Pressure dependence of Born effective charges, dielectric constant, and lattice dynamics in SiC

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The pressure dependence of the Born effective charge, dielectric constant and zone-center LO and TO phonons have been determined for $3C$-SiC by a linear response method based on the linearized augmented plane wave calculations within the local density approximation. The Born effective charges are found to increase nearly linearly with decreasing volume down to the smallest volume studied, $V/V_0 = 0.78$, corresponding to a pressure of about 0.8 Mbar. This seems to be in contradiction with the conclusion of the turnover behavior recently reported by Liu and Vohra [Phys. Rev. Lett. **72**, 4105 (1994)] for $6H$-SiC. Reanalyzing their procedure to extract the pressure dependence of the Born effective charges, we suggest that the turnover behavior they obtained is due to approximations in the assumed pressure dependence of the dielectric constant ε_∞, the use of a singular set of experimental data for the equation of state, and the uncertainty in measured phonon frequencies, especially at high pressure.

I. INTRODUCTION

Recently, Liu and Vohra[1] presented intriguing evidence regarding the pressure dependence of the Born effective charge in $6H$-SiC. These authors found that the effective charge increased initially with increasing pressure, reaching a maximum at about 0.4 Mbar. Further increasing the pressure, however, resulted in a decrease in the magnitude of the effective charge. Because of its great potential in device applications, especially in harsh environments, it is important to accurately characterize the properties of this unusual material. SiC crystallizes in hundreds of polytypes, corresponding to different stacking sequences of Si-C bilayers in the cubic [1 1 1] direction.[2] Polytypes with cubic, hexagonal, and rhombohedral symmetry are designated $3C$, nH, and nR, respectively, where n is the number of layers in the repeating unit, with the $3C$ structure corresponding to the zinc blende structure. The different polytypes have very similar properties, since differences in local atomic coordination first appear in the second-neighbor shell and the experimental equation of state for the different polytypes are very similar.[3,4] Phonon dispersion along the stacking direction is considered universal for different prototypes and this universality has been used to map out the phonon frequencies in this direction from Raman scattering measurements.[5] Indeed, a recent self-consistent study of $3C$, $2H$, and $4H$ SiC by Karch *et al.*[6] found only small differences in the calculated phonon frequencies along the stacking direction. The main purpose of the present work is to report a first-principles study of structural and dynamical properties of SiC under high pressure. In particular, the volume dependence of the Born effective charges and the dielectric constant were obtained. We find that the Born effective charge increases nearly linearly as the volume is decreased. This is in sharp contrast with the above-mentioned turnover behavior reported recently for $6H$-SiC. The likely reasons for this discrepancy will be discussed in light of the calculated results. A preliminary account of the present work has been reported.[7]

II. METHODOLOGY

First-principles total-energy calculations in the local density approximation (LDA) were performed using the linearized augmented plane wave (LAPW) method[8] to determine the ground state structural properties of $3C$-SiC at equilibrium and under pressure. Lattice dynamical properties, Born effective charges, and the dielectric constant were obtained with a linear response algorithm developed recently within the LAPW method.[9,10] To dispense with the need to treat the chemically inert localized inner core orbitals, we employ a hard Kerker-type[11] pseudopotential. The muffin-tin radii for Si and C are 1.79 and 1.50 a.u., respectively. We used the Wigner interpolation formula for the exchange-correlation potential.[12] Born effective charges and the dielectric constant were calculated using up to a $12 \times 12 \times 12$ uniform k point, mesh,[13] which corresponds to 28 special points in the irreducible Brillouin zone (BZ). At this level of convergence, the acoustic sum rule is satisfied with an error of only 0.6%. In calculating the dynamical matrices, we used an $8 \times 8 \times 8$ k-point mesh. Tests with denser meshes show that phonon frequencies are converged to better than about 0.5%. Tests with other exchange-correlation functionals also display differences at this level. Phonon dispersions in the harmonic approximation were obtained in the full BZ as follows. First, *ab initio* calculations were carried out to determine the dynamical matrix at the irreducible phonon wave vectors corresponding to a $4 \times 4 \times 4$ uniform mesh, which by symmetry gives the dynamical matrix at all mesh points. The dynamical matrix can then be obtained at arbitrary wave vectors by interpolation, first separating it into a long-range dipole-dipole term and a short-range term.[14] The former is evaluated exactly from the calculated Born effective charges and dielectric constant using the Ewald summation technique. The remaining short-range part is then interpolated using real-space force constants, which are found through Fourier transform.

TABLE I. Equilibrium state properties of SiC. The equilibrium lattice constant, bulk modulus, and its pressure derivative are represented by a_0, B_0, and B_0', respectively.

	a (Å)	B_0 (Mbar)	B_0'	Pressure range (Mbar)
Theory				
Chang et al.[a]	4.361	2.12	3.7	
Lambrecht et al.[b]	4.315	2.23	3.8	
Karch et al.[c]	4.345	2.22	3.88	
This work	4.360	2.10	3.71	
Experiment				
3C	4.360[d]	2.24[e]		
l		2.234[f]		
l		2.25[g]		
3C		2.27±0.03[h]	4.1±0.10[h]	0.425[h]
3C		2.48±0.09[i]	4.0±0.3[i]	0.25[i]
6H,15R		2.24±0.03[j]	4.3±0.3[j]	0.45[j]
3C,6H		2.60±0.09[k]	2.9±0.3[k]	0.95[k]

[a]Reference 16
[b]Reference 19.
[c]Reference 6.
[d]Reference 22.
[e]Estimated for 3C-SiC by Yean et al. (Ref. 23).
[f]Schreiber et al. (Ref. 24).
[g]R. D. Carnahan (Ref. 25).
[h]Aleksandrov et al. (Ref. 26).
[i]Strössner et al. (Ref. 27).
[j]Goncharov et al. (Ref. 3).
[k]Yoshida et al. (Ref. 4).
[l]Performed on specimens of α-SiC (hexagonal and rhombohedral phases).

III. RESULTS AND DISCUSSION

A. Structural properties, equation of state, and phase transition

LAPW total-energy calculations were performed to determine the theoretical lattice constant a_0, bulk modulus B_0, and its pressure derivative B_0' for 3C-SiC by fitting to the Murnaghan equation of state.[15] Earlier experimental and theoretical studies suggest that the pressure-volume relations for different polytypes are similar, due to the rigidity of the nearest-neighbor coordination. The equation-of-state data for the two polytypes 3C-SiC and 6H-SiC have been found to be essentially the same up to the transition pressure of 3C-SiC.[4] Theoretical calculations[6] also yield very small difference in the bulk modulus (less than 1%) between the 3C, 2H, and 4H polytypes. The calculated pressure derivative of the bulk modulus for these polytypes are different by only 7%.[6]

Results for 3C-SiC are presented in Table I and compared with other calculations and experiment for 3C and other polytypes. Our results agree well with other calculations given in the table. Slight differences may be due to the use of different forms of the exchange-correlation potential. There is nearly perfect agreement between the present calculations and those of Chang and Cohen,[16] both using the Wigner exchange-correlation potential. Karch et al.[6] used the Ceperly and Alder exchange-correlation formula[17] as parametrized by Perdew and Zunger.[18] Lambrecht et al.[19] used an LMTO basis set and the von Barth–Hedin parametrization of the exchange-correlation energy.[20] As also seen in other

systems,[21] the Wigner form tends to yield slightly larger equilibrium lattice constants than other forms, and as expected the bulk modulus is accordingly slightly smaller.

A number of high-pressure experiments have been carried out on various polytypes of SiC. While they generally show little difference between the equation of state for different polytypes, there are large discrepancies between the results of different experimental groups for the bulk modulus and its pressure derivative. Most earlier experiments report a bulk modulus around 2.25 Mbar. The recent work of Yoshida et al.[4] on SiC polytypes up to 0.95 Mbar, the highest pressurization on these materials so far, reported a relatively large bulk modulus B_0 (2.60±0.09 Mbar) and a smaller pressure derivative B_0' (2.9±0.3). They ascribed the discrepancy with the previous measurements to fitting to the larger pressure range in their experiment. Analysis of our calculated results does not support this explanation. Using our calculated total energy at various volumes, we can fit to the Murnaghan equation of state[15] for pressures up to about 0.8 Mbar. We find only small differences (both B_0 and B_0' change about 1%) compared to fitting over a smaller pressure range. The explanation is also inconsistent with the experiments of Aleksandrov et al.[26] and Goncharov et al.,[3] which were carried out, respectively, to 0.425 Mbar and 0.45 Mbar but obtained smaller bulk modulus as compared with that of Strössner et al.,[27] which went up to only 0.25 Mbar. Based on the results of all existing well-converged theoretical calculations, it seems reasonable to suggest that the lower range of the experimental bulk modulus is more likely to be correct.

TABLE II. Transition parameters from zinc blende structure to rocksalt structure for SiC. V_t is the volume of the zinc blende ($3C$) phase at transition, and V_0 is the volume at ambient pressure. $\triangle V/V_0$ denotes the percentage of volume reduction when the transition occurs.

	Pressure (Mbar)	V_t/V_0	$\triangle V/V_0$
This work	0.65	0.817	20.2%
Chang et al.[a]	0.66	0.81	18.5%
Cheong et al.[b]	0.60	0.825	
Christensen et al.[c]	0.59	0.84[d]	19%[d]
Experiment[e]	1.00	0.757	20.3%

[a]Reference 16.
[b]Reference 28.
[c]Reference 29.
[d]Quoted from Ref. 4, in which the authors derived these numbers from Fig. 12 of Ref. 29.
[e]Reference 4.

We have also determined the volume dependence of the total energy for rocksalt structure SiC. Table II compares the calculated transition parameters to other calculations and experiment. The agreement between the different calculations is good, predicting that the transformation from the zinc blende phase to the rocksalt phase takes place at about 0.65 Mbar. The volume of the zinc blende phase at the phase transition is predicted to be about 82% of its equilibrium volume at ambient pressure, and the volume reduction accompanied by the transition is predicted to be about 20%. The predicted transition pressure and the volume of the $3C$-SiC phase before the transition differ considerably from the experimental data, but the observed volume reduction is in good agreement. This may be due to the fact that the experimental transition pressure was obtained for the forward transition (from the zinc blende phase to the rocksalt phase), where an excess pressure beyond the equilibrium value appears and is included in the measurements.[4]

B. Born effective charge, dielectric constant, phonon frequencies, and elastic constants at equilibrium volume

The Born effective charge Z^* and dielectric constant ϵ_∞ are calculated at small $\mathbf{q}$ wave vector 0.01 $[1\ 1\ 1](2\pi/a)$,

where a is the lattice constant. Table III presents our results at the experimental equilibrium volume. The Born effective charges $Z^*(\mathrm{Si})$ and $Z^*(\mathrm{C})$ are converged to better than one percent when BZ integrations are performed using a 28 special k-point set in the irreducible BZ, corresponding to a $12\times12\times12$ uniform k-point sampling. The acoustic sum rule requires that $Z^*(\mathrm{Si})$ and $Z^*(\mathrm{C})$ have the same magnitude and opposite sign. Violations arise from finite k-point sampling. However, good results can be obtained with 10 special k points, especially after averaging the magnitudes of $Z^*(\mathrm{Si})$ and $Z^*(\mathrm{C})$.[30] The averaging also reduces the effect of using a small but finite wave vector. This effect was checked by using a slightly larger wave vector $\mathbf{q}=0.02$ $[1\ 1\ 1]$ $(2\pi/a)$, which yielded only a slightly larger discrepancy. Our calculations give a Born effective charge in excellent agreement with experiment and with the linear response calculations by Karch et al., using a plane wave basis set.[6] The static dielectric constant ϵ_∞ is about 7% too large, however. The tendency of the LDA to overestimate ϵ_∞ is a well-known problem that is attributed not to the density functional theory, but to the LDA used for the exchange-correlation potential.[31,32]

Our calculated phonon frequencies are shown in Fig. 1. For points along the $\Lambda[\xi\ \xi\ \xi]$ direction, we obtained the dynamical matrices as described in Sec. II, using a uniform $4\times4\times4$ phonon wave vector mesh. But along the $\Delta[\xi\ 0\ 0]$ and $\Sigma[\xi\ \xi\ 0]$ directions, we have calculated the dynamical matrices at additional points, which correspond to an $8\times8\times8$ mesh, and obtained one-dimensional interplanar force constants to perform the interpolation.[33] This improves the interpolated dispersion in the acoustic region. No neutron scattering data for zinc blende SiC is available because it is difficult to grow large enough $3C$-SiC single crystals. The filled squares in the figure are experimental phonon frequency data from Raman measurements. The experimental results on the BZ boundary (X and L) are obtained from second-order Raman scattering.[34] Others are first-order Raman data from hexagonal and rhombohedral polytypes that have been unfolded into the larger $3C$-SiC BZ.[5] The excellent agreement shows that the different stacking sequences have little influence on the vibrational properties. As mentioned, the calculated phonon frequencies of Karch et al.[6] on $2H$- and $4H$-SiC directly support this conclusion. Table IV

TABLE III. Calculated Born effective charges Z^* and ϵ_∞ at experimental volume.

	$Z^*(\mathrm{Si})$	$Z^*(\mathrm{C})$	$\dfrac{|Z^*(\mathrm{Si})|+|Z^*(\mathrm{C})|}{2}$	ϵ_∞
This work				
Number of special k points				
2	2.428	-3.392	2.910	9.426
10	2.701	-2.716	2.708	7.137
28	2.709	-2.693	2.701	7.005
Karch et al.[a]				
(at LDA volume)			2.72	6.97
Experiment			2.697[b]	6.52[c]

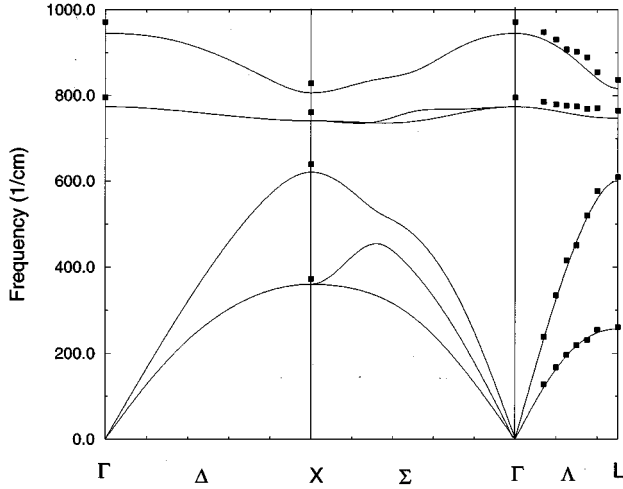[a]Reference 6.
[b]Reference 36.
[c]Reference 22.

FIG. 1. Calculated phonon frequencies of $3C$-SiC at the experimental lattice constant (solid lines). The solid square symbols are from Raman measurements (see text).

compares our calculated phonon frequencies at high-symmetry k points with those of Karch *et al.*[6] and with experiment. The zone-center ω_{LO} frequency is obtained from the calculated ω_{TO}, ϵ_∞, Z^*, and the volume of the primitive unit cell V, using the relation

$$\omega_{LO}^2 = \omega_{TO}^2 + \frac{4\pi e^2 \mathbf{Z}^{*2}}{\epsilon_\infty \mu V}, \tag{1}$$

where μ is the reduced mass. Our calculated frequencies are systematically about 1% smaller than those of Ref. 6. This is due in part to the difference in the equilibrium volume in the two calculations.

The elastic constants can be extracted from the calculated acoustic phonon dispersions. For the cubic structure, the elastic constants C_{44} and C_{11} are simply related to the velocities of transverse and longitudinal plane waves in $[1\,0\,0]$ direction as follows:[33]

$$v_T[100] = \sqrt{\frac{C_{44}}{\rho}}, \tag{2}$$

$$v_L[100] = \sqrt{\frac{C_{11}}{\rho}}, \tag{3}$$

where ρ is the mass density of SiC. The velocities of $v_T[100]$ and $v_L[100]$ can be obtained from the slopes of the acoustic transverse and longitudinal phonon dispersions at the zone center in the $[1\,0\,0]$ direction:

TABLE V. Elastic constants and bulk modulus (in Mbar) of $3C$-SiC.

	C_{44}	C_{11}	C_{12}	B_0
This work	2.41	3.84	1.32	2.16
Karch *et al.*[a]	2.53	3.90	1.34	2.19
Lambrecht *et al.*[b]	2.87	4.20	1.26	2.24
Experiment[c]	2.56	3.90	1.42	2.25

[a]Reference 6.
[b]Reference 19.
[c]The experimental data are derived by Lambrecht *et al.* (Ref. 19) from the sound velocities of Feldman *et al.* (Ref. 5).

$$v_j[100] = \frac{\partial \omega_j}{\partial k}, \tag{4}$$

where ω_j is the angular frequency of the jth branch phonon and k is the magnitude of the corresponding wave vector. Similarly, the elastic constant C_{12} can be obtained from the relationship[33]

$$v_{T_1}[110] = \sqrt{\frac{C_{11} - C_{12}}{2\rho}}, \tag{5}$$

where v_{T_1} is the velocity of transverse wave with atomic displacement along $[1\,\bar{1}\,0]$, which corresponds to the lowest acoustic branch in the Σ direction, i.e., $[1\,1\,0]$. The bulk modulus B_0 is related to these elastic constants by the relation[35]

$$B_0 = \frac{C_{11} + 2C_{12}}{3}. \tag{6}$$

The directional dependence of the transverse sound velocity in $3C$-SiC is related to the fact that the interatomic forces in $3C$-SiC are highly noncentral, which implies that the elastic constants do not satisfy the Cauchy relation ($C_{12} = C_{44}$). Table V presents the elastic constants and the bulk modulus as extracted using the equations above, together with other calculated results and experiment. Our results are in good agreement with experiment and slightly smaller than the calculations by Karch *et al.*[6] due again in part to the use of our slightly larger lattice constant. The bulk modulus B_0 determined from the elastic constants is consistent with our total energy calculations in the previous section.

TABLE IV. Comparison of phonon frequencies (cm^{-1}) in $3C$-SiC.

	Γ_{TO}	Γ_{LO}	X_{TA}	X_{LA}	X_{TO}	X_{LO}	L_{TA}	L_{LA}	L_{TO}	L_{LO}
This work	774	945	361	622	741	807	257	601	747	817
Karch *et al.*[a]	783	956	366	629	755	829	261	610	766	838
Experiment[b]	796	972	373	640	761	829	266	610	766	838

[a]Reference 6.
[b]Reference 5.

TABLE VI. Grüneisen parameters of phonon modes in 3C-SiC.

	This work	Expt.
TO(Γ)	1.07	1.02,[a] 1.102[b]
LO(Γ)	1.02	1.01,[a] 1.091[b]
TA(X)	0.12	
LA(X)	0.82	
TO(X)	1.46	1.30[a]
LO(X)	1.16	
TA(L)	-0.13	−0.28[a]
LA(L)	0.90	−0.11[a]
TO(L)	1.31	1.24[a]
LO(L)	1.15	1.30[a]

[a]Converted from the results of Olego *et al.* (Refs. 36 and 34); see text.
[b]Aleksandrov *et al.* (Ref. 26).

C. Pressure dependence of phonon frequencies, dielectric constant, and Born effective charge

The mode Grüneisen parameters, defined as

$$\gamma = -\frac{V}{\omega}\frac{\partial \omega}{\partial V}, \qquad (7)$$

describes the volume dependence of the phonon frequencies. The calculated mode Grüneisen parameters at the Γ, X, and L points in the BZ are presented in Table VI. Our results appear to be in good agreement with Karch *et al.*[6] as presented in their Fig. 9. In the text of that paper, they also gave the numerical value for the TA(X) mode, 0.13, which compares favorably with our value of 0.12. The experimental results of Olego *et al.*[34,36] and of Aleksandrov *et al.*[26] are presented for comparison. In the former work, the Grüneisen parameters were calculated from their experimental volume dependence using a bulk modulus of 3.219 Mbar. This value is likely to be too large, as discussed above. The values given in Table VI are converted from their results, assuming the bulk modulus from our calculations. The results are seen to be in generally good agreement with our calculation. A significant discrepancy exists for the LA mode at the L point. The experiment of Olego *et al.* gave a negative value, in contrast with our theoretical prediction and that of Karch *et al.*[6]

Figure 2 compares the calculated pressure dependence of the zone-center phonon frequencies of 3C-SiC with the experiments for both 3C-SiC and 6H-SiC. The numerical values of our frequencies are presented in Table VII, together with the calculated Born effective charge and dielectric constant of 3C-SiC at different lattice constants. The second row of Table VII gives the results at the equilibrium volume and the smallest lattice parameter corresponds to a pressure of about 0.8 Mbar. The calculated pressure as a function of volume was determined by fitting the volume dependence of the total energy to the Murnaghan equation of state.[15] We have also tested fitting the Birch-Murnaghan equation of state,[37] which was used by Yoshida *et al.*,[4] and find only small differences, with B_0 increasing by 1%, B_0' increasing by less than 3%, and the pressure values changing less than
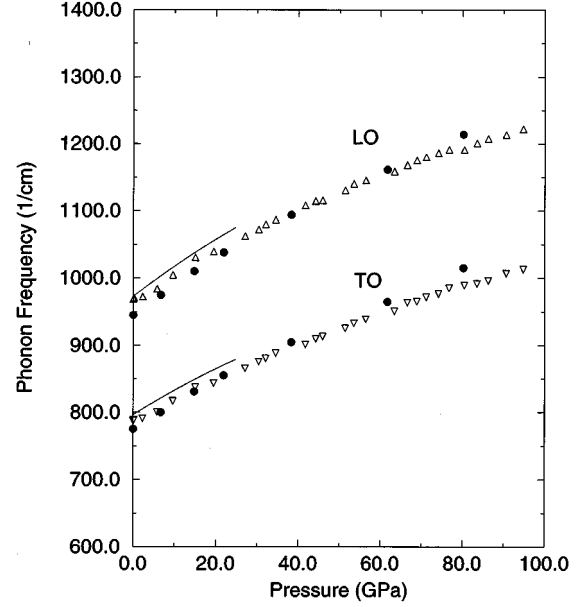

FIG. 2. Pressure dependence of zone-center phonon frequencies of SiC. Solid circles are calculated results for 3C-SiC. Solid lines are the measurements for 3C-SiC up to 25 GPa (0.25 Mbar) by Olego *et al.* (Ref. 36). Triangles are the experimental results of 6H-SiC reported by Liu and Vohra (Ref. 1) to 95 GPa (0.95 Mbar).

1%. As in the ambient pressure case mentioned above, our phonon frequencies are nearly uniformly a few percent smaller than those of 3C-SiC measured up to 0.25 Mbar by Olego *et al.*[36] Therefore the experimental pressure dependence of phonon frequencies of zone-center LO and TO modes are fairly well reproduced in our calculations. This is consistent with the agreement of zone-center mode Grüneisen parameters in Table VI between theory and experiment. Figure 2 also compares our calculations with Liu and Vohra's measurements for 6H-SiC. With increasing pressure, our calculated frequencies stiffen slightly faster than their experiment, with values initially about 2% smaller than measurements changing to 2% larger at the end. To see the differences more clearly, the resulting LO-TO splitting from theory and experiments is presented in Fig. 3. For 3C-SiC, Olego *et al.*'s measured results under pressure[36] appear to increase faster than our calculations. In 6H-SiC, Liu and Vohra[1] observed a rapidly increasing LO-TO splitting at low

TABLE VII. Volume dependence of Born effective charge Z, dielectric constant ϵ_∞, and LO-TO splitting in 3C-SiC. The lattice parameter a is in a.u. and frequencies ω are in cm^{-1}.

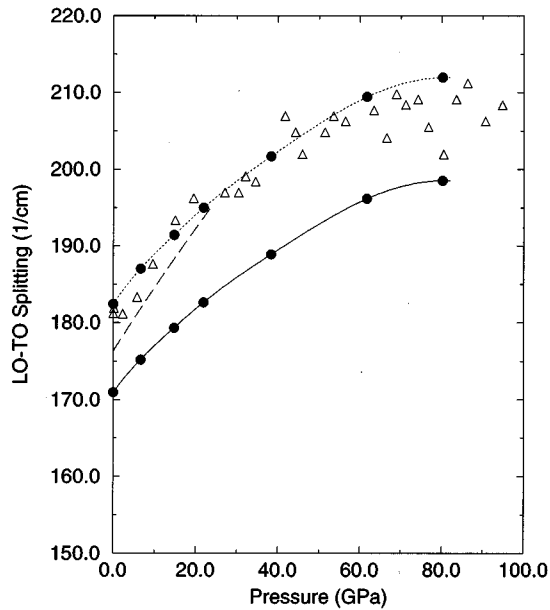| a	Z^*	ϵ_∞	ω_{TO}	ω_{LO}	ω_{LO} - ω_{TO}
8.339	2.676	7.111	744	910	166
8.239	2.701	7.005	775	945	171
8.157	2.721	6.927	800	975	175
8.069	2.744	6.852	831	1010	179
8.000	2.761	6.800	855	1038	183
7.864	2.793	6.707	905	1094	189
7.710	2.830	6.626	965	1161	196
7.610	2.850	6.575	1015	1214	199

FIG. 3. Pressure dependence of LO-TO splitting in SiC. Solid circles connected with solid lines are the theoretical results for $3C$-SiC using the calculated dielectric constants. Solid circles connected with dotted lines correspond to using the adjusted calculated dielectric constants for $3C$-SiC (see text). The dashed line represents the measurement by Olego *et al.* (Ref. 36) for $3C$-SiC up to 25 GPa (0.25 Mbar). Triangles are the experimental results of $6H$-SiC reported by Liu and Vohra (Ref. 1) to 95 GPa (0.95 Mbar).

FIG. 4. Comparison of the scaling relation in Eq. (8) to the calculated values (solid circles) of ϵ_∞ for several values of r: (a) $r=0.3$, (b) $r=0.6$, and (c) $r=0.8$.

pressure which saturates at the high end of the pressure range studied (0.9 Mbar). Our calculations compare well with the trend of the pressure dependence in their measurements, but the calculated values are smaller due to the overestimation in the dielectric constant. The pressure dependence of this overestimation is unknown, of course. However, if we assume that this is not a significant factor and reduce the calculated ϵ_∞ by 7%, the calculated LO-TO splitting increases as shown by the dotted lines in Fig. 3, which is in good agreement with the result of Liu and Vohra, except at the highest pressures.

As mentioned, using Eq. (1), Liu and Vohra[1] deduced the pressure dependence of the Born effective charges from the LO-TO splitting. Their results show that the effective charge increases at low pressure but reaches a maximum at about 0.4 Mbar and decreases as the pressure is increased further. Actually, the Born effective charges in the hexagonal polytypes are slightly anisotropic and are different for atomic displacement in the planes and perpendicular to the planes. The difference is about 7% for $2H$ and $4H$ polytypes.[6] This anisotropy in the effective charge and other physical quantities (such as the dielectric constant) was neglected in the analysis of Liu and Vohra.[1] If we consider the averaged effective charge, the results of Karch *et al.*[6] show that there is little distinction between the cubic and the hexagonal polytypes. In this sense, the results of our calculation for the cubic SiC, discussed below, are pertinent to the above-mentioned experiment.

In order to extract the pressure dependence of the effective charge from the measured LO-TO splitting, two additional pieces of information are required: (i) the equation of
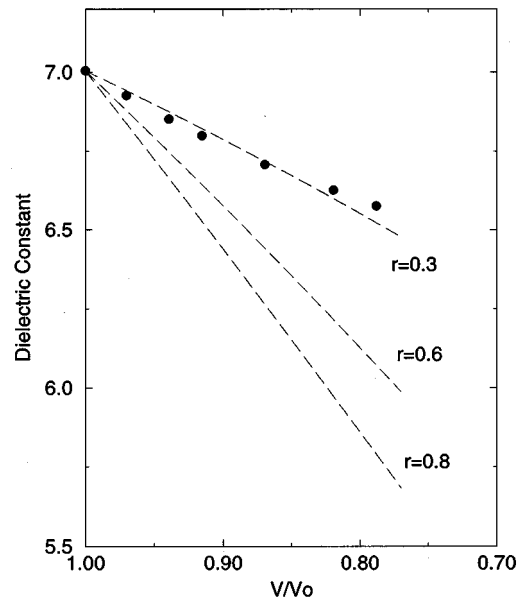
state to derive the volume from the measured pressure, and (ii) the volume dependence of ϵ_∞. By contrast, our calculated Born effective charge is determined directly and is known to be very accurate, unlike the dielectric constant which suffers from the LDA approximation. For their equation of state, Liu and Vohra used the values of Yoshida *et al.*[4] for the bulk modulus, $B=2.60$ Mbar, and its pressure derivative, $B'=2.9$ together with the Birch-Murnaghan equation of state. However, this bulk modulus is 10–20 % larger than the other measured values, and the pressure derivative is about 20–35 % smaller.

The volume dependence of ϵ_∞ has apparently never been measured for SiC. Liu and Vohra followed Olego *et al.*[36] in using the following expression:

$$\frac{\partial \ln \epsilon_\infty}{\partial \ln V} = r, \tag{8}$$

with $r=0.6$ for this range of pressures, citing earlier work on both Si and C that reported this value. Goñi *et al.*[38] have reviewed the volume dependence of the refractive index of Ge and GaAs. Their Table II shows large differences between various measurements of the volume derivative of ϵ_∞ in Eq. (8). Thus, the use of the scaling relation, Eq. (8), and the particular value $r=0.6$ must be regarded as a weak link in the experimental analysis of the volume dependence of the Born effective charge. Indeed, the present calculations suggest that this value of the exponent scaling power is too large. In Fig. 4, we compare the scaling relation Eq. (8) with the calculated volume dependence of ϵ_∞. The value $r\approx0.3$ is found to give the best fit to the calculated values. As mentioned, the LDA tends to overestimate ϵ_∞, in this case by about 7%. The volume dependence of this error is unknown, but it would have to be large to modify the above conclusions.

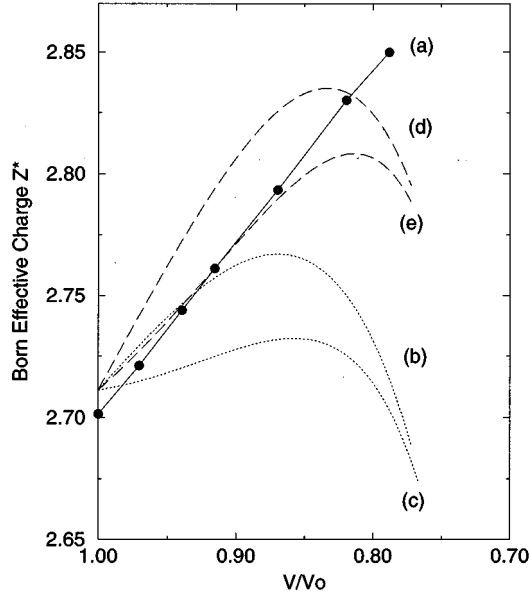FIG. 5. Volume dependence of the Born effective charge Z^*. The solid circles connected by solid lines in (a) are the calculated Z^* for $3C$-SiC. The dotted and dashed lines (b)–(e) are derived from Liu and Vohra's LO-TO splitting of $6H$-SiC but using different equations of state and scaling relations for the volume dependence of dielectric constant (see text): (b) is determined using the scaling relation with $r = 0.6$ and Yoshida *et al.*'s equation of state; (c) is determined using the scaling relation with $r = 0.6$ and our calculated equation of state; (d) is determined using the scaling relation with $r = 0.3$ and Yoshida *et al.*'s equation of state; (e) is determined using the scaling relation with $r = 0.3$ and our calculated equation of state.

In Fig. 5, we compare the volume dependence of the Born effective charge Z^* from calculations and those derived from experiment. The calculated Born effective charge for $3C$-SiC is seen to linearly increase with decreasing volume [see curve (a)], and there is no evidence of a relative maximum as is in the experimental results of Liu and Vohra for $6H$-SiC.[1] The other four curves are all derived from experiment, using Liu and Vohra's quadratic fit to the measured LO-TO splitting for $6H$-SiC, but with different choices of equation of state and volume dependence of dielectric constant. In curve (b), we have used the same input data as Liu and Vohra:[1] the scaling relation Eq. (8) with $r = 0.6$ (using the experimental $\varepsilon_\infty = 6.52$ at ambient pressure) and the equation of state ($B = 2.60$ Mbar and $B' = 2.9$) from Yoshida *et al.*[4] This curve exhibits the same peaked behavior as that shown in Fig. 3 of Liu and Vohra.[1] Curve (c), which is plotted with the same input data as for curve (b) except using our calculated equation of state ($B = 2.20$ Mbar and $B' = 3.71$), is much less peaked than curve (b), indicating that the volume dependence of Z^* derived from experiment following Eq. (1) is quite sensitive to the equation of state. The other two curves (d) and (e) are derived using the best scaling relation Eq. (8) with $r = 0.3$ (again using the experimental $\varepsilon_\infty = 6.52$ at ambient pressure). We have used the equation of state from Yoshida *et al.* for curve (d) and our calculated equation of state (for $3C$-SiC) for curve (e).

These two curves give larger Born effective charges than (b) and (c) since the scaling relation $r = 0.3$ yields larger dielectric constant under pressure than $r = 0.6$. Curve (e) is seen to agree quite well with the calculated Z^* except for volumes smaller than about $0.85\, V_0$. Examination of Liu and Vohra's measurements in Fig. 3, which shows the scatter in the experimental values of the LO-TO splitting, indicates that the greatest uncertainties occur for the higher pressures (smaller volumes) due to the pressure induced broadness of Raman and ruby peaks.[39] The magnitude of this scatter $\simeq 4$ cm^{-1} (or 2%) taken together with the questionable use of the scaling relation Eq. (8) with $r = 0.6$ and the large bulk modulus of Yoshida *et al.* undermines the conclusions of Liu and Vohra[1] regarding the peaked behavior of Z^*. Given the uncertainties in the experimental analysis, we would assert that our prediction of a linear increase of Z^* with decreasing volume, up to pressures of 0.8 Mbar is not contradicted by their measurements.

IV. CONCLUSIONS

We have presented a detailed analysis of the volume dependence of various properties of $3C$-SiC. The calculated equilibrium lattice constant, bulk modulus, and pressure derivative of the bulk modulus of $3C$-SiC were found to agree well with experiment and other LDA calculations. The transition pressure from the zincblende phase to the rocksalt phase is determined to be 0.65 Mbar, in good agreement with other theoretical results but lower than the reported experimental value (1.00 Mbar). The volume reduction, however, is in good agreement. The discrepancy may be due in part to the fact that the experimental transition pressure obtained in a diamond-anvil apparatus is for the forward transition (from zincblende phase to rocksalt phase), which requires an excess pressure[4] beyond the equilibrium value. The equilibrium calculated Born effective charge Z^* is in excellent agreement with experiment, but the dielectric constant is about 7% too large, as is typical in LDA calculations. The phonon dispersion and the elastic constants agree with available experiment data, demonstrating that the different stacking sequences in silicon carbides have little influence on the vibrational properties. The experimental Grüneisen parameters are well reproduced, and predictions are given for those experimentally unavailable. In $3C$-SiC, we find that (i) the dielectric constant ϵ_∞ decreases with increasing pressure, and (ii) the Born effective charge increases monotonically with pressure, without any evidence of a relative maximum as reported for $6H$-SiC by Liu and Vohra.[1] After analyzing the procedure used to extract the experimental Born effective charges Z^* of $6H$-SiC in Ref. 1, we suggest that the turnover behavior of Z^* reported by Ref. 1 is due to the assumptions regarding the volume dependence of dielectric constant ϵ_∞, the use of a singular set of experiment data for B_0 and B_0', and uncertainties in the measured phonon frequencies, especially at high pressure. Our calculations predict a linear increase of Z^* with decreasing volume, up to pressures of 0.8 Mbar.

Note added. Since the submission of the manuscript, two recent publications[40,41] have come to our attention. A theoretical study using molecular dynamics simulations with an

empirical potential model[40] raised the possibility of amorphization of SiC under high pressure. This seems to be inconsistent with the experiment of Yoshida *et al.*,[4] which observed a direct polymorphic transition to the rocksalt structure at 1 Mbar. Thus further experimental and theoretical work needs to be done to see if this is a real effect. Reference 41 presented calculated Born effective charges of 3*C*-SiC under low pressure, in good agreement with this work.

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