC polytypes, each atom is surrounded by four atoms of the other kind. The polytypes are built up of double layers of Si and C atoms, which occur in hexagonal $(\ldots ABA\ldots)$ and/or cubic $(\ldots ABC\ldots)$ environment, where A, B, C represent the different position of the atoms in the (1120) plane. The 4H structure with alternating hexagonal and cubic Si-C stacking layers is shown in Fig. 1. The 2H structure consists of only hexagonal double stacking layers, whereas no bond twisting appears in the cubic 3C structure (see Fig. 1). Consequently, the smaller anisotropy of the 4H structure can be attributed to the partially cubic environments of the atoms within the unit cell. The structural anisotropy given by the Poisson ratio μ and the ratio $\beta_{\perp}/\beta_{\parallel}$ increases slightly (linearly) with increasing external hydrostatic pressure. The corresponding values of the linear coefficients of μ and $\beta_{\perp}/\beta_{\parallel}$ for 2H (4H) SiC are $\partial \mu / \partial p = 6.03 \times 10^{-3}$ (3.18×10⁻³) Mbar⁻¹ and $\partial (\beta_{\perp} / \beta_{\parallel}) / \partial p = 6.08 \times 10^{-3} (3.43 \times 10^{-3}) \text{ Mbar}^{-1}.$

The deviations from an ideal form of the hexagonal cell can be described by the ratio c/a of the hexagonal lattice constants. The ratio c/a of 2*H* and 4*H* SiC is plotted in Fig. 2, as a function of pressure. As can be seen from this figure,



FIG. 2. Pressure dependence of the ratio c/a of 2H (a) and 4H (b) silicon carbide. The filled circles indicate the values obtained from the minimization of the static total energy $\mathcal{E}(V)$ at a given pressure. The solid lines are the linear least-square fits to these calculated data.

the ratios c/a of both polytypes decrease linearly with increasing hydrostatic pressure. The equilibrium c/a ratio of 2H (1.644) and 4H (3.276) SiC are very close to the ideal value $c/a = n\sqrt{2/3}$ and indicate an almost negligible structural anisotropy at zero pressure. Moreover, the variation of the ratio c/a of both hexagonal polytypes in the pressure range up to 1.25 Mbar is less than 0.2%. This tiny variation of the ratio c/a matches well with the calculated Poisson ratio μ of these SiC phases. Because of the occurrence of cubically stacked Si-C bilayers in the unit cell of 4H SiC, the pressure variation of the ratio c/a for this phase is weaker than for 2H SiC.

The deviations of the n/2 independent structural parameters of the hexagonal nH polytypes of SiC from the corresponding ideal values are rather small for zero pressure.²² In order to estimate their pressure variation and their importance for different pressure-dependent properties of SiC, we determined the pressure dependence of the internal parameter u of 2H SiC. The hydrostatic pressure variation of this internal parameter is shown in Fig. 3 (see also Table II). The calculated parameter u decreases for small pressures and saturates for pressures higher than 0.5 Mbar. However, the relative change of the internal parameter u of 2H SiC, in the pressure range up to 1.25 Mbar, is less than 0.1%. Moreover, the influence of the pressure variation of this internal parameter on the lattice-dynamical and dielectric properties of 2H SiC is found to be negligible. Therefore, for the calculation of the equilibrium geometry of 4H SiC at a given volume of the unit cell (external hydrostatic pressure), we dis-



FIG. 3. Pressure dependence of the internal parameter u of 2H SiC. Same key as Fig. 2.

TABLE II. Calculated static equilibrium lattice constant *a* (a.u.), the ratio c/a, bulk modulus B_0 (Mbar), pressure derivative of the bulk modulus B'_0 , and ionicity factor *g* for high-pressure phases of SiC, using the Vinet equation of state.

Phase	а	c/a	B_0	B_0'	g
NaCl	7.635		2.523	4.26	0.487
NiAs	5.392	1.657	2.438	4.96	0.491
anti-NiAs	5.404	1.764	2.185	4.14	0.502
CsCl	4.972		1.819	4.32	0.447

regard the pressure variation of the internal structural parameters and restrict ourselves to the variation of the ratio c/a.

The theoretical p-V relationship of 3C, 2H, and 4H SiC is plotted in Fig. 4, together with a variation of c/a on the same scale. It is obvious that the variation of the ratio c/a of the hexagonal nH polytypes is only of minor influence. In the wide range of pressures $p \leq 0.5$ Mbar, there are practically no apparent differences between the p-V results for the three considered polytypes. The almost identical behavior of the volume compression of these SiC polytypes is due to the very similar values of the corresponding bulk moduli and their pressure derivatives (see Table I). The similarity of the structural and elastic properties is caused by the locally identical structure up to second neighbors in all polytypes. The rather similar course of the p-V relation for the different polytypes agrees well with experimentally found identical equation of state for 3C and 6H SiC in the pressure range up to 1.0 Mbar.⁶

B. High-pressure phases

1. Enthalpies and pressure-induced phase transitions

The thermodynamic potential that governs the crystal stability at a given pressure and temperature is the Gibbs free energy G = U + pV - TS. However, a complete calculation of this quantity requires the knowledge of the full phonon spectrum, too. In our calculations, we restrict ourselves to the discussion of the low-temperature case, more strictly speaking to the enthalpy $H = \mathcal{E} + pV$ with the internal energy



FIG. 4. (a) Pressure dependence of the reduced volume V(p)/V(p=0) for 3*C* (solid line), 2*H* (dotted line), and 4*H* (dashed line). In addition, the pressure dependence of the reduced c/a ratio of 2*H* SiC is also plotted as dot-dashed line.



FIG. 5. (a) Total energy per Si-C pair of 3C (solid line), NaCl (dotted line), NiAs (short-dashed line), anti-NiAs (long-dashed line), and CsCl (dot-dashed line) phases of SiC, as a function of reduced volume. The experimental volume V_0 of the zinc-blende structure of SiC has been taken as the reference one. (b) Enthalpy per Si-C pair of these SiC phases, as a function of external hydrostatic pressure.

 $U(V) \cong \mathscr{E}(V)$ described by the Vinet EOS. The zero-point motional energy is neglected. Such an approach is sufficient for the discussion of the pressure-induced properties of hard materials like diamond, silicon carbide, and even silicon for temperatures below $T^* = \hbar \omega_{\text{max}}/k_B$ given by the maximum frequency of the phonon spectrum.²³

As possible high-pressure phases of the zinc-blende (3C) structure of SiC, we consider the rocksalt (NaCl), heteropolar β -tin (β -Sn), hexagonal nickel arsenide (NiAs) and anti-NiAs, and cesium chloride (CsCl) structures. 3C is a fourfold-coordinated structure, NaCl and the β -Sn are sixfold-coordinated structures, and CsCl is an eightfoldcoordinated structure. In the NiAs structure the sites of the two different ions are not equivalent. For the ideal ratio $c/a = \sqrt{8/3}$ of the lattice constants the anions (As) establish a hexagonal close-packed structure (hcp), whereas the cations (Ni) form a simple hexagonal structure (sh). Each cation has four nearest neighbors (anions) and possesses the same environment as in the rocksalt structure. In contrast, each anion has six nearest neighbors, four cations and two anions. The latter ones form a linear chain parallel to the c axis. The NiAs and the anti-NiAs structures (arising from interchanging the positions of the anions and cations in the NiAs structure) are not equivalent, due to the different environments of their ions.

The self-consistently calculated total energy $\mathcal{E}(V)$ per Si-C pair is shown in Fig. 5(a) as a function of reduced volume for the the 3*C*, NaCl, NiAs, anti-NiAs, and CsCl

TABLE III. Calculated critical transition pressure p (Mbar), initial volume V_I , and final volume V_F for the transition from zinc blende (3*C*) to NaCl, NiAs, anti-NiAs, and CsCl structure of SiC using Vinet (*V*) and Murnaghan (*M*) equation of state. The volumes are given in units of the experimental equilibrium volume of the 3*C* phase.

		р	V_I	V_F
→ NaCl	V	0.666	0.815	0.671
	М	0.665	0.819	0.672
\rightarrow NiAs	V	0.798	0.792	0.665
	M	0.791	0.799	0.667
\rightarrow anti-NiAs	V	2.063	0.652	0.575
	М	1.906	0.685	0.592
\rightarrow CsCl	V	3.607	0.560	0.489
	М	3.536	0.600	0.527

structure. The corresponding structural parameters *a*, *c/a*, B_0 , and B'_0 are given in Tables I and II. In addition, the ionicity coefficient *g* of the Si-C bonds has been calculated using the approach of Garcia and Cohen.²⁴ With the exception of the CsCl structure the high-pressure phases of SiC exhibit higher ionicity than the zinc-blende phase of SiC (g = 0.476). The smaller ionicity of the CsCl phase may be explained by its pronounced metallic character, as can be seen from the corresponding band structure and valence-charge density.

The enthalpies H(p) of the high-pressure phases of SiC are plotted as a function of pressure in Fig. 5(b). The crossing of two curves indicates a pressure-induced phase transition between the two structures. The corresponding transition pressures, as well as the critical initial volumes V_I of the zinc-blende structure and final volumes V_F of the considered high-pressure phases are listed in Table II. Our results are also in good agreement with those of former ab initio calculations,⁸ where a zinc-blende to rocksalt phase transition has been found. The transition pressure of 0.66 ± 0.05 Mbar, as well as the corresponding volumes $V_I = 0.81V_0$ and $V_F = 0.66V_0$, with the equilibrium volume of 3C SiC $V_0 = 10.369$ Å³ from Ref. 8, are very close to our data shown in Table III. Furthermore, the theoretical data approach well the experimental transition volumes, $V_I = 0.76V_0$ and $V_F = 0.60 V_0$.⁶ However, the theoretical transition pressure is much lower than the experimental one found at about 1.0 Mbar.⁶ The underestimation of the critical pressure for a structural phase transition seems to be a general problem of the DFT-LDA calculations. The stiffness of the materials against hydrostatic pressure is usually not correctly described using LDA.^{25,26} It has been shown that this deficiency of the LDA calculations can be partially overcome using generalized gradient approximation for the exchange-correlation energy; In the case of silicon and germanium, the gradient corrections shift the transition pressure towards the experimental value.27

The phase transition from the zinc blende into the rocksalt structure of SiC under external hydrostatic pressure can be interpreted in terms of a relative atomic displacement of the Si and C atom in the unit cell of the fcc structure parallel to the [111] direction. Such an interpretation for a high-pressure phase transition from a given hexagonal nH polytype into

the rocksalt structure is not possible. The stretching of the bonds parallel to the c axis cannot be accompanied by the same displacements for atoms in bonds oriented by an angle of about 70.5° to the c axis. Such a unique behavior of the different Si-C bonds in the unit cell would require an additional twisting of the bonds in the hexagonal Si-C bilayers. We found that this process automatically enlarges the energy barrier for a pressure-induced phase transition. Perhaps this is the reason why a pressure-induced phase transition of the hexagonal polytypes has not yet been observed experimentally. Considering the p-V relation and the enthalpy versus pressure, the transitions from the hexagonal phases into rocksalt structure should be expected at similar critical volumes and pressures as for 3C SiC. Our calculations show that the 2H (4H) phase of SiC may transform into rocksalt structure at a slightly smaller (higher) pressure than 3C SiC: 0.653 (0.673) Mbar. The corresponding critical volume is 81.9%(81.3%) of the equilibrium one.

2. Electronic properties. Metallicity

The self-consistent LDA band structure and the corresponding electronic density of states of 3C, NaCl, NiAs, and CsCl phases of SiC is plotted in Fig. 6. The maximum of the valence bands (the Fermi energy) has been taken as the energy zero for the semiconducting (metallic) phases. Because of the well-known failure of the LDA the calculated band gaps are underestimated, e.g., the indirect gap $\Gamma_{15v} \rightarrow X_{1c}$ of 3*C* SiC amounts to 1.37 eV, and the direct gap $X_{3v} \rightarrow X_{1c}$ of 3C SiC to 2.89 eV, whereas the corresponding experimental values are 2.39 and 3.10 eV, respectively.²⁸ Reliable values of the band-gap energies can be calculated by including many-body quasiparticle effects.²⁹ Nevertheless, the dispersion of the LDA energy bands is quite reasonable. Our band structure and transition energies of the 3C SiC agree well with those from similar LDA calculations.^{22,30} In our calculation, the indirect band gap $\Gamma_{15v} \rightarrow X_{1c}$ disappears already for the NaCl phase, due to a remarkable displacement of the lowest conduction band at X towards lower energies. Chang and Cohen⁸ found that the rocksalt phase is still semiconducting, even if the pressure is increased up to about 3.0 Mbar. We believe that the discrepancy between their results and the present calculations may be due to lacking convergence, with respect to the BZ sampling in Ref. 8. In case of semimetallic or metallic phases, a correct description of the features of the band structure requires large sets of special points in the irreducible BZ. In addition, we have used a smearing technique to describe the Fermi surface in our calculations. The local density of states is convoluted with a Gaussian function.^{31,32} The narrowing of the indirect band gap $\Gamma_{15v} \rightarrow X_{1c}$ under hydrostatic pressure has been also observed for several III-V compounds.33,34

The similarities between the band structures of the rocksalt and hexagonal NiAs phase of SiC (Fig. 6) and also between their ground-state energies [Fig. 5(a)] are not fortuitous, but are related to the structural resemblance of both phases. According to the structural analogy between zincblende and wurtzite structure, the rocksalt and hexagonal NiAs structures can be built up by stacking hexagonal planes with atoms of the same kind: AbCaBcAbCaBc (rocksalt) and AbCbAbCbAbCb (NiAs structure).²¹ The general shape



FIG. 6. DFT-LDA band structure and the corresponding density of states calculated at the equilibrium volume for the 3*C*, NaCl, NiAs, and CsCl phases of SiC. The top of the valence bands (Fermi energy) is taken as the energy zero for the semiconducting (semimetallic or metallic) phases.

of the electronic density of states is approximately the same for both structures. Moreover, the weakly pronounced semimetallic character, due to the lowering of the conduction band at the *K* point in the NiAs structure, is in accordance to the lowering of the corresponding conduction band of the rocksalt structure. The different positions of the conduction band minima may be traced back to the different configuration of the second- and higher-neighbor shells. The band structure of the anti-NiAs high-pressure phase exhibits a more pronounced semimetallic character than that of the NiAs phase. The minimum of the lowest conduction band is found at the *K* point at -2.32 eV below the Fermi energy compared to -1.60 eV in the case of the NiAs phase.

In contrast to the NaCl, NiAs, or anti-NiAs high-pressure phases, the CsCl structure exhibits a pronounced metallic character. Here, the ionic gap in the valence bands completely disappears, whereas there is a gap feature just above the Fermi energy in the density of states for the NaCl and NiAs structures in the energy region of the ionic gap of SiC.



FIG. 7. The total energy per atom versus the c/a ratio of the lattice constants of the tetragonal structure of SiC. The equilibrium energy of the zinc-blende structure of SiC has been taken as the reference one. The c/a ratio of the ideal β -tin $(2/\sqrt{15})$ and zinc-blende structure $(\sqrt{2})$ are indicated by arrows. The solid (dotted) line corresponds to the energy curve calculated at the equilibrium volume (0.8 times equilibrium one) of the 3*C* phase of SiC.

The metallic character of the CsCl phase of SiC can also be seen in the degree of uniformity of the charge density distribution in the unit cell. The increasing metallicity upon compression causes a charge transfer from the bond to the interstitial region. The maximum of the charge density along the bonding direction decreases from 1.96 (3*C* phase) to 1.64 $e/Å^3$ (CsCl phase), whereas the charge density minimum in the interstitial space increases from 5.9 × 10⁻² (3*C* phase) to 2.2 × 10⁻¹ $e/Å^3$ (CsCl phase).

3. Stability

The β -tin structure (space group I4m2) is made up of two interpenetrating body-centered-tetragonal (bct) sublattices displaced against each other by the vector (0, a/2, c/4). In the ideal β -tin structure with the ratio $c/a=2/\sqrt{15}$, the atoms are sixfold coordinated with the nearest-neighbor distance of $2 a/\sqrt{15}$. The fourfold-coordinated zinc-blende structure (space group $F\overline{4}3m$) is built up of two interpenetrating fcc sublattices displaced against each other by onequarter of the body diagonal. A continuous transition between the two structures can be described by a change of the c/a ratio of the lattice constants c and a of the tetragonal unit cell. The increase of the ratio to $c/a = \sqrt{2}$ yields the zinc blende, a further increase to $c/a \approx 4$ gives rise to an eightfold-coordinated structure, where each atom has eight nearest neighbors, four cations and four anions. Increasing coordination number with pressure is a common feature of structural phase transitions and can be traced back to the relevance of the interionic Coulomb interaction at high pressures and small unit-cell volumes.

The change of the total energy, which arises from a $3C \rightarrow \beta$ -Sn transition at fixed volume, is plotted in Fig. 7 versus the ratio c/a of the tetragonal lattice constants. While for both unit-cell volumes, the total energy as a function of c/a exhibits a minimum at the ratio $c/a = \sqrt{2}$, which corresponds to the zinc-blende structure, no local minimum exists around $c/a = 2/\sqrt{15}$, which could be identified as the heteropolar β -Sn structure. There is only a bend in the curves around $c/a \approx 0.6$, due to the behavior of the Ewald energy of the ions, which approaches a minimum at about $c/a \approx 0.57$.



FIG. 8. Calculated total energy per atom of a simple cubic structure of SiC, as a function of the position of carbon atom along the [111] direction (in units of $2\pi/a$). The hypothetical equilibrium volume of the CsCl high-pressure phase (see Table I) has been used as the reference one.

The absence of a local minimum in the total energy for $c/a < \sqrt{2}$, in particular, around $c/a = 2/\sqrt{15}$, indicates that the heteropolar β -tin structure is neither a stable nor a meta-stable high-pressure phase of 3*C* SiC for external hydrostatic pressures less than 2.8 Mbar.

Despite their common pronounced covalent bonding character, the tetrahedrally coordinated III-V and II-VI semiconductors transform into different crystal structures under applied external hydrostatic pressure.^{33–39} The nonuniform behavior of these semiconductors have been traced back to the different relevance of the ionic contribution to their bonding. Theoretical arguments provide a relationship between the ionicity and the crystal structure to which a given tetrahedrally coordinated semiconductor prefers to transform under pressure: Semiconductors with strong ionic character tend to transform into the rocksalt structure, whereas those with predominantly covalent character transform into the heteropolar β -tin structure.^{24,40,41} Indeed, theory and experiment show that AlAs (Ref. 34), ZnS (Ref. 37), BN (Ref. 36), and AlN,^{42,43} transform into the NaCl structure, whereas the high-pressure phase of InSb (Ref. 38), Si (Ref. 39), Ge (Ref. 39), and GaP (Ref. 44) has the β -tin structure. Considering the low ionicity $f_i = 0.177$ of 3C SiC within the Phillips scale,⁴⁰ this result is somehow surprising. The behavior of SiC can be immediately understood if the ionicity scale g of Garcia and Cohen²⁴ is used. The intermediate ionicity g = 0.476 places SiC between materials with high ionicity like AlN (g=0.796) and ZnS (g=0.673) and rather covalently bonded semiconductors. The remarkable variation of the ionicities arising from the different scales of Ref. 24 and Ref. 40 is typical for compounds containing first-row elements, such as B, C, or N. This can be traced back to the lack of p electrons in their cores and therefore to the small core size and large electronegativity of these elements.

The instability of the sixfold-coordinated β -tin structure suggests that metastable SiC phases with a coordination number greater than six are unlikely to occur. Indeed, the CsCl high-pressure phase of SiC is neither a stable nor a metastable structure at the corresponding equilibrium volume given by the minimum of the static total energy. To demonstrate this fact, the total energy of a simple cubic SiC structure with two atoms per unit cell is shown in Fig. 8, as a function of the displacement of the carbon atom along the



FIG. 9. Total energy per atom of an fcc structure of SiC, as a function of the displacement of carbon atom along [111] direction (in units of $2\pi/a$). The solid (dotted) line corresponds to the energy curve calculated at the equilibrium volume (critical transition volume V_I) of the zinc-blende phase of SiC.

body diagonal with a fixed position of the silicon atom at the origin. The energy curve has been determined using the calculated equilibrium volume of the CsCl phase of SiC (cf. Table II). At the position of the carbon ion corresponding to that of the CsCl structure no minimum is observed, rather a local maximum as indicated by the double-well behavior of the energy. This means that the total energy of SiC possesses a saddle point at the CsCl structure, and the CsCl structure of SiC cannot be a stable phase at zero pressure of this phase, which corresponds to 0.75 Mbar external hydrostatic pressure applied to the zinc-blende phase of SiC. The instability of SiC in the CsCl structure is due to the high-energy barrier for the breaking of the tetrahedral sp^3 bonds and subsequent formation of unfavorable weak octahedral bonds. A similar behavior has been found for diamond.45 Therefore, we conclude that the instability of SiC phases with an atomic coordination number greater than six follows from the intrinsic strong bonding properties of the carbon atom.

A possible transformation path for the transition from zinc blende to rocksalt structure can be described by a displacement of the carbon atom along the [111] direction with a fixed position of the silicon atom at the origin. The anions have to be displaced from tetrahedral positions at one-quarter of the body diagonal to the body-centered position within the fcc unit cell. The corresponding total energy variation is plotted in Fig. 9 for the equilibrium (V_{3C}) , as well as the transition (V_I) volume of 3C SiC to rocksalt structure (cf. Table II). At the anion position in the NaCl structure, the total energy curves calculated at the equilibrium volume exhibits a maximum. Only when the volume is reduced, i.e., after the application of an external hydrostatic pressure, a local minimum appears in the total energy. Therefore, the NaCl structure represents a metastable phase, which transform spontaneously into the 3C phase upon depressurization. This behavior associated with the zinc blende to rocksalt transition is indeed observed experimentally.⁶ The energy barrier between the 3C and the NaCl phase being visible from Fig. 9 is about 1.2 eV per unit cell.

The calculated ratio c/a = 1.657 of the lattice constants of the hexagonal NiAs structure is about 2% larger than the ideal value indicating an instability towards structures with coordination number lower than six. Furthermore, the anti-NiAs structure is energetically clearly unfavorable. We found an increase of the total energy of about 1.97 eV per unit cell in comparison to the NiAs structure. This behavior agrees well with the experimental finding that, in structures related to NiAs, the more metallic atom—in the case of SiC silicon—forms usually a hcp structure, whereas the more metalloid element—here carbon—forms the sh structure.

C. Lattice dynamical and dielectric properties

1. Static and high-frequency dielectric tensor

The total macroscopic polarization P of a crystal can formally be written in the limit of long wavelengths $(\mathbf{q}\rightarrow \mathbf{0})$ as⁴⁶

$$\boldsymbol{P} = \frac{1}{\Omega} \sum_{\kappa} \boldsymbol{Z}^{B}(\kappa) \cdot \boldsymbol{u}(\kappa) + \frac{1}{4\pi} [\boldsymbol{\epsilon}(\infty) - \boldsymbol{1}] \cdot \boldsymbol{E}, \qquad (1)$$

where Ω is the unit cell volume, $\boldsymbol{u}(\kappa)$ is the displacement of the κ th ion, $\boldsymbol{\epsilon}(\infty)$ is the high-frequency dielectric tensor (at a frequency much larger than the eigenfrequencies of the lattice vibrations, but much smaller than the electronic excitation frequencies), \boldsymbol{E} is the macroscopic (screened) electric field, and $\mathbf{Z}^{B}(\kappa)$ the tensor of the Born effective charge, satisfying the acoustic sum rule,

$$\sum_{\kappa} Z^{B}_{\alpha\beta}(\kappa) = 0, \qquad (2)$$

as is evident from the invariance of P against uniform displacement of all the ions. The macroscopic polarization P can be decomposed into a pure ionic

$$\boldsymbol{P}^{\text{ion}} = \frac{1}{\Omega} \sum_{\kappa} Z(\kappa) \boldsymbol{u}(\kappa)$$
(3)

and an electronic part

$$\boldsymbol{P}^{\rm el} = \frac{1}{N\Omega} \int \mathbf{r} \Delta n(\mathbf{r}) \mathbf{d}^3 \mathbf{r}, \qquad (4)$$

where *N* is the number of the unit cells of the crystal, $Z(\kappa)$ is the bare ionic charge of the κ th ion, and $\Delta n(\mathbf{r})$ is the density response to a given external perturbation.¹⁵ The high-frequency dielectric tensor $\epsilon(\infty)$ relates the total macroscopic field *E* to the external homogeneous field E^0 ,

$$\boldsymbol{\epsilon}_{\alpha\beta}(\infty) = \frac{\partial E_{\alpha}}{\partial E_{\beta}^{0}} = \delta_{\alpha\beta} + 4\pi \frac{\partial P_{\alpha}^{\text{el}}}{\partial E_{\beta}}\Big|_{\{\boldsymbol{u}\}=0}.$$
 (5)

The high-frequency dielectric tensor $\epsilon(\infty)$ accounts for electronic polarization effects. The static dielectric constant $\epsilon(0)$, which describes also the lattice-vibrational polarization contributions, can be derived from a generalized Lyddane-Sachs-Teller relation⁴⁷

$$\prod_{\lambda=1}^{r} \frac{\omega_{\lambda}^{2}(\hat{\mathbf{q}})}{\omega_{\lambda}^{2}(0)} = \frac{\hat{\mathbf{q}} \cdot \boldsymbol{\epsilon}(0) \cdot \hat{\mathbf{q}}}{\hat{\mathbf{q}} \cdot \boldsymbol{\epsilon}(\infty) \cdot \hat{\mathbf{q}}},$$
(6)

where $\hat{\mathbf{q}}$ denotes the direction of the wave vector \mathbf{q} , r is the number of infrared (IR) active modes, and $\omega_{\lambda}(\hat{\mathbf{q}})$ ($\omega_{\lambda}(0)$) are the corresponding phonon frequencies calculated with (without) consideration of the macroscopic electric field E. In case of hexagonal symmetry the static and high-frequency dielectric tensors have two independent components, one



FIG. 10. Pressure dependence of the high-frequency $\epsilon(\infty)$ and the static $\epsilon(0)$ dielectric tensor of 2*H* (a and c) and 4*H* SiC (b and d). The calculated parallel components of $\epsilon(\infty)$ and $\epsilon(0)$ are denoted by open diamonds, the perpendicular component by open triangles. The solid lines correspond to the static and high-frequency dielectric constants of 3*C* SiC.

corresponding to the direction parallel to the *c* axis, $\epsilon_{\parallel} = \epsilon_{zz}$, and the other being characteristic for the plane perpendicular to *c* axis, $\epsilon_{\perp} = \epsilon_{xx} = \epsilon_{yy}$.

The pressure dependence of the two independent components of $\epsilon(\infty)$ for 2H and 4H phases of SiC is shown in Fig. 10 and compared with the behavior of the dielectric constant of 3C. The calculated components, in particular, the parallel component, of the high-frequency dielectric tensor of 2H and 4H SiC display a tendency to saturate in the limit of high pressures. For the two hexagonal polytypes experimental data are available neither for $\boldsymbol{\epsilon}(\infty)$ nor for its pressure derivative. Nevertheless, the magnitude of the splitting between the parallel and perpendicular component of $\epsilon(\infty)$ for 4HSiC at zero pressure $\left[\Delta\epsilon(\infty)=0.22\right]$ agrees well with the experimental results for 6H SiC $\left[\epsilon_{\parallel}(\infty)=6.70,\right]$ $\epsilon_{\perp}(\infty) = 6.52, \ \Delta \epsilon(\infty) = 0.18$ taken from Ref. 48. Because of the anisotropy of the 4H structure (with the hexagonality parameter h = 50%), the difference $\Delta \epsilon(\infty)$ is expected to be somehow larger than for the 6H structure with the h = 33.3% hexagonality.

Several semiempirical^{4,49,50} approaches have been proposed to describe the volume (pressure) dependence of the dielectric constant for ionic and covalent compounds, which are based either on the dielectric theory of the chemical bond⁴⁰ or on the tight-binding method. However, these approaches yield partially contradictory results for the pressure dependence of the dielectric constants. In addition, a critical judgement on the reliability of these different procedures

TABLE IV. Calculated and experimental polynomial expansion coefficients of various pressure-dependent vibrational quantities of 3C SiC. Frequencies are given in cm⁻¹; the Born effective charge is given in units of the elementary charge.

		$lpha_0$	α_1	α_2	α ₃	$lpha_4$
LO-TO	Theory	173.6	68.7	-75.8	64.1	-23.1
	Expt. ^a	176.5 ± 0.3	87 ± 9	-30 ± 40		
$\epsilon(\infty)$	Theory	7.019	-1.342	2.013	-1.715	0.571
. /	Expt. b	6.52				
$\epsilon(0)$	Theory	10.495	-2.404	2.791	-2.177	0.698
	Expt. b	9.73				
Z^B	Theory	2.719	0.331	-0.349	0.277	-0.092
	Expt. ^a	2.697				

^aReference 4.

^bReference 28.

cannot be made, because a comparison between theoretical and experimental results is not possible due to the missing experimental data.

We find that the widely used assumption $\partial \ln \epsilon(\infty)/\partial \ln V = \kappa$ for the volume dependence of the highfrequency dielectric constant is not valid for homopolar, as well as for heteropolar semiconductors^{4,7,51} far away from the equilibrium volume. Moreover, the value of the logarithmic derivative of the high-frequency dielectric constant is not universal and differs considerably with $\kappa = 0.413$ for 3C, $\kappa = 0.407$ (0.410), and $\kappa = 0.374$ (0.390), for the parallel (perpendicular) component of $\epsilon(\infty)$ for 2H and 4H SiC from the value $\kappa = 0.6$ suggested in Ref. 4. As indicated by the increase of the splitting between $\epsilon_{\parallel}(\infty)$ and $\epsilon_{\perp}(\infty)$, the anisotropy of dielectric properties of the hexagonal polytypes of SiC increases with increasing hydrostatic pressure. The anisotropy of the high-frequency dielectric tensor of 2H and 4H SiC increases much faster with increasing hydrostatic pressure than the anisotropy of the structural parameters of both polytypes (see Sec. III A). We have described this nonlinear behavior of the hydrostatic pressure variation of the high-frequency dielectric tensor of the zinc-blende 3C and of both hexagonal polytypes, using a fourth-order Taylor expansion around zero pressure (see Tables IV, V, and VI).

The calculated parallel and perpendicular components of the static dielectric tensor $\epsilon(0)$ of 2H and 4H SiC are plotted in Fig. 10, as functions of hydrostatic pressure. For comparison, also the pressure dependence of the static dielectric constant of 3C SiC is shown in this figure. As can be seen from Fig. 10, the static dielectric tensor decreases faster with increasing hydrostatic pressure than the high-frequency dielectric tensor (see Tables II and III). The logarithmic derivative of the average value $\overline{\epsilon}$ [1/3 of the trace of $\epsilon(0)$], $\partial \ln \overline{\epsilon}(0)/\partial p$, for 2H and 4H SiC amounts to -0.212 and -0.211, whereas the logarithmic derivative of the average value of the $\epsilon(\infty)$ is -0.176 and -0.170, respectively. This behavior can be explained in terms of the lattice polarization. As the lattice expands, the restoring forces between the ions decrease. The lattice polarization is approximately inversely proportional to the forces acting between the ions and increases with decreasing pressure. It is important to recognize that the displacement of the ions are accompanied by a deTABLE V. The calculated Taylor expansion coefficients up to the fourth order in pressure p (Mbar) for various pressuredependent properties of 2H SiC.

		$lpha_0$	α_1	α_2	α ₃	$lpha_4$
c/a	Theory	1.6444	-0.0026			
	Expt. ^a	1.6409				
и	Theory	0.3755	-0.0012	0.0019	-0.0014	0.0004
	Expt. ^a	0.3760				
LO-TO	Theory	166.73	61.67	-54.65	37.31	-10.86
	Expt. ^b	169.3				
LO-TO_{\perp}	Theory	193.77	81.77	-68.72	43.35	-12.03
	Expt. ^b	204.7				
$\boldsymbol{\epsilon}_{\parallel}(\infty)$	Theory	7.277	-1.276	1.657	-1.224	0.368
$\epsilon_{\perp}^{(\infty)}$	Theory	6.878	-1.218	1.469	-1.079	0.324
$\boldsymbol{\epsilon}_{\parallel}(0)$	Theory	11.369	-2.355	2.436	-1.673	0.488
$\boldsymbol{\epsilon}_{\perp}(0)$	Theory	10.230	-2.200	2.158	-1.466	0.424
$\mathbf{Z}^{B}_{\parallel}(Si)$	Theory	2.870	0.382	-0.323	0.221	-0.066
$\mathbf{Z}_{\perp}^{B}(\mathrm{Si})$	Theory	2.674	0.328	-0.298	0.197	-0.056

^aReference 20.

^bReference 55.

^cReference 54.

formation of the electronic charge distribution. This effect adds a considerable contribution to the resulting polarization.

2. Tensor of the Born effective charge

By definition, the Born (transverse) effective charge tensor $\mathbf{Z}^{B}(\kappa)$ gives the total macroscopic polarization induced by a unit sublattice displacement of the κ th ions in zero macroscopic electric field.⁴⁷ $\mathbf{Z}^{B}(\kappa)$ also describes the coupling between transverse lattice vibrations and light; hence the term *transverse*. Using the macroscopic polarization Pgiven by Eqs. (3) and (4), we can see that the Born effective charge tensor $\mathbf{Z}^{B}(\kappa)$ is composed of an ionic and an electronic contribution,

TABLE VI. The calculated Taylor expansion coefficients up to the fourth order in pressure p (Mbar) for various pressuredependent properties of 4H SiC.

		u	α_2	α_3	α_4
Theory	3.2761	-0.0020			
Expt. ^a	3.2711				
Theory	168.73	58.94	-50.07	30.00	-9.58
Expt. b	170				
Theory	182.23	73.93	-71.66	53.77	-17.53
Expt. b	189				
Theory	7.169	-1.189	1.722	-1.420	0.475
Theory	6.946	-1.202	1.650	-1.358	0.455
Theory	10.900	-2.232	2.475	-1.877	0.609
Theory	10.352	-2.218	2.386	-1.807	0.585
Theory	2.782	0.350	-0.316	0.229	-0.073
Theory	2.692	0.327	-0.317	0.234	-0.075
	Theory Expt. ^a Theory Expt. ^b Theory Expt. ^b Theory Theory Theory Theory Theory Theory	Theory 3.2761 Expt. a 3.2711 Theory 168.73 Expt. b 170 Theory 182.23 Expt. b 189 Theory 7.169 Theory 6.946 Theory 10.352 Theory 2.782 Theory 2.692	Theory 3.2761 -0.0020 Expt. a 3.2711	Theory 3.2761 -0.0020 Expt. a 3.2711 -50.07 Theory 168.73 58.94 -50.07 Expt. b 170 -50.07 -50.07 Theory 182.23 73.93 -71.66 Expt. b 189 -50.07 -50.07 Theory 182.23 73.93 -71.66 Expt. b 189 -50.07 -50.07 Theory 7.169 -1.189 1.722 Theory 6.946 -1.202 1.650 Theory 10.900 -2.232 2.475 Theory 10.352 -2.218 2.386 Theory 2.782 0.350 -0.316 Theory 2.692 0.327 -0.317	Theory 3.2761 -0.0020 Expt. a 3.2711 -0.0020 Theory 168.73 58.94 -50.07 30.00 Expt. b 170 -0.0020 -0.0020 -0.0020 Theory 168.73 58.94 -50.07 30.00 Expt. b 170 -0.002 -0.002 -0.002 Theory 182.23 73.93 -71.66 53.77 Expt. b 189 -0.002 -1.420 Theory 7.169 -1.189 1.722 -1.420 Theory 6.946 -1.202 1.650 -1.358 Theory 10.900 -2.232 2.475 -1.877 Theory 10.352 -2.218 2.386 -1.807 Theory 2.782 0.350 -0.316 0.229 Theory 2.692 0.327 -0.317 0.234

^aReference 21.

^bReference 54.



FIG. 11. Pressure dependence of the tensor of the Born effective charges of 2H SiC. The open diamonds (triangles) denote the parallel (perpendicular) components, whereas the full line corresponds to the Born effective charge of 3C SiC.

$$Z^{B}_{\alpha\beta}(\kappa) = Z(\kappa) \,\delta_{\alpha\beta} + \Omega \left. \frac{\partial P^{\rm el}_{\alpha}}{\partial u_{\beta}(\kappa)} \right|_{E=0},\tag{7}$$

where $\partial P_{\alpha}^{el}/\partial u_{\beta}(\kappa)|_{E=0}$ is the linear variation of the electronic polarization upon lattice distortion at zero electric field. In the unit cell of hexagonal *nH* polytypes there are n/2 independent tensors of the Born effective charges for the silicon and for the carbon ions. Moreover, due to the uniaxial symmetry of the crystal each $\mathbf{Z}^{B}(\kappa)$ possesses two independent components, a parallel and a perpendicular one to the *c* axis. The only restriction, which is imposed on $\mathbf{Z}^{B}(\kappa)$, is the neutrality condition given by Eq. (2).

The pressure dependence of the independent components of the Born effective charges $\mathbf{Z}^{B}(\kappa)$ of 2*H* and 4*H* SiC is plotted in Figs. 11 and 12, respectively. For comparison, the Born effective charge of 3*C* SiC is also displayed. The parallel and perpendicular components of $\mathbf{Z}^{B}(\kappa)$ for 2*H* and 4*H* SiC bracket the value of 3*C* SiC. In addition, one ob-



FIG. 12. Pressure dependence of the tensor of the Born effective charges of 4H SiC for the two independent silicon (a) and carbon atoms (b). The open (filled) diamonds denote the perpendicular components, the open (filled) triangles correspond to the parallel component of the tensor of the Born effective charges of the inequivalent atom 1 and 2, respectively. The sites of the equivalent and inequivalent atoms are indicated in Fig. 1.



FIG. 13. (a) Pressure dependence of the estimated average parallel (solid triangles) and perpendicular (open triangles) component of the tensor of the Born effective charges $\overline{\mathbf{Z}}^{B}(Si)$ of 4*H* SiC, using $\partial \ln \epsilon_{\alpha\beta}(\infty)/\partial \ln V=0.6$ as in Ref. 7 for the volume dependence of the high-frequency dielectric tensor. The correct values of the average parallel and perpendicular component of $\overline{\mathbf{Z}}^{B}(Si)$ are plotted as full and dotted lines, respectively. (b) Parallel (solid circles) and perpendicular (open circles) component of $\overline{\mathbf{Z}}^{B}(Si)$ for 4*H* SiC derived from LO-TO splitting. The solid and open triangles denote the parallel and perpendicular components of $\overline{\mathbf{Z}}^{B}(Si)$ derived from LO-TO splitting, using $\partial \ln \epsilon_{\alpha\beta}(\infty)/\partial \ln V=0.6$ as in Ref. 7 for the volume dependence of $\boldsymbol{\epsilon}(\infty)$.

serves an increasing splitting between the parallel and perpendicular components of the Born effective charges with increasing pressure. Contrary to the cubic and the special case of the wurtzite structure, there is generally no local dynamical charge neutrality for a given bond of an nH polytype. A stronger anisotropy appears for the silicon and carbon atoms in the hexagonal bilayers, where bond twisting occurs with respect to the cubic stacking layers (see Fig. 1). The splitting between the parallel and perpendicular components of $\mathbf{Z}^{B}(\kappa)$ for 2H and 4H SiC increases with increasing hydrostatic pressure and indicates therefore an increasing anisotropy under hydrostatic pressure. We observe a tendency of the effective charges to saturate for ultrahigh pressures. However, a pronounced maximum of \mathbf{Z}^{B} , as extracted from Raman measurements⁷ for 6H SiC, is absent in our theoretical curves for 2H and 4H polytypes.

Three reasons may be mentioned to give an idea for the explanation of this discrepancy. In order to relate the LO-TO splitting to an average transverse effective charge of 6H SiC, a simplified formula is used in Ref. 7 that is only valid for crystals with cubic symmetry. The possible errors caused by this assumption and their order of magnitude will be discussed in the next section. Moreover, the tensor character of $\boldsymbol{\epsilon}(\infty)$ and \mathbf{Z}^{B} is neglected and an incorrect volume dependence of $\boldsymbol{\epsilon}(\infty)$ is assumed. To estimate the influence of this incorrect volume (pressure) dependence of $\epsilon(\infty)$, $\partial \ln \epsilon_{\alpha\beta}(\infty)/\partial \ln V = 0.6$, we rescaled the values of the average components of the tensor of the Born effective charge of silicon ions $\overline{Z}^{B}_{\alpha\beta}(Si) = 1/2\Sigma_{\kappa}Z^{B}_{\alpha\beta}(\kappa|Si)$ in 4*H* SiC. The rescaled values of $\overline{Z}^{B}_{\alpha\beta}(Si)$ are shown in Fig. 13(a) and compared with the correct theoretical components of $\overline{\mathbf{Z}}^{B}(Si)$. Because of the ASR, see Eq. (2), $\overline{\mathbf{Z}}^{B}(\mathbf{C})$ is equal to $-\overline{\mathbf{Z}}^{B}(\mathbf{S}i)$. As can be seen from Fig. 13(a), there are not only considerable deviations between the rescaled and correct values of $\overline{Z}_{\alpha\beta}^{B}$ (Si), in particular for high pressures, but we are able also to mimic the behavior for the pressure dependence of the Born effective charge of 4*H* SiC, as has been derived experimentally for 6*H* SiC (Ref. 7), using an incorrect volume dependence of the high-frequency dielectric tensor. The rescaled average value of the parallel and perpendicular component of \overline{Z}^{B} (Si) for 4*H* SiC exhibits a weak, flat maximum at about 0.6 Mbar. The difference between the maximum and zero pressure value amounts to 0.042. The same difference for the experimental estimated average Born effective charge of 6*H* SiC is about 0.055.⁷ Deviations caused by the use of different equations of state (Birch and Vinet EOS) are found to be only of minor influence.

The dynamic ionicity of a crystal is exhibited in the splitting of the longitudinal and transverse optical modes at the zone center and can be related to the Born effective charges. Recently, an *ab initio* approach to the static ionicity of a solid based on the asymmetry of the ground-state valencecharge density was proposed by Garcia and Cohen.²⁴ Both the static ionicity described by the charge asymmetry coefficient g (Ref. 24) of 3C, 2H, 4H, and 6H (Ref. 52) SiC, and the trace of $\Sigma_{\kappa} \mathbf{Z}^{B}(\kappa | \mathbf{Si})$ show a similar behavior as functions of applied hydrostatic pressure. Therefore, we assume that the static and dynamic ionicity approaches can be used as almost equivalent ionic scales.

3. Zone-center frequencies

In polar materials, the longitudinal optic modes in the limit $\mathbf{q} \rightarrow 0$ couple to the macroscopic electric field caused by the long-range part of Coulomb forces. This leads to a nonanalytic behavior of the force constants and thus of the dynamical matrix at the Γ point. The complete information for describing this nonanalytic behavior is contained in the knowledge of the tensor \mathbf{Z}^B of the Born effective charges and the tensor $\boldsymbol{\epsilon}(\infty)$ of the macroscopic high-frequency dielectric constant; the *nonanalytic* part of the dynamical matrix can be written as⁴⁷

$$D^{\mathrm{na}}_{\alpha\beta}(\kappa\kappa'|\mathbf{q}\to\mathbf{0}) = \frac{4\pi}{\Omega\sqrt{m_{\kappa}m_{\kappa'}}} \frac{[\mathbf{Z}^{B}(\kappa)\cdot\hat{\mathbf{q}}]_{\alpha}[\hat{\mathbf{q}}\cdot\mathbf{Z}^{B}(\kappa')]_{\beta}}{\hat{\mathbf{q}}\cdot\boldsymbol{\epsilon}(\infty)\cdot\hat{\mathbf{q}}},$$
(8)

where m_{κ} is the atomic mass of the κ th ion. The *analytic* part D^{an} of the dynamical matrix for polar compounds is calculated self-consistently in the framework of the first-order DFPT, neglecting any macroscopic polarization effects.¹⁵

The pressure dependence of the zone-center phonon frequencies of 2*H* and 4*H* SiC is displayed in Fig. 14 for two different propagation directions. The optical modes exhibit a strong increase with applied hydrostatic pressure. This effect is much weaker in the case of the folded longitudinal acoustic (LA) modes; the folded transverse acoustic (TA) modes even decrease slightly with increasing pressure. The general trend is the same for the two propagation directions under consideration. The modes polarized parallel to the *c* axis may be interpreted to arise from a folding procedure of the Γ -*L* phonon modes of the 3*C* structure with an effective wave vector *q* in units of $n\pi/c$ (n=2,4). Raman scattering studies performed on 6*H* and 15*R* polytypes of SiC report



FIG. 14. Pressure dependence of the Γ point frequencies of 2*H* and 4*H* SiC for phonon propagation parallel to the *c* axis [0001] (a) and (c) and perpendicular to the *c* axis along the [11 $\overline{20}$] direction (b) and (d).

also a decrease of the TA modes near the BZ boundary upon pressure; in particular, at 0.3 Mbar, a shift of 2.0, -1.7, and -3.0 cm^{-1} was observed for the q=0.4, q=0.67, and q=0.8 mode, respectively.⁵³ Our theoretical results of a shift of -0.5 (-2.4 for the high-frequency part of the doublet) and -5.8 cm^{-1} for the reduced wave vector q=0.5 (4H) and q=1.0 (2H) comply well with the experimental findings.

The calculated pressure dependence of the LO-TO splitting of the strong Raman modes for phonon propagation parallel and perpendicular to the *c* axis of 2*H* and 4*H* SiC is shown in Fig. 15 and compared with the LO-TO splitting of 3*C* SiC. In case of the *nH* structures, we plot the splitting between A_{1l} and A_{1t} (E_{1l} and E_{1t}) modes for the parallel (perpendicular) propagation. The difference in the



FIG. 15. Pressure dependence of the LO-TO splitting for two different phonon propagation directions, parallel along the [0001] direction (open circles) and perpendicular to the *c* axis along [1120] direction (filled circles) of 2*H* (a) and 4*H* SiC (b). The solid line indicates the LO-TO splitting of 3*C* SiC.



FIG. 16. Volume dependence of the LO-TO splitting for two different phonon propagation directions, parallel along the [0001] direction (dotted line) and perpendicular to the *c* axis along $[11\overline{20}]$ direction (solid line) of 2*H* SiC. The open (solid) circles denote the LO-TO splitting calculated using a unit cell compressed along the *c* axis.

pressure dependence for optical modes propagating parallel and perpendicular to the c-axis gives some indication for increasing anisotropy of the nH polytypes of SiC upon applied hydrostatic pressure. Our theoretical results for the LO-TO splittings at zero pressure for 3C (174 cm⁻¹), 2H $(167 \text{ and } 194 \text{ cm}^{-1})$, and 4H (183 and 168 cm⁻¹ for the $[11\overline{2}0]$ and [0001] direction) reproduce well the first-order Raman scattering data for 3C (176 cm⁻¹),⁵⁴ 2H (169 and 204 cm⁻¹),⁵⁵ and 4H (189 and 170 cm⁻¹).⁵⁴ The curves in Fig. 15 nearly reproduce the pressure dependences found experimentally for 3C and 6H SiC.4,7 For 3C, the linear increase for small pressure is well reproduced.⁴ In the 2H and 4H case, we notice a tendency towards a saturation in the LO-TO splitting for the parallel phonon propagation direction. However, this tendency is much weaker, as found experimentally for 6H SiC.⁷ The existing discrepancy between our theoretical calculation of the LO-TO splitting of 2H and 4H SiC and experimental data for 6H SiC might be due to the use of the presumably nonhydrostatic and quasihydrostatic pressure for the measurements in the ultrahighpressure region.⁷ Moreover, the variance of the experimental data in this high-pressure region is quite large.⁷ The authors of Ref. 7 assumed that the experiments performed under hydrostatic, quasihydrostatic, and presumably nonhydrostatic pressure gave the same general trend for the saturation of the LO-TO splitting, and that the extreme flattening of the LO-TO splitting in the ultrahigh-pressure region was independent of the nonhydrostatic pressure effects. To estimate a possible influence of a nonhydrostatic uniaxial compression of the unit cell of nH polytypes of SiC on the LO-TO splitting for the parallel and perpendicular phonon propagation direction, we calculated the zone-center phonon frequencies of 2H SiC at different volumes. In doing so, we used c/aratios, which were 2% smaller than the the corresponding equilibrium c/a ones (see Sec. III A). Furthermore, for a given unit cell volume and c/a ratio, we minimized the static total energy with respect to the internal parameter u. As illustrated in Fig. 16, there are considerable deviations, in particular, in the high-pressure region, between the LO-TO splitting data obtained under hydrostatic and nonhydrostatic pressure. Therefore, we presume that the extreme saturation behavior of the experimentally found LO-TO splitting for 6H SiC (Ref. 7) might be partially caused by nonhydrostatic pressure conditions.

In order to relate the experimental LO-TO splitting to the Born effective charges, a simplified formula is used in Ref. 7 that is only valid for binary compounds with cubic symmetry,

$$\omega_{\rm LO}^2 - \omega_{\rm TO}^2 = \frac{4 \pi (Z^B)^2}{\mu \Omega \epsilon(\infty)},\tag{9}$$

where μ is the reduced mass. This might be another reason for a discrepancy between the experimentally derived Born effective charge of 6*H* SiC (Ref. 7) and our results for 2*H* and 4*H* polytypes of SiC. In general, for crystals of arbitrary symmetry, Eq. (9) has to be replaced by a generalized one,

$$\sum_{\lambda=1}^{r} \left[\omega_{\lambda}^{2}(\hat{\mathbf{q}}) - \omega_{\lambda}^{2}(0) \right] = \frac{4\pi}{\Omega} \sum_{\kappa\alpha} \frac{1}{m_{\kappa}} \frac{\left[\mathbf{Z}^{B}(\kappa) \cdot \hat{\mathbf{q}} \right]_{\alpha}^{2}}{\hat{\mathbf{q}} \cdot \boldsymbol{\epsilon}(\infty) \cdot \hat{\mathbf{q}}}, \quad (10)$$

where r is the number of the IR-active modes, and the righthand side of this equation is the trace of the nonanalytical part of the dynamical matrix at the Γ point, see Eq. (8).⁵⁶ As pointed out in Refs. 47 and 56 in the case of low-symmetry crystals, the splitting between the IR-active phonon frequencies $\omega_{\lambda}(\hat{\mathbf{q}})$ and their regular (analytical) part $\omega_{\lambda}(0)$ is not necessarily the LO-TO splitting for the particular direction $\hat{\mathbf{q}}$. To determine the magnitude of the possible error made by this approximation, we estimated the pressure dependence of the average parallel and perpendicular components of $\overline{\mathbf{Z}}^{B}(Si)$ using, Eq. (9) and the correct volume dependence of $\epsilon_{\alpha\beta}(\infty)$. As can be seen from Fig. 13(b), there is a slight deviation between the so determined components of $\overline{\mathbf{Z}}^{B}(Si)$ and the correct ones. The most significant result from Fig. 13(b) is, however, the inverted order of the parallel and the perpendicular component of $\overline{\mathbf{Z}}^{B}(Si)$ and the more pronounced saturation behavior of the perpendicular component in the high-pressure region. This behavior joined together with the incorrect volume dependence of the high-frequency dielectric constant, $\partial \ln \epsilon_{\alpha\beta}(\infty)/\partial \ln V = 0.6$, results in a pronounced maximum of the perpendicular component of the average Born effective charge $\overline{Z}^B_{\parallel}(Si) \approx 2.736$ around 0.46 Mbar and a decrease beyond this pressure to $\overline{Z}^B_{\parallel}(Si) \approx 2.7$ at 1.13 Mbar. Therefore, we believe that the unusual behavior of the Born effective charge of 6H SiC derived from the LO-TO splitting in Ref. 7 can be related to the use of the incorrect pressure dependence of the high-frequency dielectric constant, to the simplified relation for the splitting between the IR-active phonon frequencies $\omega_{\lambda}(\hat{\mathbf{q}})$ and their regular (analytical) part $\omega_{\lambda}(0)$, to the neglect of the anisotropy of the uniaxial 6H structure, and to uncertainties of the experimental procedure.

IV. CONCLUSIONS

In conclusion, we have presented the first *ab initio* study on the pressure dependence of the structural, latticedynamical, and dielectric properties of cubic 3*C* and uniaxial 2*H* and 4*H* polytypes of SiC. In our calculation, NaCl, NiAs, CsCl, and β -Sn structures of SiC have been considered as candidates for high-pressure phases. The transition as well as the stability of the high-pressure phases are discussed in terms of relative displacements between Si and C atoms and the metallicity of these phases. In agreement with the partial ionic binding of 3C SiC, we find a pressure-induced phase transition from the zinc blende to the rocksalt structure at a critical pressure of 0.67 Mbar. However, the calculated transition pressure is lower than the experimental one. We favor a high-pressure transition to the NaCl structure, not only for 3C, but also for 2H and 4H SiC. The corresponding critical pressure is found to be smaller (larger) for hexagonal polytypes with a hexagonality larger than (less than or equal) 50%.

Moreover, we determined the pressure dependence of the optical zone-center phonon frequencies, the high-frequency dielectric constant, and the Born effective charge of 3C, 2H, and 4H SiC. Our results are in good agreement with the available experimental data, in particular, in the low-pressure region. Discrepancies between theory and experiment with respect to the pressure dependences of the Born effective charges of the hexagonal polytypes at ultrahigh pressures can be mainly traced back to the neglect of their tensor character, to the use of a simplified relation for the splitting between IR-active phonon frequencies and their regular (analytical) part, and, finally, to an incorrect volume dependence of the high-frequency dielectric constant. On the other hand, the pressure dependences of the LO-TO splittings also at ultra-

high pressures are essentially reproduced by the calculations. We predict a different pressure behavior of the optical phonons in nH polytypes of SiC in dependence on the propagation direction, although the anisotropy of the hexagonal polytypes of SiC at ambient pressure is rather small.

Our study shows that *ab initio* density-functional perturbational-theory calculations of ultrahigh-pressure dependence are feasible and that such properties can also be tackled for uniaxial crystals with more than two atoms in the unit cell. Nevertheless, in order to solve the remaining problems, more experimental and theoretical studies must be performed on SiC. Remarkable differences caused by applied hydrostatic pressure are found for the dynamical and dielectric properties of the 3C, 2H, and 4H SiC. This is in contrast to the ground-state properties, which are rather independent of the polytype.

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- ¹ Proceedings of the Fifth Conference on Silicon Carbide and Related Materials, edited by M. G. Spencer, R. P. Devaty, J. A. Edmond, M. Asif Khan, R. Kaplan, and M. Rahman, IOP Conf. Proc. No. 137 (Institute of Physics and Physical Society, Bristol, 1994).
- ²A. Addamiano, in *Silicon Carbide—1973*, edited by R. C. Marshal, J. W. Faust, Jr., and C. E. Ryan (University of South Carolina, Columbia, 1974), p. 179.
- ³W. J. Choyke, in *The Physics and Chemistry of Carbides, Nitrides and Borides*, Vol. 185 of *NATO Advanced Study Institute, Series E: Applied Science*, edited by R. Freer (Kluwer, Dordrecht, 1990), p. 563.
- ⁴D. Olego, M. Cardona, and P. Vogl, Phys. Rev. B **25**, 3978 (1982); **25**, 1151 (1982).
- ⁵I. V. Aleksandrov, A. F. Goncharov, S. M. Stishov, and E. V. Yakovenko, Pis'ma Zh. Éksp. Teor. Fiz. **50**, 116 (1989) [JETP Lett. **50**, 127 (1989)].
- ⁶M. Yoshida, A. Onodera, M. Ueno, K. Takemura, and O. Shimomura, Phys. Rev. B 48, 10 587 (1993).
- ⁷J. Liu and Y. K. Vohra, Phys. Rev. Lett. **72**, 4105 (1994).
- ⁸K. J. Chang and M. L. Cohen, Phys. Rev. B **35**, 8196 (1987).
- ⁹B. H. Cheong, K. J. Chang, and M. L. Cohen, Phys. Rev. B 44, 1053 (1991).
- ¹⁰P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
- ¹¹N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).
- ¹²D. J. Chadi and M. L. Cohen, Phys. Rev. B 8, 5747 (1973).
- ¹³P. Vinet, J. Ferrante, J. R. Smith, and J. H. Rose, J. Phys. C 19, L467 (1986).
- ¹⁴S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. 58, 1861 (1987).

- ¹⁵P. Giannozzi, S. De Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991).
- ¹⁶X. Gonze and J. P. Vigneron, Phys. Rev. B **39**, 13 120 (1989).
- ¹⁷K. Karch, P. Pavone, W. Windl, O. Schütt, and D. Strauch, Phys. Rev. B **50**, 17 054 (1994).
- ¹⁸F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. 50, 697 (1944).
- ¹⁹F. Birch, J. Geophys. Res. **83**, 316 (1978).
- ²⁰H. Schultz and K.H. Thiemann, Solid State Commun. **32**, 783 (1979).
- ²¹R. W. G. Wyckoff, Crystal Structure (Wiley, New York, 1963).
- ²²P. Käckell, B. Wenzien, and F. Bechstedt, Phys. Rev. B 50, 17 037 (1994).
- ²³K. Karch, F. Bechstedt, P. Pavone, and D. Strauch (unpublished).
- ²⁴A. Garcia and M. L. Cohen, Phys. Rev. B 47, 4215 (1993).
- ²⁵L. L. Boyer, E. Kaxiras, J. F. Feldman, J. Q. Broughton, and M. J. Mehl, Phys. Rev. Lett. **67**, 715 (1991).
- ²⁶G. Kresse and J. Hafner, Phys. Rev. B 49, 14 251 (1994).
- ²⁷N. Moll, M. Bockstedte, M. Fuchs, E. Pehlke, and M. Scheffler, Phys. Rev. B **52**, 2550 (1995).
- ²⁸ Physics of Group IV Elements and III-V Compounds, edited by O. Madelung, M. Schulz, and M. Weiss, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. a (Springer, Berlin, 1982).
- ²⁹B. Wenzien, G. Cappellini, and F. Bechstedt, Phys. Rev. B **51**, 14 701 (1995).
- ³⁰C. H. Park, B.-H. Cheong, K.-H. Lee, and K. J. Chang, Phys. Rev. B **49**, 4485 (1994).
- ³¹C. L. Fu and K.-M. Ho, Phys. Rev. B 28, 5489 (1983).
- ³²M. Methfessel and A. T. Paxon, Phys. Rev. B 40, 3616 (1989).
- ³³S. B. Zhang and M. L. Cohen, Phys. Rev. B **35**, 7604 (1987).
- ³⁴S. Froyen and M. L. Cohen, Phys. Rev. B 28, 3258 (1983).

- 17
- ³⁵S. T. Weir, Y. K. Vohra, C. A. Vanderborgh, and A. L. Ruoff, Phys. Rev. B **39**, 1280 (1989).
- ³⁶R. M. Wentzcowitsch, M. L. Cohen, and P. K. Lam, Phys. Rev. B 36, 6058 (1987).
- ³⁷J. E. Jaffee, R. Pandey, and M. J. Seel, Phys. Rev. B 47, 6299 (1993).
- ³⁸G. Y. Guo, J. Crain, P. Blacha, and W. M. Temmerman, Phys. Rev. B 47, 4841 (1993).
- ³⁹M. T. Yin and M. L. Cohen, Phys. Rev. B 26, 5668 (1982).
- ⁴⁰J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic Press, New York 1973).
- ⁴¹J. R. Chelikowsky and J. K. Burdett, Phys. Rev. Lett. 56, 961 (1986).
- ⁴² M. Ueno, A. Onodera, O. Shimomura, and K. Takemura, Phys. Rev. B **45**, 10 123 (1992).
- ⁴³I. Gorczyca, N. E. Christensen, P. Perlin, I. Grzegory, J. Jun, and M. Bockowski, Solid State Commun. **79**, 1033 (1991).
- ⁴⁴ J. Wangel, V. Arnold, and A. L. Ruoff, J. Appl. Phys. 47, 2821 (1976).
- ⁴⁵S. Fahy and S. G. Louie, Phys. Rev. B 36, 3373 (1987).
- ⁴⁶M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).

- ⁴⁷W. Cochran and R. A. Cowley, J. Phys. Chem. Solids 23, 447 (1962).
- ⁴⁸L. Patrick and W. J. Choyke, Phys. Rev. B 2, 2255 (1972).
- ⁴⁹D. L. Camphausen, A. G. Neville Connell, and W. Paul, Phys. Rev. Lett. **26**, 184 (1971).
- ⁵⁰W. A. Harrison, *Electronic Structure and Properties of Solids* (Freeman, San Fransisco, 1980).
- ⁵¹G. S. Spencer, A. C. Ho, J. Menendez, R. Droopad, H. Fathollahnejad, and G. N. Maracas, Phys. Rev. B 50, 14 125 (1994).
- ⁵²G. Wellenhofer, K. Karch, P. Pavone, U. Rössler, and D. Strauch, Phys. Rev. B 53, 6071 (1996).
- ⁵³A. F. Goncharov, E. V. Yakovenko, and S. M. Stishov, Pis'ma Zh. Éksp. Teor. Fiz. **52**, 1092 (1990) [JETP Lett. **52**, 491 (1990)].
- ⁵⁴D. W. Feldman, J. H. Parker, Jr., W. J. Choyke, and L. Patrick, Phys. Rev. **173**, 787 (1968).
- ⁵⁵S. Nakashima, A. Wada, and Z. Inoue, J. Phys. Soc. Jpn. 56, 3375 (1987).
- ⁵⁶G. Venkataraman, L. A. Feldkamp, and V. C. Sahni, *Dynamics of Perfect Crystals* (MIT, Cambridge, 1900).
- ⁵⁷R. D. Carnahan, J. Am. Ceram. Soc. **51**, 223 (1968).