Pressure dependences of band gaps and optical-phonon frequency in cubic SiC

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The high-pressure behavior of the direct and indirect band gaps in zinc-blende-structure SiC is examined with use of self-consistent *ab initio* pseudopotential calculations. The fundamental band gap from Γ_{15}^v to X_1^c is found to decrease linearly with pressure up to 200 kbar. This result disagrees with a recent experimental finding of strong sublinear behavior at pressures of 10 to 15 kbar. The linear pressure coefficients of the fundamental band gap and the transverse-optical-phonon frequency at the Γ point in the Brillouin zone are in good agreement with measured values.

In recent years, *ab initio* density-functional calculations based on the local-density approximation (LDA) have been successful in describing the structural properties of solids.[1] However, the LDA band gaps of semiconductors and insulators have been consistently underestimated by about 30–50 % compared with experiments.[2] Despite the discrepancies between the calculated and measured band gaps, the pressure variations of the band gaps in semiconductors have been correctly described.[3–5] Since most of the band gaps vary linearly with pressure for very low pressures, the calculations of the pressure coefficients for the gaps were usually performed by reducing the volume isotropically on the order of 1–2 % near the equilibrium volume. This volume reduction corresponds to a pressure of about 10 kbar. The sublinear behavior of the band gaps becomes appreciable only at higher pressures.

Silicon carbide occurs in numerous hexagonal and orthorhombic structures in addition to the cubic form. In recent first-principles theoretical calculations,[6–9] the explored ground-state properties of SiC in the zinc-blende (β or 3*C*-type) and wurtzite (2*H*) structures were shown to be in good agreement with experiment. The calculations suggested that the cubic phase of SiC transforms into the more ionic rocksalt structure as pressure is applied above 600 kbar.[6] For SiC in the cubic structure, recent experiments showed that the fundamental gap varies linearly with pressure up to 10 kbar, but strong sublinear behavior is exhibited for pressures of 10 to 15 kbar.[10] Although this measured linear pressure coefficient of the band gap agrees well with one previously reported theoretical result,[6] the pressure variation of the gaps at very high pressures has not been previously calculated.

In this paper we examine the sublinear behavior of the band gaps in cubic SiC for pressures up to 600 kbar. We find the linear pressure dependence of the indirect and direct gaps up to 200 kbar. For the fundamental band gap from Γ_{15}^v to X_1^c, the calculated linear pressure coefficient is in good agreement with experiment. However, the sublinear coefficient is found to be much smaller than the measured value. Other band gaps ($\Gamma_{15}^v \rightarrow \Gamma_1^c$ and

$\Gamma_{15}^v \rightarrow L_1^c$) are shown to increase with pressure and have pressure coefficients larger by an order of magnitude than that for the fundamental gap. For the direct Γ_{15}^v-Γ_1^c gap, sublinear behavior is found to be more significant above 200 kbar and its second-order pressure coefficient is much larger compared to that of the fundamental gap.

In the present calculations we use the *ab initio* total-energy–pseudopotential method[1] within the framework of the local-density approximation.[11] The exchange and correlation functional is approximated by the Wigner interpolation formula.[12] The nonlocal pseudopotentials are generated from the scheme proposed by Hamann, Schlüter, and Chiang.[13] The crystal total energies are calculated self-consistently in momentum space.[14] The pseudo-wave-functions are expanded in a plane-wave basis set with a kinetic-energy cutoff (E_{pw}) of up to 60 Ry. This size of the Hamiltonian matrix was shown to be successful in providing accurate ground-state properties of cubic SiC.[6] The lattice constant (a_0), the bulk modulus (B_0), and the pressure derivative of the bulk modulus (B_0') were calculated to be 4.361 Å, 2.12 Mbar, and 3.7, respectively, while the measured values for a_0 and B_0 are 4.360 Å and 2.24 Mbar, respectively.[15,16] However, we are not aware of the experimental value for B_0'. The summation of the charge density over the Brillouin zone is done using uniform grids of **k** points. A grid of ten **k** points in an irreducible wedge of the Brillouin zone is chosen for the zinc-blende structure.

In Fig. 1, the calculated equation of state for the zinc-blende structure of SiC is plotted. This curve is obtained from the Murnaghan equation of state,[17] to which the volume-dependent energies were fitted, and drawn for pressures up to 600 kbar. This pressure represents the transition pressure for the zinc-blende to rocksalt phase transformation[6] and it is achieved by a volume compression down to about $0.825V_0$. At this point, the lattice constant is isotropically reduced by about 6% from its equilibrium value. It is noted that nonlinearity in the equation of state occurs above 100 kbar. Because of this
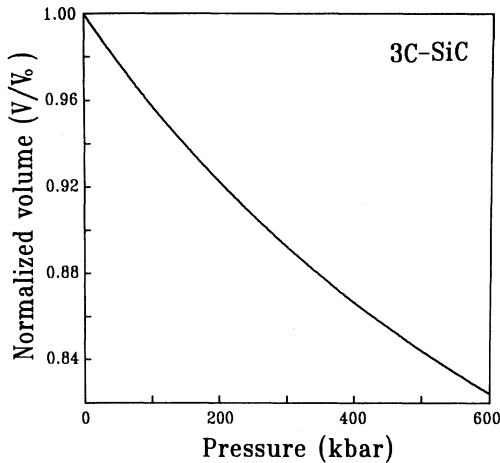
FIG. 1. The equation of state for cubic SiC is drawn for pressures up to 600 kbar.
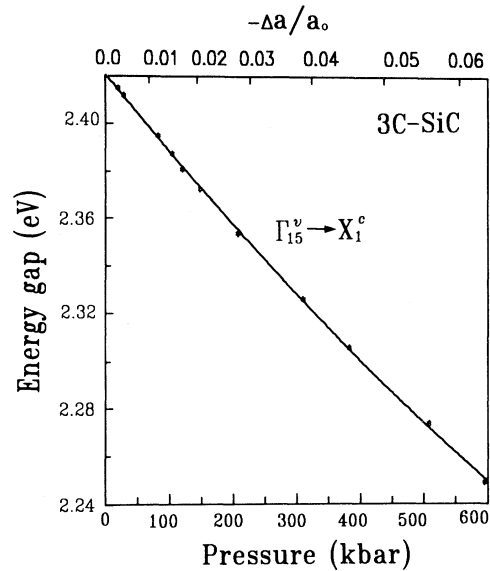

FIG. 2. The pressure dependence of the fundamental band gap ($\Gamma_{15}^v \rightarrow X_1^c$) in SiC is plotted as functions of relative lattice compression (upper scale) and pressure (lower scale). The solid line represents a least-squares fit to the calculated points. On the y axis, energies are shifted to produce the correct band gap of 2.42 eV at zero pressure.

nonlinear behavior, the simple use of the bulk modulus to convert volume changes into pressures, which is usually used to calculate the pressure coefficients and is considered to be accurate near the equilibrium volume, produces large uncertainties in the region of very high pressures. To avoid these uncertainties, in the present calculations we use the pressures converted from the volume changes through the equation of state.

We find the fundamental band gap of cubic SiC to be indirect from Γ_{15}^v to X_1^c. The calculated value of 1.21 eV for this band gap is underestimated by 50%, compared with the measured value of 2.42 eV.[18] This underestimate is attributed to the use of the LDA. The pressure variations of the fundamental gap and other Γ_{15}^v-Γ_1^c and Γ_{15}^v-L_1^c gaps are shown in Figs. 2 and 3, respectively, for pressures up to 600 kbar. With increasing pressure, all the band gaps are found to vary linearly up to 200 kbar; above 200 kbar, the sublinear behavior becomes appreciable. Compared with the recent experimental result that the strong sublinear behavior occurs at about 10 kbar,[10] our calculated pressure for the nonlinear pressure deviation of the fundamental gap is much higher. Since the experiments were done for pressures up to 15 kbar, experimental data at higher pressures are needed for more precise comparisons.

In Table I, the calculated linear and sublinear pressure coefficients are listed for each band and compared with experiment. For the fundamental optical gap, the calculated linear pressure coefficient of -0.33 meV/kbar is consistent with the previous calculation in which the bulk modulus was used to estimate pressures corresponding to volume changes. This coefficient is also in good agreement with the measured value of -0.34 meV/kbar.[10] However, the sublinear coefficient is an order of magnitude smaller than experiment. For the Γ_1^c and L_1^c conduction bands, both the linear and sublinear coefficients are found to be an order of magnitude larger than for the fundamental gap.

Compared with III-V heteropolar semiconductors, much of the ionic character of SiC is believed to result from the difference in the core sizes of C and Si. Al-

though the charge density of SiC resembles those of ionic crystals,[6] its lattice constant, bulk modulus, cohesive energy, and pressure coefficients of the band gaps are fairly well described by choosing the average of the values for Si and C. For Si and C, their fundamental gaps are found to vary almost linearly with the pressure coefficients of
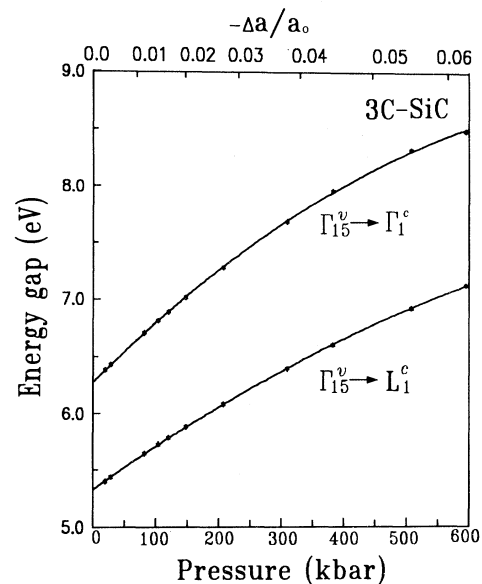

FIG. 3. The pressure dependences of the $\Gamma_{15}^v \rightarrow \Gamma_1^c$ and $\Gamma_{15}^v \rightarrow L_1^c$ band gaps are plotted as functions of relative lattice compression (upper scale) and pressure (lower scale). The solid lines represent least-squares fits to the calculated points.

TABLE I. Band energies (E_{nk} in eV), linear (dE_{nk}/dP in meV/kbar), and sublinear (d^2E_{nk}/dP^2 in meV/kbar^2) pressure coefficients for cubic SiC at symmetry points (with respect to the top of the valence bands). Values in parentheses are experimental data.

	E_{nk}	dE_{nk}/dP	d^2E_{nk}/dP^2
Γ_{15}^{v}	0.0		
Γ_{1}^{c}	6.27	5.50	-2.97×10^{-2}
	$(6.0)^{a}$		
X_{1}^{c}	1.21	-0.33	8.03×10^{-4}
	$(2.42)^{a}$	$(-0.34)^{b}$	$(1.06 \times 10^{-2})^{b}$
L_{1}^{c}	5.32	3.95	-1.58×10^{-2}
	$(4.2)^{a}$		

[a]Reference 18.
[b]Reference 10.

−1.5 and 0.58 meV/kbar, respectively, up to 200 kbar, as shown in Figs. 4 and 5. We also find the pressure coefficients at the X_{1}^{c} points to be close to those for the minimum conduction bands. Thus, it is unlikely that the strong sublinear behavior in SiC appears below 200 kbar. In fact, the magnitude of the calculated value of −0.33 meV/kbar for the linear pressure coefficient of the fundamental gap in SiC is a little smaller than the magnitude of
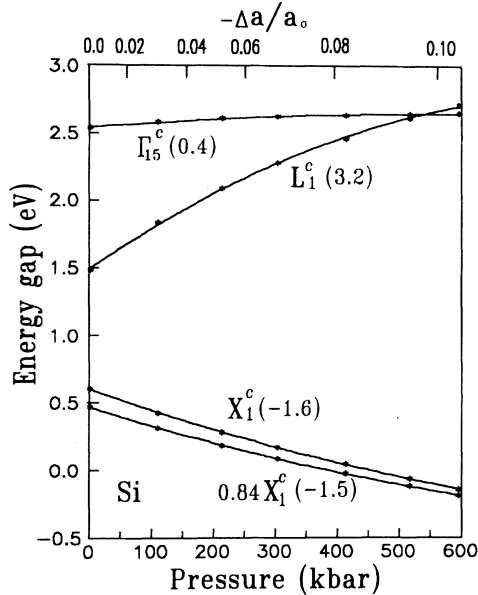

FIG. 4. The pressure dependences of the band gaps for Si in the diamond structure are plotted as functions of relative lattice compression (upper scale) and pressure (lower scale). The solid lines represent least-squares fits to the calculated points. The values in parentheses are the pressure coefficients of the band gaps in units of meV/kbar. The negative band gaps shown for pressures above 400 kbar at the X_{1}^{c} and $0.84X_{1}^{c}$ (i.e., $k = 0.84k_{\Gamma X_{1}^{c}}$) points are resulted from the underestimation in the LDA calculations. In fact, the diamond structure is only stable up to about 100 kbar because of the structural phase transition into the β-Sn phase.
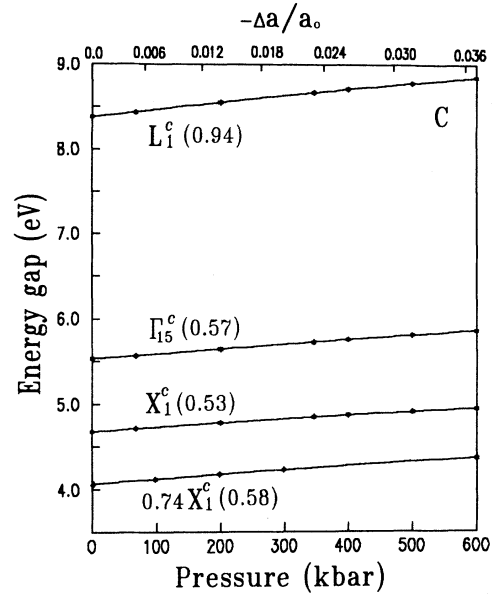

FIG. 5. The pressure dependences of the band gaps for C in the diamond structure are plotted as functions of relative lattice compression (upper scale) and pressure (lower scale). The solid lines represent least-squares fits to the calculated points. The values in parentheses are the pressure coefficients of the band gaps in units of meV/kbar.

the average (−0.46 meV/kbar) of the coefficients for Si and C.

An interesting property of SiC is that the magnitude of the pressure coefficient for the X_{1}^{c} conduction band is much smaller than for group-IV elemental (Si and Ge), III-V, and II-VI compound semiconductors, which have values around −1.5 meV/kbar.[3] This small pressure coefficient for SiC results from the fact that the X_{1}^{c} conduction band in C has a positive coefficient of 0.53 meV/kbar. Since the d state in C is absent in the low-lying valence states, the d-state energy is much higher than that for Si.[5] Although the charge densities for the X_{1}^{c} conduction bands in semiconductors are mostly d-like,[19] the d-state contribution to the charge density at the X_{1}^{c} point is less for SiC and much less for C as compared to Si. Thus, the X_{1}^{c} band in SiC decreases very slowly with pressure while it increases in C.

In Fig. 6, the pressure dependence of the transverse optical (TO) vibration mode at the Γ point in the Brillouin zone is shown. For each volume considered, the total energies are expanded in the atomic displacement u, and then the phonon vibrational frequency is calculated from a harmonic term. Since the coefficient of the u^3 term is found to be negative, the bond depression costs more energy than for the stretching along the [111] direction. Compared with the experimentally fitted phonon frequency[20] up to second order in pressure,

$$\omega_{TO} = (796.2 \pm 0.3) + (3.88 \pm 0.88) \times 10^{-1}P$$

$$- (2.2 \pm 0.4) \times 10^{-4}P^2 . \tag{1}$$

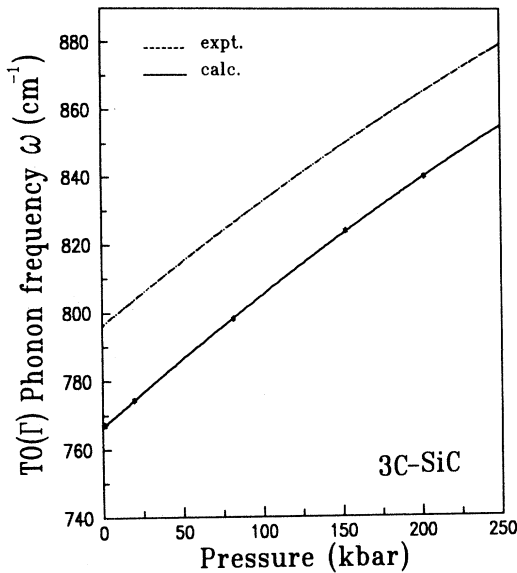Our fitted expression for the phonon frequency is

FIG. 6. The pressure dependence of the TO(Γ) phonon frequency is plotted as a function of pressure. The dashed and solid lines represent the experimental data from Ref. 20 and the present calculations, respectively.

TABLE II. Calculated TO(Γ) phonon frequency (v) and mode-Grüneisen parameter (γ) for cubic SiC at an equilibrium volume of 20.7 $\text{\AA}^3$ per molecule.

	v (THz)	γ
Present calc.	23.0	1.12
Other calc.	22.8[a]	1.01[a]
Expt.	23.9[b]	1.56[b]
		1.03[c]

[a]Reference 7.
[b]Reference 19.
[c]This value is obtained by using our results for B_0 and B_0' (see the text for details).

$$\omega_{\text{TO}} = 766.4 + 4.13 \times 10^{-1} P - 2.34 \times 10^{-4} P^2 , \qquad (2)$$

where ω and P are given in units of cm^{-1} and kbar, respectively. Thus, the calculated values for ω_{TO} (see Table II) and its linear and second-order pressure coefficients are in good agreement with experiments. We find ω_{TO} to increase linearly with pressure up to 100 kbar with no abrupt changes up to 250 kbar considered here. From the linear pressure coefficient, we estimate the mode-Grüneisen parameter $\gamma = -\partial \ln\omega / \partial \ln V$ for the TO(Γ) mode to be 1.12. This calculated value is consistent with other theoretical results,[7] but it is a little smaller than one previously reported experimental value of 1.56.[20] Since these experimental data were obtained from crude estimates for B_0 and B_0', which were taken from an average value of those for C and Si, a direct comparison cannot be made. However, if we use our results for B_0, B_0', and a_0, we find a value of 1.03 for γ, which is in better agreement with our calculational result.

In conclusion we have found an almost linear pressure behavior for the fundamental band gaps in cubic SiC, Si, and C up to 200 kbar. Although the linear pressure coefficient in SiC is in good agreement with experiment, the second-order pressure coefficient is much smaller than the measured value. Thus, we suggest that further experiments at very high pressures are needed to resolve such a discrepancy. For the TO(Γ) phonon mode, the calculated vibrational frequency and its pressure dependence are in good agreement with experiment.

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