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Ab initio pseudopotential study of structural and high-pressure properties of SiC

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An *ab initio* pseudopotential method is used to study the structural properties of SiC at low and high pressures. For cubic SiC, the calculated ground-state properties, such as the equilibrium lattice constant, bulk modulus, and cohesive energy, are in good agreement with experiment. The indirect band gap of cubic SiC is predicted to decrease with increasing pressure; this behavior is similar to Si but not to C. To study the structural phase stability at high pressures, the rocksalt and tetragonal β-Sn phases are considered. Our calculations suggest that the zinc-blende structure of SiC transforms into the rocksalt phase under a hydrostatic pressure of 660 ± 50 kbar. The calculated value should be regarded as an upper bound for the pressure of a structural phase transition from the zinc blende. The valence-charge distribution for cubic SiC resembles those for other zinc-blende semiconductors.

In contrast to 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; thus the charge density of SiC resembles those of ionic crystals. There are however some differences between SiC and other zinc-blende compounds. Cubic (β or 3*C*-type) SiC was suggested to have a low ionicity ($f_i=0.177$) by Phillips,[1] and although for most zinc-blende semiconductors the transverse effective charge which is a qualitative measure of ionicity is found to decrease with hydrostatic pressure, the effective charge for cubic SiC was observed to increase with pressure.[2] This latter result was explained[2] by the fact that the ionicity of SiC is caused by the presence of the strong potential of C rather than the difference in valency.

There have been many first-principles theoretical studies of the structural properties of the group-IV elements, C,[3-6] Si,[7-9] Ge,[7,10,11] and Sn.[12] The IV-IV compound SiC has received less attention, but recently pseudopotential calculations were done for the ground-state properties of cubic SiC at zero pressure.[13,14] The present study extends these investigations and explores high-pressure properties of SiC.

For C and Si, it has been shown theoretically[4-6] that the diamond structure of C transforms into the body-centered-cubic structure with eight atoms per unit cell B-8 ("BC-8") at 12 Mbar and for Si (experimentally and theoretically[7-9]) into the β-Sn phase at about 100 kbar. At higher pressures, the crystal structure of C was predicted to change to the simple cubic phase[5] at 27 Mbar while Si theoretically and experimentally was found to undergo successive phase transitions[7-9] to the simple hexagonal structure at 130–160 kbar and to the hexagonal close-packed structure above 400 kbar. In contrast, the B-8 phase of Si was found theoretically to be metastable.[5,6]

For SiC, there exist numerous modifications of the crystal structure at atmospheric pressure. These polytypes of SiC differ by the stacking order of the layers, and the atoms in the different polytypes form tetrahedral bonds characterizing the strong covalent behavior. As a result of the polytypism and the nearly covalent character of SiC, the band gaps are variable but the structures are very stable chemically with high bulk moduli, However, little is known about the structure at high pressures. Since cubic SiC may be considered to have characteristics between Si and C, its crystal structures at high pressures are expected to be the rocksalt, β-Sn or B-8. Because of the localized $2p$ orbital of the C atom, the calculations using pseudopotentials and plane waves are extensive. Hence, in this study, we choose only the cubic structure to analyze the structural properties.

We present the results of *ab initio* pseudopotential calculations for studying the ground state properties of zinc-blende SiC. These include the zero pressure lattice constant, bulk modulus, cohesive energy, and the deformation potentials of the direct and indirect band gaps. We also study the structural stability of phases with increasing pressure and find that the zinc-blende structure changes into the rocksalt phase above 660 kbar where this estimate should be considered as an upper bound for a structural transition. To investigate the ionicity of SiC, the valence charge distribution is presented and compared to other ionic compounds.

The present calculation is based on the *ab initio* total-energy pseudopotential method[15] within the framework of the local density approximation.[16] The exchange and correlation functional is approximated by the Wigner interpolation formula.[17] The details of the theoretical method and its successful applications to solids are given in Refs. 7 and 15. The ionic pseudopotentials for the C and Si atoms were previously tested to study the structural and dynamical properties of C and Si.[3,4,7-9]

The total energy is calculated self-consistently in momentum space.[18] The wave functions are expanded in a plane-wave basis set with a kinetic energy cutoff (E_{PW}) of up to 60 Ry. The size of the Hamiltonian matrix is about 1200 for the equilibrium volume and the full matrix is diagonalized without using perturbation (e.g., Löwdin perturbation) methods. For the C atom, the $2p$ orbital is strongly localized because of the lack of p core states, thus, a large number of plane waves are required to achieve a high degree of accuracy. The summation of the charge density over the Brillouin zone is done using a uniform grid of **k** points; samplings of 2, 2, and 39 points are chosen in the zinc-blende, rocksalt, and β-Sn irreducible Brillouin zones, respectively. The lattice constant a, the bulk modulus B_0, and the pressure derivative of the bulk modulus B_0' are calculated by fitting the volume-dependent energies to the Murnaghan equation of state.[19] The transition pressure and volume are calculated by considering the Gibbs free energy at zero temperature.

In Table I, the calculated values for a, B_0, and B_0' in the present study are compared with the results of other calculations[5,7,13,14,20,21] and experiments[22–24] for diamond C, Si, and zinc-blende SiC. The lattice constants and bulk moduli are in good agreement with the measured values. The result for B_0' of SiC is estimated to be 3.7 which is close to one other calculated value[13] of 3.2; experimental data for B_0' is not available. The lattice constant of zinc-blende SiC is smaller by 0.138 Å than the average of those for Si and C. This reduction of the lattice constant is an exception to Vegard's rule and results from the charge transfer from the Si atom to the C atom arising from the strong $2p$ potential of C when the Si—C bond is formed. The bulk modulus of 2.12 Mbar is smaller than those calculated or measured for diamond or first-row zinc-blende compounds, C (4.43 Mbar), zinc-blende BN (Ref. 25) (3.67 Mbar) and zinc-blende BeO (Ref. 26) (2.97 Mbar), but it is larger than that of isoelectronic BP (Ref. 25) (1.65 Mbar). The value for B_0 of SiC is also 28% smaller than the average (2.71 Mbar) of C and Si.

TABLE I. Calculated lattice constants, bulk moduli, their pressure derivatives, and cohesive energies for C, Si, and SiC. Kinetic energy cutoffs (E_{PW}) of 20, 60, and 60 Ry are used for Si, C, and SiC, respectively.

	a_0 (Å)	B_0 (Mbar)	B_0'	E_{coh} (eV/atom)
		C		
Present Calc.	3.561	4.38	3.5	7.94
Other Calc.[a]	3.55	4.7	4.2	8.06
Expt.[b]	3.567	4.43	4.0	7.37
		Si		
Present Calc.	5.433	0.92	3.6	4.84
Other Calc.[a]	5.43	0.88	4.0	4.85
Expt.[b]	5.429	0.99	4.2	4.63
		SiC		
Present Calc.	4.361	2.12	3.7	6.66
Other Calc.	4.326[c]	2.49[c]	3.2[c]	
	4.365[d]	2.00[d]	7.3[d]	
		2.11[e]		
Expt.	4.360[f]	2.24[g]		6.34[h]

[a] Reference 20 ($E_{\mathrm{PW}}=20$ Ry for Si and 50 Ry for C).

[b] See references in Refs. 5 and 7.

[c] Reference 13 ($E_{\mathrm{PW}}=24$ and 48 Ry for SiC using Löwdin perturbations).

[d] Reference 14 ($E_{\mathrm{PW}}=29.7$ Ry for SiC).

[e] Reference 21 (empirical formula $1761d^{-3.5}$ is used where d is the nearest-neighbor distance).

[f] Reference 22.

[g] Reference 23.

[h] Reference 24.

For the cohesive energy, we include the spin-polarized energies of 103 and 58 mRy for the C and Si atoms, respectively, and the zero-point vibrational energies. The results for C, Si, and SiC agree with the measured values to within 5 to 10%. Since the calculated cohesive energy of SiC (6.66 eV) is larger than the average (6.38 eV) of C and Si, the enthalpy of formation of cubic SiC is -0.28 eV per atom and this value is in reasonable agreement with the measured heat of formation[24] of -0.33 eV per atom. Therefore, the zinc-blende structure of SiC is thermodynamically stable and this is consistent with other calculated results.[27] In contrast, for zinc-blende SiGe, a positive enthalpy of formation was found to cause the instability of the zinc-blende structure.[27]

Figure 1 shows the calculated valence charge densities for zinc-blende SiC. Superposition of the atomic charges for the C and Si atoms show fairly spherical distributions around each atom. Because of the strong $2p$ potential of C, the charge density is localized near the C atom. As a result of self-consistent charge redistribution, the charges at the atomic sites diminish while the bond charges increase. As shown in Fig. 2, some charges around the Si atom move to the bonding region. This charge transfer gives rise to the ionic character of SiC and is similar to that found in III-V compounds where the transfer is caused by the difference in valency, but compared to the III-V's the ionicity of SiC was suggested to be small.[1] The charge transfer into the bonding regions results in a decrease of the total energy, i.e., the strongly attractive C potentials cause an increase of the cohesion of SiC with respect to the energies of the separated atoms. The Si-C bonds become stable and their formation contributes to the stabilization of the zinc-blende structure. Upon compression of the crystal, the charge densities are found to move into the interstitial and nonbonding regions while they decrease in the bonding region. This is consistent with the results of Ref. 13; however, this behavior does not account for the observed increase of the transverse effective charge with hydrostatic pressure.[2]

We summarize the results of the calculations for the band structure in Table II. The band gap of cubic SiC is found to be indirect from Γ to X with an energy separation of 1.21 eV. As in the case of C and Si, the calculated value for the band gap is smaller than the measured band gap of 2.39 eV, and this error is expected because of the use of the local-density approximation. The average of the band gaps for C and Si is 3.32 eV which is larger than that of SiC.

Assuming hydrostatic pressure, by varying the lattice constant, the deformation potentials of several conduction

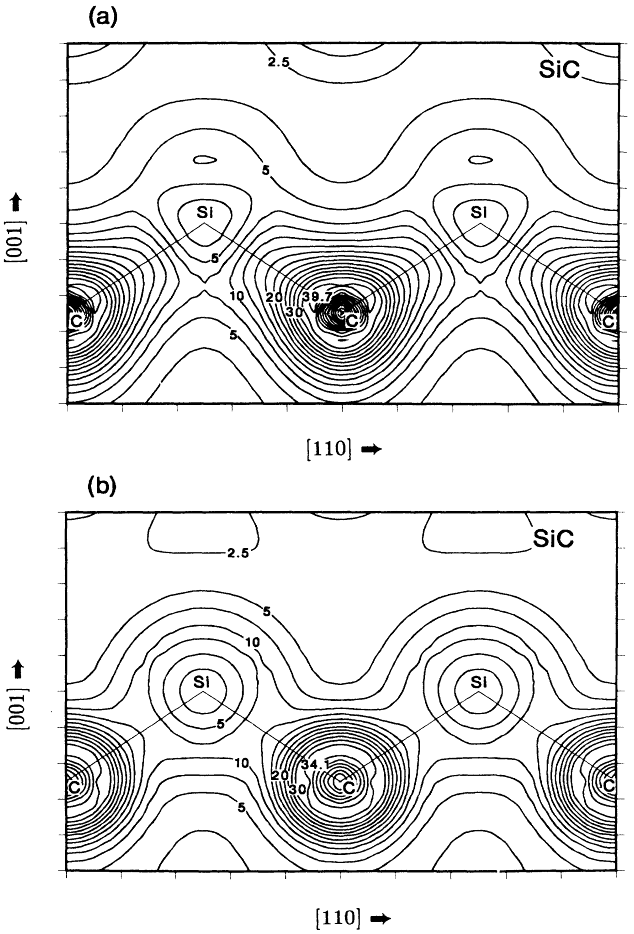

FIG. 1. Contour plots of the valence charge densities in the $(1\bar{1}0)$ planes for the zinc-blende phase of SiC: (a) self-consistent charge density and (b) superposition of atomic charge densities. An atomic volume of 10.369 Å^3 is used. Steps are in units of 2.5 electrons per cell volume.

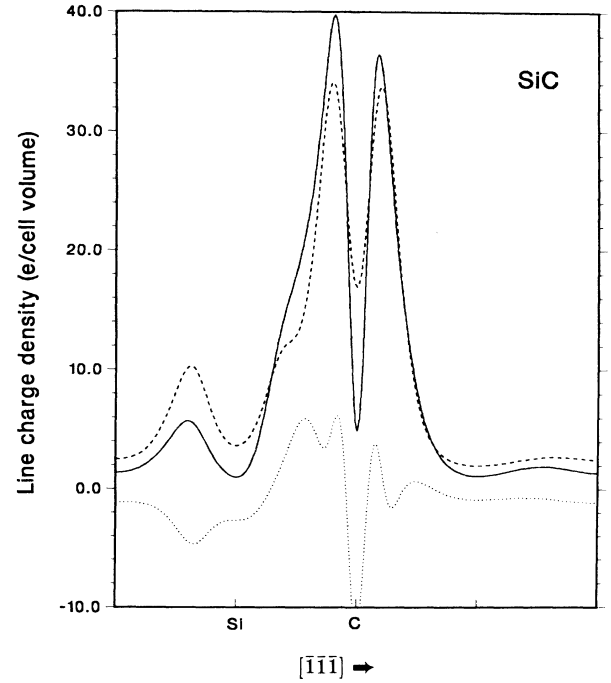

FIG. 2. Line plots of the valence charge densities along the $[\bar{1}\bar{1}\bar{1}]$ direction for the zinc-blende phase of SiC. Solid, dashed, and dotted lines denote the charge density for the self-consistent, the superposition of the atomic charges, and the difference of the two charge densities, respectively. An atomic volume of 10.369 Å is used.

band states are calculated. We find that the pressure coefficient of the indirect gap is different from those found in Si and C. With increasing pressure, it was found that the indirect gap for C increases with a coefficient[22] of 0.5 meV/kbar while for Si the coefficient[28] has the opposite sign with -1.4 meV/kbar. Using the calculated bulk modulus, we obtain a pressure coefficient of the fundamental band gap of -0.36 meV/kbar for cubic SiC and this value is a little larger than the average $(-0.42$ meV/kbar) of the coefficients for C and Si.

In Fig. 3, the calculated total energies are compared for the zinc-blende, rocksalt, and β-Sn structures. The zinc-blende structure is found to be stable up to 660 kbar where a transformation to the rocksalt phase is predicted. We have tested the effect of using different numbers of **k** points for sampling the charge density in the self-consistent calculations of the transition pressure and estimated a possible error of about 50 kbar. Theoretically, the diamond structure of C was predicted to change to the B-8 phase[5,6] at 12 Mbar and then transform into the simple cubic phase[5] at 27 GPa. For Si and Ge, it is well known that the first diamond to β-Sn phase transition occurs at about 100 kbar.[7–11] In contrast, the metallic β-Sn phase of C was found to be unstable with respect to the simple cubic phase. As shown in Fig. 3, we find that like C, the rocksalt structure (equivalent to the simple cubic structure with two types of atom) of SiC is more stable than the β-Sn structure. Because other possible phases like the B-8 structure are not tested, the calculated pressure is only considered to be an upper bound for the transition pressure from zinc-blende to another structure. The predicted values for the transitions volumes are given in Table III.

We find that the rocksalt phase is still semiconducting even if the pressure is increased up to about 3 Mbar (corresponding to a volume of $\sim 0.5V_0$ where V_0 is the equili-

TABLE II. Band energies ($E_{n\mathbf{k}}$ in eV) and deformation potentials for cubic SiC at symmetry points (with respect to the top of the valence bands). The calculated bulk modulus given in Table I is used. Experimental values are from Ref. 2.

	$E_{n\mathbf{k}}^{\text{calc}}$	$E_{n\mathbf{k}}^{\text{expt}}$	$-dE_{n\mathbf{k}}/(B_0 d\ln V)$
Γ_1^v	-15.36		
Γ_{15}^v	0.0	0.0	
Γ_1^c	6.27	6.0	0.57
Γ_{15}^c	7.07		0.33
X_1^c	1.21	2.39	-0.36
L_1^c	5.32	4.2	0.43

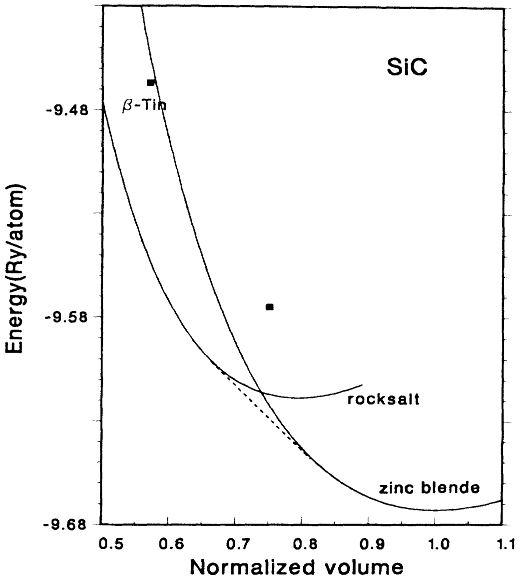

FIG. 3. Crystal energies versus volume normalized by the calculated equilibrium volume of 10.369 Å^3 per atom for the zinc-blende phase of SiC. Dashed line is the common tangent of the two energy curves. Square points denote the energies for the β-Sn phase; the axial ratios are 0.8 and 0.6 for $0.57V_0$ and $0.75V_0$, respectively. For $V=0.57V_0$, the energy for the β-Sn phase changes only by 16 mRy per atom when c/a varies from 0.8 to 0.6.

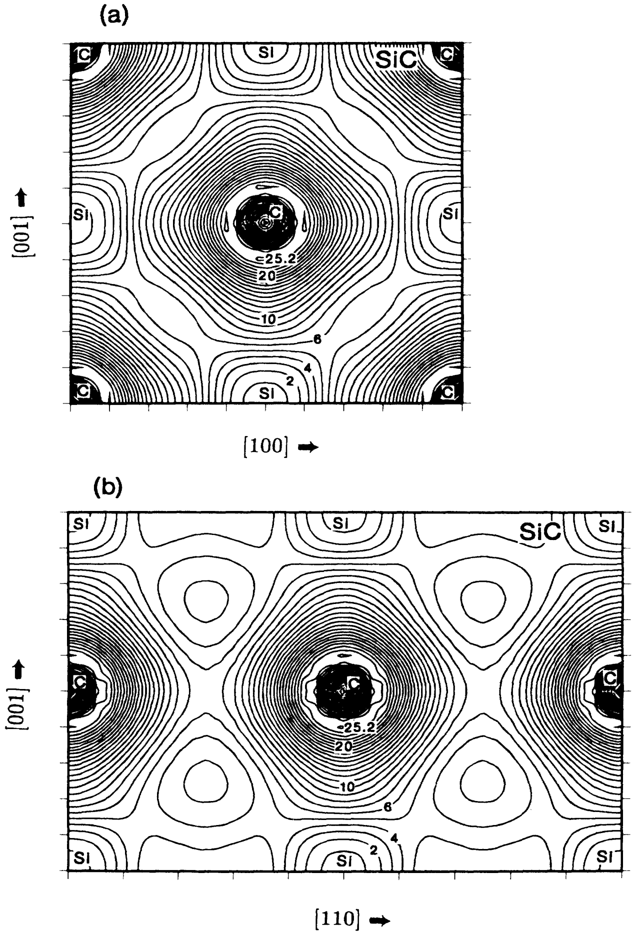

FIG. 4. Contour plots of the self-consistent valence charge densities in the (a) (010) and (b) $(1\bar{1}0)$ planes for the rocksalt phase of SiC. A volume of $0.57V_0$ is used. Steps are in units of one electron per cell volume. The dark regions around the C atom are caused by a rapid change of the charge density and poor resolution of the contour lines.

brium volume), while the β-Sn phase is metallic. Since the simple cubic structure for C and Si is metallic, the rocksalt phase for SiC might be expected to be metallic, too. However, a symmetry breaking arising from the heteropolarity of SiC basis splits the degeneracies of the energy bands at the L point in the face-centered cubic (fcc) Brillouin zone of the simple cubic structure; the degeneracy arises at the L point when the R point in the simple cubic Brillouin zone is folded into the Γ point when mapping from the simple cubic to the fcc lattice.[29] Thus, a gap develops near the Fermi level. Furthermore, a smaller negative pressure coefficient for the Γ to X transition is not sufficient to induce band overlap metallization. The rocksalt structure of usual III-V semiconductors has been shown to be metallic at high pressure[30] because of the band overlap between the occupied Γ and unoccupied X states. The charge density for rocksalt SiC (see Fig. 4) shows still localized distributions around the C atom although the volume is compressed to $0.57V_0$. Since the p-state potential of the C atom is strongly attractive for small radial distances up to about 0.38 Å, a reduction of the lattice constant does not alter the localized behavior of the potential. This ioniclike charge distribution keeps the semiconducting behavior for the rocksalt structure, thus this structure is stabilized as we shall see next.

TABLE III. Transition pressure and transition volume for the cubic zinc-blende to rocksalt transition. The volume are normalized by the calculated equilibrium volume of 10.369 Å^3 per atom for the zinc-blende structure.

	V_t(zinc blende)	V_t(rocksalt)	P_t (kbar)
Present Calc.	0.81	0.66	660±50

For a volume of $0.57V_0$, the energy of the β-Sn phase is higher by about 80 mRy per atom than that of the rocksalt phase; this energy is lower by about 12 mRy per atom than the zinc-blende structure. For a larger volume of $0.75V_0$, the β-Sn structure is found to be higher in energy than both the zinc-blende and rocksalt phases. Considering only the Ewald energy, the axial ratio of the β-Sn structure is determined to be 0.54 where the energy is minimum. However, when the axial ratio changes from 0.55 to 1.5, keeping the volume constant ($0.57V_0$), the total energy is found to be lowest for $c/a \simeq 0.8$ where this value is a little large than that of the β-Sn phase. Around $c/a=\sqrt{2}$ which is the c/a for the zinc-blende phase, the energy also has a minimum. When the axial ratio becomes close to $\sqrt{2}$, the metallic behavior of the β-Sn phase disappears. This is because the metallicity of the β-Sn phase results from the band overlapping when two new homopolar bonds are formed by reducing the c/a ratio of the zinc-blende structure. In the case of the zinc-blende structure, the semiconducting band structure is caused by the sp^3 tetrahedral bonds (all are heteropolar bonds).

Based on an ionicity argument, it was suggested that the transition pressure of highly ionic semiconducting compounds from the zinc-blende to the rocksalt phases increases with decreasing ionicity.[31] For less ionic materials, the β-Sn phase is generally stable with respect to the rocksalt phase. Since the ionicity of SiC is small, the β-Sn phase is expected to be more stable than the rocksalt phase. However, for SiC and C, we suggest that the relation of the rocksalt phase stability to ionicity is not applicable to elements and compounds with atoms in the first row and localized wave functions caused by the absence of occupied p core states.

Among polytypes of SiC, the $2H$ and $4H$ hexagonal structures differ from the zinc-blende phase by the stacking order along the [111] direction of the cubic lattice. Because the zinc-blende, $2H$, and $4H$ structures have similar tetrahedral bonds, the energy differences are expected to be small. Recent pseudopotential calculations showed that the energies for the $2H$ phase are higher by 10 (Ref. 9) to 16 (Ref. 7) meV and 14 (Ref. 10) to 15 (Ref. 7) meV per atom for Si and Ge, respectively, compared to the cubic diamond structure. The hexagonal $4H$ structure of Ge was found to be metastable with respect to the diamond phase and the energy difference is about 5 meV per atom.[10] A study of stacking faults in Si[32] reported that stacking faults energies are 25.8 and 20.4 meV for the intrinsic and extrinsic stacking faults, respectively, along the diagonal axis. These small energy differences are caused by the different stacking patterns since breaking a tetrahedral bond would cost a much higher energy of 2.3 and 1.9 eV for Si and Ge, respectively.

For SiC, the wurtzite ($2H$) structure is found to be higher in energy by about 3 meV per atom compared to the zinc-blende phase for the equilibrium volume whereas the calculated Si—C bond energy is 3.33 eV. In this case, we use the axial ratio of 1.645 obtained by energy minimization. This value for the c/a ratio is in good agreement with the measured value[22] of 1.641. In addition, a kinetic energy cutoff of 50 Ry is used and samplings of 19 and 27 **k** points are chosen in the zinc-blende and wurtzite irreducible Brillouin zone, respectively. We find that the energy of the zinc-blende phase changes only by 26 meV per atom when the kinetic energy cutoff varies from 50 to 60 Ry. Since the energies are accurate to within 6 meV by varying the number of **k** points, the stability of the zinc-blende and wurtzite structures is at the limits of the accuracy of the calculations. Based on bond-orbital coordinates r_σ and r_π, SiC was found to be on the boundary separating the zinc-blende and wurtzite structures along with ZnS.[33] This classification of crystal structures is in good agreement with the present results since the calculated energy difference between the zinc-blende and wurtzite structures is extremely small. Although we have not attempted the calculations of the total energy at high pressures for the $2H$ structure, we expect that the $2H$ phase has a phase transition into the rocksalt phase as the case found in the zinc-blende structure since the energy difference is small, i.e., bulk moduli and cohesive energies are expected to be similar.

In conclusion, we have studied the ground state properties of SiC using the pseudopotential-total-energy method and the results are found to be in good agreement with experiment. The rocksalt and β-Sn phases are considered as candidates for the high-pressure phase. A transition pressure of 660 kbar is suggested as an upper bound for the pressure-induced structural transition of SiC from the zinc-blende. At this pressure a transition to rocksalt is likely, but transitions to other phases at lower pressures are not ruled out. We found that the semiconducting rocksalt phase is more stable than the metallic β-Sn phase. The valence charge distribution for zinc-blende SiC resembles those found in III-V zinc-blende semiconducting compounds. Despite the different sizes of the atomic cores in SiC, the valence charges are found to transfer from the atomic sites and the nonbonding region to the bonding region near the C atom.

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