

# Calculated elastic constants and deformation potentials of cubic SiC

W. R. L. Lambrecht and B. Segall

*Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106*

M. Methfessel

*Fritz-Haber Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, W-1000 Berlin 33, Germany*

M. van Schilfgaarde

*SRI International, 333 Ravenswood Avenue, Menlo Park, California 94025*

(Received 7 March 1991)

The full-potential linear-muffin-tin-orbital method in combination with the local-density-functional theory is used to calculate the equilibrium lattice constant, the cohesive energy, the bulk modulus and its pressure derivative, the elastic constants, the Kleinman internal displacement parameter  $\zeta$ , the zone-center transverse-optical-phonon frequency, its Grüneisen parameter and the corresponding energy-band strain, and optical-mode deformation potentials of cubic SiC. The results for equilibrium properties and the transverse-optical phonon at the center of the Brillouin zone are shown to be in good agreement with the available experimental data and previous first-principles calculations. The elastic constants of 3C-SiC are transformed to a trigonal symmetry tensor along the  $\langle 111 \rangle$  direction, which allows a comparison to experimental data on hexagonal SiC. The agreement is found to be good. The elastic constants are also shown to be in good agreement with experimental data on the Young's and shear moduli and the Poisson ratio for polycrystalline SiC and with the Young's modulus of 3C-SiC whiskers along the  $\langle 111 \rangle$  direction, which is related to the theoretical cleavage strength. Predictions are also made for the deformation potentials, which have not yet been measured. The discrepancies with previous atomic-sphere-approximation calculations for the trigonal strain and optical-mode deformation potentials indicate the importance of nonspherical terms in the potential for these deformations. The absolute deformation potential of the valence-band maximum is computed by means of a heterojunction calculation between strained and unstrained materials. This procedure is shown to give good agreement with previous calculations for Si.

## I. INTRODUCTION

In view of the recent increased interest in SiC both for electronic and structural applications,<sup>1</sup> accurate values of its elastic constants and band-structure deformation potentials have become matters of considerable importance. From a thorough investigation of the literature it appears that this information is not available. Here we present the results of first-principles calculations of the elastic properties and the strain deformation potentials of cubic (or 3C-) SiC.

We use the recently developed full-potential version<sup>2</sup> of the linear-muffin-tin-orbital method<sup>3</sup> in conjunction with the density-functional method in the local-density approximation<sup>4</sup> (LDA) using the von Barth-Hedin parametrization of the exchange-correlation energy.<sup>5</sup> This approach was recently shown to provide an accurate description of the elastic properties of Si and C in the diamond structure.<sup>2</sup> Because of the similarity in structure of 3C-SiC (zinc blende) to diamond, similar accuracy is expected for SiC. We note that there are no shape approximations to the all-electron potential or charge density. Furthermore, since a variational approach is used, the desired accuracy of the total energy results can be obtained

by increasing the size of the multiple- $\kappa$  muffin-tin-orbital basis set (to be defined below). There are thus basically no approximations except for the use of the LDA.

We will show that the results of our calculations are in excellent agreement with experimental and previous first-principles theoretical data that are available for 3C-SiC. These include the equilibrium lattice constant, the bulk modulus and its pressure derivative, the cohesive energy, the TO phonon frequency at  $\Gamma$ , and its mode Grüneisen parameter. Unfortunately, the elastic constants of 3C-SiC single crystals have not been measured. However, we will show that our results are in good agreement with the experimental data on the Young's modulus for single crystal whiskers of 3C-SiC and the Young's and shear moduli of polycrystalline SiC. Furthermore, we will show that good agreement is obtained with values of the elastic constants that we derive from experimental data on the longitudinal and transverse sound velocities and the bulk modulus. Finally, our results for the cubic SiC elastic constants are found to be in fair agreement with the measured elastic constants of hexagonal SiC. This comparison is achieved by transforming the results in the cubic system to a trigonal system with the threefold rotation axis along the cubic  $\langle 111 \rangle$  direction.<sup>6</sup>

The other quantities we are concerned with are the band-structure deformation potentials. Since the elastic constants are obtained by studying the total energy as a function of hydrostatic and traceless strains, the resulting self-consistent band structures as a function of strain contain the desired information about the *relative* strain deformation potentials. We also obtain the optical-mode deformation potentials from the  $\Gamma_{\text{TO}}$  frozen phonon calculation. We have calculated all the relevant deformation potentials for the  $\Gamma$  and  $X$  states in the upper valence and lower conduction bands. The *absolute* deformation potential of the valence-band maximum, which then fixes all other deformation potentials on an absolute scale, cannot be obtained directly from self-consistent band-structure calculations for the bulk crystal as a function of hydrostatic strain since the latter cannot provide a unique reference potential. The absolute deformation potential was obtained by the calculation of the valence-band offset for a heterojunction consisting of strained and unstrained material.

The paper is organized as follows. The existing experimental and theoretical information about the elastic constants is briefly reviewed in Sec. II. Section III gives the necessary details about the computational method. The results for elastic constants are presented and discussed in Sec. IV. Section V is devoted to the deformation potentials and Sec. VI summarizes our conclusions.

## II. LITERATURE OVERVIEW

The literature on elastic constants of SiC is extremely inaccurate and confusing as was noted earlier by Feng, Choyke, and Powell.<sup>7</sup> To the best of our knowledge there has been no direct determination of the full set of elastic constants of 3C-SiC. This is primarily due to the unavailability of single crystals of 3C material of the required size. Larger crystals of hexagonal polytypes (mainly 6H) obtained by a modified Lely process<sup>8</sup> have, however, been available for some time. Since the pioneering work of Tairov and Tsvetkov,<sup>9</sup> a modified sublimation process has recently led to significant improvements in the quality and size of single-polytype single crystals of hexagonal SiC. Because of the similarity in the local tetrahedral bonding in the cubic and hexagonal polytypes, one may expect their elastic properties to be very closely related. A comparison of the properties of the two is made possible by transforming the elastic stiffness tensor of cubic SiC to a set of Cartesian coordinates with the  $z$  axis along the  $\langle 111 \rangle$  direction. In other words, we view the tensor as one with trigonal symmetry along  $\langle 111 \rangle$  rather than as a tensor with cubic symmetry.<sup>6</sup> The cubic  $\{111\}$  planes are physically equivalent to the basal planes  $\{0001\}$  of the hexagonal system. As is well known, the various polytypes of SiC differ only in the stacking of these planes. Recent progress has also been made in epitaxial growth of 3C-SiC films on Si  $\{001\}$  (Ref. 10) and 6H-SiC  $\{0001\}$  substrates.<sup>11</sup>

Hasselman and Batha<sup>12</sup> measured the Young's modulus of mostly 6H single crystal platelets in the basal plane to be  $\sim 450$  GPa using a bending test. This Young's modulus should correspond to  $1/S_{11}^h$ , where the super-

script  $h$  stands for hexagonal. Slack<sup>13</sup> used Hasselman and Batha's value along with an estimated value of the Poisson ratio of  $\nu = 0.25$  and the anisotropy ratio of  $A \equiv 2C_{44}/(C_{11} - C_{12}) = 1.4$  to obtain the full set of elastic constants. The resultant values are

$$C_{11} = 540, \quad C_{12} = 180, \quad C_{44} = 250 \text{ GPa},$$

from which one obtains a bulk modulus  $B = 300$  GPa. This result, however, is based on a misinterpretation of Hasselman and Batha's Young's modulus as being  $E = 1/S_{11}^c$ , with the superscript  $c$  standing for cubic, rather than the Young's modulus for a direction in the  $\{111\}$  plane which is given by<sup>14</sup>

$$E_{\{111\}} = 4/(2S_{11}^c + 2S_{12}^c + S_{44}^c). \quad (1)$$

Using the correct equation with Slack's estimates of  $\nu$  and  $A$  one obtains

$$C_{11} = 444, \quad C_{12} = 148, \quad C_{44} = 207 \text{ GPa},$$

giving a bulk modulus  $B = 247$  GPa. We will show in Sec. IV, however, that the value of  $A$  is close to 2 and that Hasselman and Batha's value for the Young's modulus is somewhat low.

Values of the Young's modulus  $E$  and shear modulus  $G$  of polycrystalline SiC measured by acoustical methods were reported by several authors.<sup>15–20</sup> These measurements were made on ceramic samples, which were polypotypic, polycrystalline, and had a certain degree of porosity. Carnahan's study<sup>18</sup> contained the samples of the lowest porosity and used the most convincing extrapolation to zero porosity. His values, which are  $E = 448$ ,  $G = 192$  GPa are thus probably the most accurate. They yield a bulk modulus  $B = 225$  GPa and an average Poisson ratio  $\nu = 0.168$ . We note that this value of  $B$  is considerably lower than the one obtained from Slack's estimate, even after the correction mentioned above. Yean and Riter,<sup>21</sup> whose paper is often cited for the experimental value of the bulk modulus, in fact, made a semiempirical estimate of the bulk modulus on the basis of molecular force constants. They find  $B = 224$  GPa, which we will show to be very close to our calculated value.

Arlt and Schodder<sup>22</sup> measured the complete set of elastic constants except for  $C_{13}$  of Lely grown single crystal 6H-SiC by two different electroacoustical methods. We will make a detailed comparison to their values which are given in Table II in Sec. IV. More recently Helbig, Karmann, and Stein<sup>23</sup> measured a few of the elastic and piezoelectric constants of both the 6H and 4H polytypes. The results for the two structures were found to be very close to each other. They also measured the temperature dependence down to 5 K. The temperature dependence up to 1000 °C has been discussed by Li and Bradt.<sup>24</sup> Essentially they use data on the temperature dependence of the polycrystalline Young's and shear moduli to deduce the temperature dependence of the cubic elastic constants. Finally, Petrovic *et al.*<sup>25</sup> measured the Young's modulus of 3C-SiC whiskers along the  $\langle 111 \rangle$  direction and found an average value of 581 GPa with a spread of  $\pm 60$  GPa.

The values of the transverse and longitudinal sound

velocities were reported by Schreiber and Soga<sup>17</sup> to be  $v_t = 7.69$  km/s,  $v_l = 12.21$  km/s for a sample with a porosity of 1%. Feldman *et al.*<sup>26</sup> obtained  $v_t = 7.24$  km/s and  $v_l = 13.27$  km/s by fitting the phonon frequencies at finite wave vectors along the  $\langle 111 \rangle$  direction to a sine curve. The phonon frequencies at  $\Gamma$  of a series of polytypes were determined by means of Raman spectroscopy and related to the phonon frequencies of cubic SiC at finite wave vectors along the  $\langle 111 \rangle$  axis assuming the appropriate folding relations between their Brillouin zones. From these sound velocities and the known density of SiC  $\rho = 3.2145$  g cm<sup>-3</sup>, one can obtain some of the elastic constants<sup>27</sup> using

$$\begin{aligned}\rho v_t^2 &= C_{44}^h = (C_{11}^c - C_{12}^c + C_{44}^c)/3, \\ \rho v_l^2 &= C_{33}^h = (C_{11}^c + 2C_{12}^c + 4C_{44}^c)/3,\end{aligned}\quad (2)$$

where the assumption is made that the sound velocities in hexagonal and cubic SiC along the above-mentioned axes are the same. This gives  $C_{44}^h = 168$  GPa and  $C_{33}^h = 566$  GPa. Combining Eq. (2) with the equation for the bulk modulus

$$B = (C_{11} + 2C_{12})/3, \quad (3)$$

one can obtain an estimate of the complete set of cubic elastic constants. Using the above value  $B = 225$  GPa, one obtains

$$C_{11} = 390, \quad C_{12} = 142, \quad C_{44} = 256 \text{ GPa.}$$

On the theory side, Tolpygo<sup>28</sup> calculated the elastic constants for the 3C phase on the basis of a semi-empirical force model with parameters obtained by interpolation between those of Si and C. These elastic constants were subsequently used by Kunc, Balkanski, and Nusimovici<sup>29</sup> in a study of the phonon spectra. Lee and Joannopoulos<sup>30</sup> presented a tight-binding model for a study of the phonon spectrum with parameters fitted to “experimental data” of the elastic constants, for which, however, they did not give a reference. It is rather unfortunate that these values whose origin we were unable to trace back were later cited as experimental values in the reference work of Landolt and Börnstein.<sup>31</sup> A very extensive set of first-principles pseudopotential calculations of the polytypes in SiC was conducted by Heine and co-workers.<sup>32,33</sup> To the best of our knowledge, however, they did not report calculated values for the elastic constants, except for the bulk modulus. They did, however, report several frozen phonon calculations. The calculation of the transverse-optical-phonon frequency at  $\Gamma$  is directly related to the internal displacement that occurs in the trigonal distortion giving the  $C_{44}$  elastic constant. We can thus compare our phonon results to theirs and to the experimental values determined by Raman spectroscopy by Olego and Cardona.<sup>34</sup>

### III. COMPUTATIONAL METHOD

We first briefly describe our procedure for calculating the elastic constants. Basically we obtain the elastic constants by calculating the ground-state energy of SiC under applied hydrostatic, tetragonal, and trigonal strains. First, we calculate the total energy as a function of vol-

ume. The equilibrium lattice constant  $a$ , the equilibrium bulk modulus  $B$ , and its pressure derivative  $B'$  are obtained by fitting the energy-volume curve to the Rose-Ferrante-Smith equation of state.<sup>35</sup> By subtracting the atomic energies calculated within the same LDA approximation but including spin polarization, we also obtain the cohesive energy. For completeness, we add a zero-point correction  $9k\Theta_D/4$  with  $\Theta_D$  the Debye frequency and  $k$  Boltzmann’s constant to the solid’s total energy. Next, from the total energy as a function of a traceless tetragonal strain, we obtain the value of  $C_{11} - C_{12}$ . Similarly, the imposition of a trigonal strain yields  $C_{44}$ . However, in calculating the total energy under the trigonal strain, the position of the two atoms in the cell is allowed to “relax” relative to each other along the  $\langle 111 \rangle$  direction, thereby yielding the so-called “internal displacement.” This displacement pattern is equivalent to that for the center of the Brillouin zone transverse optical phonon. A separate calculation of the energy as a function of the above frozen phonon displacement for zero strain gives us the phonon frequency  $\omega_{\Gamma}^{\text{TO}} = 2\pi\nu_{\Gamma}^{\text{TO}}$ . The volume dependence of this frequency gives us the corresponding mode Grüneisen parameter  $\gamma_{\Gamma}^{\text{TO}} = -(d\omega_{\Gamma}^{\text{TO}}/\omega_{\Gamma}^{\text{TO}})/(d\Omega/\Omega)$ , where  $\Omega$  is the unit cell volume. The unrelaxed ( $C_{44}^0$ ) and relaxed ( $C_{44}$ ) are related by

$$C_{44} = C_{44}^0 - \Omega^{-1}\mu \left( \omega_{\Gamma}^{\text{TO}} \zeta \frac{a}{4} \right)^2, \quad (4)$$

where  $\mu$  is the reduced mass and  $\zeta$  is the Kleinman internal displacement parameter.<sup>36</sup> See, e.g., Nielsen and Martin<sup>37</sup> for a clear exposition of these relations.

In contrast to the work of Nielsen and Martin,<sup>38</sup> we do not use the Hellman-Feynman theorem to calculate the stress tensor, but rather obtain the elastic constants directly from numerical second derivatives of the total energy. These calculations are quite demanding for the required precision. In order to stay within the harmonic range, one is limited to very small strains of the order of 2%. The total energy differences from the unstrained state are then of the order of a few mRy and a precision of a few percent in the elastic constants thus requires one to calculate the total energy difference with a precision of 0.01 mRy. In practice, we compute the energies for compressive and tensile strains of equal magnitude and take their average so as to eliminate the third-order terms. The energy differences from the unstrained state are then fitted to a parabolic expression in the strain. The phonon frequency is obtained in a similar manner by numerical differentiation as a function of the atomic displacement parameter. The full-potential linear-muffin-tin-orbital method has previously been shown to achieve the required accuracy for Si and diamond.<sup>2</sup> The method has been described elsewhere.<sup>2</sup>

A key feature of the method is the use of a multiple- $\kappa$  basis set, where  $\kappa^2$  is the kinetic energy of the muffin-tin-orbital envelope function, the part relevant to the interstitial region. The latter is a Hankel function and  $\kappa$  determines its decay length. A multiple- $\kappa$  basis set is found to be necessary because of the requirement that the muffin-tin spheres be nonoverlapping. We emphasize that the muffin-tin potential is only used in the con-

struction of the basis set. The potential and charge densities of the Hamiltonian are completely general—they are nonspherical inside the spheres and nonconstant in the interstitial region. The charge density and potential in the interstitial region are represented by a separate set of Hankel functions. This representation reduces the three-center integrals of the Hamiltonian matrix elements to two-center integrals. The required expansion coefficients are obtained by interpolation between the spheres. For details, see Methfessel.<sup>2</sup> We used a set of Hankel functions with two decay lengths ( $\kappa^2 = -1$  and  $-3$  Ry), and  $0 \leq l \leq 4$  as in the previous work for Si and diamond. The muffin-tin sphere radii were chosen to be nearly touching, that is as large as possible without overlaps and kept fixed during volume-conserving deformations and scaled according to the lattice constant for the hydrostatic deformation. They varied between 1.72 and 1.75 a.u. and we checked explicitly that the results are independent of this choice to within the limits of the accuracy we need.

For the muffin-tin-orbital basis set we used  $s$ ,  $p$ , and  $d$  orbitals for two  $\kappa$  values and centered both on the atomic and empty sphere sites at the tetrahedral interstices. This amounts to a very complete basis set of 72 orbitals per cell. The second  $\kappa$   $p$  and  $d$  orbitals were found to contribute less than 1 mRy. The addition of a third  $\kappa$   $s$  orbital to this basis set led to a linearly dependent basis set. The effect of a third  $\kappa$   $s$  orbital was studied separately for basis sets not including empty sphere orbitals. It was found to be similar to the effect of adding a single  $\kappa$   $s$  and  $p$  orbital on the empty spheres. A 38-orbital  $dds$  basis set (i.e., the set with up to  $d$ ,  $d$ , and  $s$  orbitals, respectively, for the three  $\kappa$ 's and with no use of empty sphere orbitals in the basis set) gave only a 6-mRy higher total energy. For diamond Si and C Methfessel and co-workers<sup>2</sup> found the 44-orbital per cell basis set  $ddp$  to be converged to 1 mRy. Here, we conclude that an even smaller  $dps$  basis set (of only 28 orbitals), which gives a 15-mRy higher energy (than the 72-orbital basis set), is probably adequate for most purposes since one can expect a good deal of cancellation of errors for the energy differences that one is usually concerned with. It is thus possible to eliminate the empty sphere orbitals completely and still achieve  $\sim 1$  mRy precision. For the present application, the calculation of elastic constants, where, as noted above, extreme accuracy below 1 mRy is desirable, we decided to use the large basis set (atom  $dd$ , empty sphere  $dd$ ). Since the unit cell is small, this is not prohibitive. Of the various basis sets we studied, this one yields the lowest total energy, and, from the above is judged to be absolutely converged to 1 mRy or better. Care was taken that the Brillouin zone summations and self-consistency iterations were converged to a numerical precision of 0.01 mRy.

#### IV. EQUILIBRIUM PROPERTIES AND ELASTIC CONSTANTS

Our results for the equilibrium properties, the elastic constants, and the above-discussed phonon properties for 3C-SiC are given in Table I. The equilibrium lattice con-

stant is 1% smaller than the experimental value as is usually the case in the LDA and is in excellent agreement with the previous LDA calculations of Churcher, Kunc, and Heine.<sup>32</sup> The calculated cohesive energy is about 17% larger than the experimental value,<sup>39</sup> a typical error for this quantity in the LDA. It is mainly due to the difficulty of the LDA in describing the open-shell atomic systems. The bulk modulus is in excellent agreement with the experimental and previous theoretical values. The pressure derivative of the bulk modulus is not known experimentally, but is in fair agreement with the previous calculations. These results are also in excellent agreement with previous atomic-sphere-approximation (ASA) calculations of Lambrecht and Segall<sup>40</sup> that give  $a = 4.32$  Å,  $B = 233$  GPa,  $B' = 3.8$ ,  $E_{\text{coh}} = 14.06$  eV/pair. The bulk modulus is only 4% larger and the cohesive energy 5% smaller in the ASA, which shows that the latter yields quite good results for symmetric structures. The phonon frequency and its mode Grüneisen parameter are also in excellent agreement with both previous theory and experiment. We note that Olego and Cardona actually reported a value of 1.56 for  $\gamma_{\text{F}}^{\text{TO}}$ , but as discussed in Churcher, Kunc, and Heine,<sup>32</sup> their analysis made use of an earlier incorrect value for the bulk modulus and its pressure derivative. The value quoted in the table is obtained from a new analysis of the experimental data of Olego and Cardona by Churcher, Kunc, and Heine.<sup>32</sup>

We now turn to the elastic constants and properties directly related to them. We first compare our results with the results of the semiempirical calculations of Tolpygo<sup>28</sup> and Lee and Joannopoulos.<sup>30</sup> Our value of  $C_{11}$  is somewhat larger and our  $C_{12}$  smaller than their values. The differences are such that the resulting values of  $B$  are fairly close. We note that the  $C_{44}$  values of Lee and Joannopoulos<sup>30</sup> are significantly smaller than ours and Tolpygo's. This is also reflected in their much smaller value of the anisotropy  $A$ . We note that for an isotropic crystal  $A = 1$ . Tolpygo's and our calculation yield a rather high anisotropy for 3C-SiC, for example, compared to Si and diamond C, for which Polatoglou and Methfessel's<sup>2</sup> results give  $A = 1.57$  and 1.21, respectively. These values are in fair agreement with those of Nielsen and Martin<sup>37</sup> for Si ( $A = 1.73$ ) and Nielsen<sup>41</sup> for diamond C ( $A = 1.19$ ). The value we obtain for the Poisson ratio  $\nu = -S_{12}/S_{11}$  is 0.23, which is close to Slack's estimate<sup>13</sup> of 0.25. We note that the Kleinman internal displacement parameter  $\zeta$  has not been reported before and is important for the optical-mode deformation potential, discussed in Sec. V.

We now turn to the elastic constants derived from experimental data. The agreement between our calculated elastic constants and the experimental values derived from the two sound velocities determined by Feldman *et al.*<sup>26</sup> and the bulk modulus in Sec. II, using Eqs. (2) and (3), is quite good (the deviation is  $\sim 10\%$ ). The latter also support a high value of the anisotropy close to  $A = 2$ .

Next, we compare with the data on the Young's and shear moduli and the average Poisson ratio for polycrystalline material. We note that for isotropic materials there are only two independent elastic constants and thus

the value of  $\nu$  actually follows from that of  $E$  and  $G$ . The Young's modulus  $E$ , shear modulus  $G$ , and Poisson ratio  $\nu$  for an arbitrary set of mutually perpendicular directions  $(1', 2')$  are defined by<sup>6</sup>

$$1/E = S'_{11}, \quad (5)$$

$$1/G = 2(S'_{11} - S'_{12}), \quad (6)$$

$$\nu = -S'_{12}/S'_{11}, \quad (7)$$

where<sup>6,14</sup>

$$S'_{11} = S_{11} - 2(S_{11} - S_{12} - \frac{1}{2}S_{44})(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2), \quad (8)$$

$$S'_{12} = S_{12} + (S_{11} - S_{12} - \frac{1}{2}S_{44})(l_1^2 m_1^2 + l_2^2 m_2^2 + l_3^2 m_3^2),$$

with  $(l_1, l_2, l_3)$  and  $(m_1, m_2, m_3)$  the direction cosines of the two perpendicular directions with respect to the cubic axes. Expressions for the compliances  $S_{ij}$  in terms of the stiffnesses  $C_{ij}$  and vice versa can be found in Nye.<sup>6</sup> The average over all orientations of the angular factors

$$\langle l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2 \rangle = \frac{1}{5}, \quad (9)$$

$$\langle l_1^2 m_1^2 + l_2^2 m_2^2 + l_3^2 m_3^2 \rangle = \frac{1}{5},$$

gives the so-called Reuss averages<sup>42,43</sup>

$$1/E_R = (3S_{11} + 2S_{12} + S_{44})/5, \quad (10)$$

$$1/G_R = (4S_{11} - 4S_{12} + 3S_{44})/5, \quad (11)$$

of the Young's and shear moduli relevant to polycrystalline material if there are no preferred orientations. The Reuss averages clearly correspond to orientational averages of the compliances. Different averages, the so-called Voigt averages<sup>44,43</sup> result if one averages elastic stiffnesses over orientation. Using

$$G = (C'_{11} - C'_{12})/2,$$

$$C'_{11} = C_{11} - 2(C_{11} - C_{12} - 2C_{44})(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2), \quad (12)$$

$$C'_{12} = C_{12} + (C_{11} - C_{12} - 2C_{44})(l_1^2 m_1^2 + l_2^2 m_2^2 + l_3^2 m_3^2),$$

averaging over the angular factors as in Eq. (9) and using Eq. (3) which is invariant under the averaging procedure and

$$E = 9GB/(G + 3B), \quad (13)$$

one obtains the Voigt averages

$$E_V = \frac{(C_{11} - C_{12} + 3C_{44})(C_{11} + 2C_{12})}{2C_{11} + 3C_{12} + C_{44}}, \quad (14)$$

$$G_V = (C_{11} - C_{12} + 3C_{44})/5.$$

TABLE I. Equilibrium, phonon, and elastic properties of 3C-SiC. FP-LMTO, present full-potential linear-muffin-tin-orbital calculation; CKH, Churcher, Kunc, and Heine (Ref. 32); T, Tolpygo (Ref. 28); LJ, Lee and Joannopoulos (Ref. 30) theory and (experiment); Expt., experimental values as indicated by footnotes.

Property	FP-LMTO	CKH	T	LJ	Expt.
$a$ (Å)	4.315	4.31			4.3596 <sup>a</sup>
$E_{\text{coh}}$ (eV/pair)	14.83				12.68 <sup>b</sup>
$B$ (GPa)	223	224	211	225–236 <sup>d</sup>	225 <sup>c</sup>
$B'$	3.8	3.2			
$\nu_{\text{TO}}^{\text{TO}}$ (THz)	23.88	22.75		23	23.87 <sup>e</sup>
$\gamma_{\text{TO}}^{\text{TO}}$	0.99	1.13			1.0 <sup>e</sup>
$\zeta$	0.49				
$C_{11}$ (GPa)	420		352.3	371 (363)	390 <sup>f</sup>
$C_{12}$ (GPa)	126		140.4	169 (154)	142 <sup>f</sup>
$C_{44}$ (GPa)	287		232.9	176 (149)	256 <sup>f</sup>
$A \equiv 2C_{44}/(C_{11} - C_{12})$	1.95		2.20	1.74 (1.43)	2.00 <sup>f</sup>
$\nu \equiv -S_{12}/S_{11}$	0.231		0.284	0.313 (0.299)	0.267 <sup>f</sup>
$E_{\langle 111 \rangle}$ (GPa)	603		511	423 (366)	581( $\pm 10\%$ ) <sup>g</sup>
$E_{\langle 100 \rangle}$ (GPa)	362		272	265 (271)	
$E_R$ (GPa)	476		378	342 (320)	
$E_V$ (GPa)	516		424	363 (329)	
$\bar{E}$ (GPa)	496		401	352 (325)	448 <sup>c</sup>
$G_R$ (GPa)	208		157	136 (127)	
$G_V$ (GPa)	231		182	146 (131)	
$\bar{G}$ (GPa)	219		169	141 (129)	192 <sup>c</sup>
$\bar{\nu}$	0.146		0.201	0.259 (0.261)	0.168 <sup>c</sup>

<sup>a</sup>Landolt and Börnstein (Ref. 31).

<sup>b</sup>Wagman *et al.* (Ref. 39).

<sup>c</sup>Carnahan (Ref. 18).

<sup>d</sup>Lee and Joannopoulos (Ref. 30) fit to  $B = 225$  but their resulting  $(C_{11} + 2C_{12})/3 = 236$  GPa.

<sup>e</sup>Olego and Cardona (Ref. 34) see discussion in the text for  $\gamma_{\text{TO}}^{\text{TO}}$ .

<sup>f</sup>Obtained from sound velocities of Feldman *et al.* (Ref. 26), and bulk modulus, see text.

<sup>g</sup>Petrovic *et al.* (Ref. 25).

We define an average Poisson ratio by

$$\bar{\nu} = -\bar{S}_{12}/\bar{S}_{11}, \quad (15)$$

where the averages denoted by overbars are taken over the angular factors as in Eq. (9). This value is close to  $(E_R/2G_R) - 1$  but somewhat larger than  $(E_V/2G_V) - 1$ . From the fact that

$$G_V/G_R = [13 + 6(A + 1/A)]/25, \quad (16)$$

it can be seen that the minimum value of  $G_V/G_R$  occurs for  $A = 1$ , in which case  $G_V = G_R$ . It then also follows from Eq. (13) that  $E_V \geq E_R$  with the equality holding for  $A = 1$ . Using an energy density argument Hill<sup>45</sup> showed that one expects the physical averages, here denoted by overbars, to be intermediate between the Reuss and Voigt averages.

$$E_R \leq \bar{E} \leq E_V, \quad (17)$$

$$G_R \leq \bar{G} \leq G_V.$$

From our calculations and the above considerations we conclude that

$$\bar{E} \approx 500 \text{ GPa} \pm 4\%, \quad \bar{G} \approx 220 \text{ GPa} \pm 5\%,$$

where  $\bar{E}$  and  $\bar{G}$  denote the mean value of the Reuss and Voigt averages. Our values are slightly larger than the experimental values, the discrepancy being about 10–15%. We note that values of  $E$  up to 464 GPa (Shaffer and Jun<sup>19</sup>) and  $G$  up to 203 GPa (McHenry and Tressler<sup>20</sup>) have been reported. In Table I, it can be seen that both the Reuss and Voigt averages deduced from our elastic constants are higher than the experimental values while the ones derived from Tolpygo's<sup>28</sup> or Lee and Joannopoulos's<sup>30</sup> elastic constants are lower. While the

latter are definitely too low, Tolpygo's and our results seem to be in about equally good agreement with the experimental values. The fair agreement with our calculation indicates that the random orientation hypothesis applies reasonably well to the ceramic samples. If there were a strong preferred orientation along the  $\langle 111 \rangle$  direction, for example, one would expect a significantly larger value ( $\sim 600$  GPa), while a significantly lower value ( $\sim 360$  GPa) is expected along the  $\langle 100 \rangle$  direction. These directions correspond to the maximum and minimum values. Plots of the directional dependence of the Young's and shear moduli and Poisson ratio calculated on the basis of Tolpygo's values can be found in Li and Bradt.<sup>46</sup>

Of particular significance is the comparison to the Young's modulus along the  $\langle 111 \rangle$  direction measured by Petrovic *et al.*,<sup>25</sup> since, to our knowledge, this is the only measurement that refers to single crystals of 3C-SiC. It was measured by a tensile test experiment on whiskers with their long axis in the  $\langle 111 \rangle$  direction. Our value, which differs from the average of his data by only 4%, is in much better agreement with experiment than are the other calculated values. We note, however, that Petrovic *et al.*'s experiments<sup>25</sup> give a fairly wide range of values ( $\pm 60$  GPa or  $\pm 10\%$ ), which is presumably related to experimental difficulties in measuring elastic constants from tensile tests.

According to the Orowan expression,<sup>47</sup> the theoretical cleavage strength  $\sigma_{\max}$  is given by

$$\sigma_{\max} = \frac{1}{2} \sqrt{E\gamma/a}, \quad (18)$$

where  $E$  is the Young's modulus (here along the  $\langle 111 \rangle$  direction),  $\gamma$  is the surface tension, and  $a$  is the lattice constant. The surface energy is not very well known for SiC  $\{111\}$  but can be estimated from the cohesive energy<sup>40</sup> to be  $\sim 3 \text{ J m}^{-2}$ . This leads to an estimated theoretical

TABLE II. Elastic constants of 3C-SiC transformed to trigonal symmetry along the  $\langle 111 \rangle$  direction compared to measured values of hexagonal SiC.

Property	Present	Tolpygo <sup>a</sup>	Expt. <sup>b</sup>
$C_{11}$ (GPa)	560	479	502( $\pm 4\%$ )
$C_{12}$ (GPa)	79	98	95( $\pm 30\%$ )
$C_{13}$ (GPa)	33	56	
$C_{14}$ (GPa)	66	60	$\equiv 0$
$C_{33}$ (GPa)	607	521	565( $\pm 2\%$ )
$C_{44}$ (GPa)	194	148	169( $\pm 2\%$ )
$C_{66} \equiv (C_{11} - C_{12})/2$ (GPa)	240	191	203( $\pm 3\%$ )
$S_{11}$ ( $10^{-12} \text{ m}^2/\text{N}$ )	1.933	2.389	2.03( $\pm 2\%$ ), 2.05 <sup>c</sup>
$S_{12}$ ( $10^{-12} \text{ m}^2/\text{N}$ )	-0.356	-0.619	-0.421( $\pm 5\%$ ), -0.43 <sup>c</sup>
$S_{13}$ ( $10^{-12} \text{ m}^2/\text{N}$ )	-0.086	-0.189	
$S_{14}$ ( $10^{-12} \text{ m}^2/\text{N}$ )	-0.780	-1.21	
$S_{33}$ ( $10^{-12} \text{ m}^2/\text{N}$ )	1.657	1.958	
$S_{44}$ ( $10^{-12} \text{ m}^2/\text{N}$ )	5.685	7.720	5.92
$S_{66} \equiv 2(S_{11} - S_{12})$ ( $10^{-12} \text{ m}^2/\text{N}$ )	4.378	6.016	4.915

<sup>a</sup>Tolpygo (Ref. 28) semiempirical theory.

<sup>b</sup>Arlt and Schodder (Ref. 22) average of two measurements.

<sup>c</sup>Helbig, Karmann, and Stein (Ref. 23).

strength of  $\sim 30$  GPa. The theoretical strength is thus about 5% of the Young's modulus. The highest whisker strength measured in Petrovic *et al.*'s investigation<sup>25</sup> was 23.74 GPa.

In order to compare with the experimental values of elastic constants of hexagonal SiC, we transformed our results to elastic constants corresponding to trigonal symmetry, as discussed in Sec. II. In Table II we give both the stiffnesses and compliances for which the transformation formula can be found in Nye.<sup>6</sup> We quoted the average value of the two measurements, reported by Arlt and Schodder,<sup>22</sup> along with the maximum of the quoted uncertainties, which reflect differences between different samples. Also included are the values one obtains by transforming Tolpygo's<sup>28</sup> elastic constants and the measured values of the compliances by Helbig, Karmann, and Stein,<sup>23</sup> which are in good agreement with Arlt and Schodder's.<sup>22</sup> It can be seen that our transformed  $C_{ij}$  and  $S_{ij}$  compare well with the data for 6H, given the intrinsic uncertainties in this comparison. Nevertheless, the agreement is not always within the quoted error bars. Arlt and Schodder<sup>22</sup> mention that some fragments of other polytypes and a significant concentration of impurities were present in their samples. In addition, there were voids in their material which lead to a density 1.5% lower than the ideal value. From Carnahan's study<sup>18</sup> of the elastic constants as a function of porosity of the sample, one may expect a 6% decrease in the stiffnesses from the ideal value for a porosity of 1.5%. Correcting for the porosity of Arlt and Schodder's samples<sup>22</sup> accounts for about half of the discrepancy with our calculated values. The remaining discrepancies are  $\sim 20$  GPa.

Finally, we note that the Young's modulus in the basal plane given by  $1/S_{11}^h$  from our calculated values is 517 GPa and from Arlt and Schodder's<sup>22</sup> measured  $S_{11}^h$  is 488 GPa. This value should be compared to Hasselman and Batha's<sup>12</sup> value of 450 GPa. The values for  $C_{33}^h = 566$  GPa and  $C_{44}^h = 168$  GPa, deduced from the sound velocities by means of Eq. (2), are in excellent agreement with Arlt and Schodder's<sup>22</sup> and thus also in fair agreement with our calculated values.

## V. DEFORMATION POTENTIALS

Along with the strain calculations discussed above, we obtain the corresponding deformation potentials of the energy bands. We restrict our discussion to the eigenvalues at the  $\Gamma$  and  $X$  points in the upper valence and lower conduction bands. We follow the group-theoretical notation of Kane.<sup>48</sup> For the valence-band maximum  $\Gamma_{15}^v$ , the splittings under  $\langle 001 \rangle$  and  $\langle 111 \rangle$  strains are given in Kane<sup>48</sup> Eqs. (3.39)–(3.42) after substituting the single band deformation potentials  $d_i$  for the exciton deformation potentials  $D_i$  discussed by Kane. The  $\Gamma_1$  states are only affected by hydrostatic strain. The corresponding equations for the  $X_1$ ,  $X_3$ , and  $X_5$  levels are given in Kane<sup>48</sup> Tables II and III. For the trigonal strain deformation potentials, the internal displacement of the two sublattices with respect to each other must be taken into account. The latter is related to the optical-mode de-

mation potential, which has the same symmetry as the  $\langle 111 \rangle$  strain. Following Pötz and Vogl,<sup>49</sup> we use the notation  $d_{5o}$  for the optical-mode deformation potential of the  $\Gamma_{15}$  level. The corresponding trigonal strain deformation potential  $d_5$  in the absence of the internal displacement is denoted by  $d_5'$  and the two are related by

$$d_5 = d_5' - \frac{1}{4}\zeta d_{5o}. \quad (19)$$

For the splitting of the  $X_5$  level under trigonal strain and the optical-phonon deformation, a similar decomposition is used for the deformation potential  $d_4$ . We note that a different notation due to Pikus and Bir<sup>50</sup> is often used for the deformation potentials of the  $\Gamma_{15}$  level. The correspondence is as follows:  $d_1 = \sqrt{3}a$ ,  $d_3 = \sqrt{3}b$ , and  $d_5 = \sqrt{2}d$ . To our knowledge, the only deformation potentials which have previously been calculated for SiC are  $d_5'$  and  $d_{5o}$ .<sup>51,49</sup>

The results are given in Table III. The comparison to Brey, Christensen, and Cardona's<sup>51</sup> calculation indicates that the "warped" ASA calculation, including nonspherical terms inside the atomic spheres but using a constant average potential in the interstitial region included through the combined correction term,<sup>3</sup> overestimates the nonspherical effects. The present values are close to the average of Brey, Christensen, and Cardona's pure ASA and warped ASA results. Pötz and Vogl obtained  $d_{5o} = 98.0$  eV, which is about a factor of 3 larger than our present value.

Finally, we note that for the absolute hydrostatic deformation potential, there is a "reference-level" problem. The fact is that one cannot uniquely define an electrostatic reference level in a periodic crystal.<sup>52</sup> Thus to obtain a meaningful shift of a single eigenvalue under hydrostatic strain, we need the eigenvalue in the unstrained and in the strained part of the same crystal with respect to a common reference level. We must thus consider the interface between the strained and the unstrained parts of the crystal. In general, there will be some charge transfer across this interface, and as a result the creation of an interface dipole potential. In principle, the latter can depend on the interface orientation. This results in a different long-wavelength limit for the coupling to acoustical phonons for different directions, in other words a nonanalyticity as discussed by Lawaetz.<sup>53</sup> For a recent discussion of this problem and explicit calculations, see Cardona and Christensen,<sup>54</sup> Van de Walle and Martin,<sup>55</sup> and Resta, Colombo, and Baroni.<sup>56</sup>

Basically, the problem is equivalent to a heterojunction band offset problem. Lambrecht, Segall, and Andersen<sup>57</sup> have recently developed a so-called self-consistent dipole theory of band offsets. Here, we use essentially the same approach for the absolute deformation potential of the valence-band maximum. This part of our study is performed within the ASA. We used a supercell of five layers of strained and five layers of unstrained SiC along the  $\langle 110 \rangle$  direction. The two regions are matched parallel to the interface. The spacing between the layers in the strained region was expanded by 3%. We used an intermediate interplanar spacing at the interface. The volume filling atomic sphere radii were appropriately scaled in

TABLE III. Deformation potentials of 3C-SiC (in eV).

Eigenvalue	Energy <sup>a</sup> (eV)	Deformation	FP <sup>b</sup>	ASA <sup>c</sup>	“Warped” ASA <sup>c</sup>
$\Gamma_{15}^v$		$d_1$	7.45		
		$d_3$	-3.81		
		$d_5'$	-4.61	-7.83	-3.38
		$d_{5o}$	34.62	26.45	43.56
		$d_5$	-8.85		
$\Gamma_1^c$	6.79	$d_1$	-12.99		
$\Gamma_{15}^c$	7.43	$d_1$	-4.56		
		$d_3$	1.61		
		$d_5'$	-26.18		
		$d_{5o}$	-14.50		
		$d_5$	-24.40		
$X_1^c$	1.30	$d_1^1$	8.87		
		$d_1^3$	7.72		
$X_3^c$	4.34	$d_1^1$	1.33		
		$d_1^3$	14.61		
$X_5^v$	-3.24	$d_1^1$	10.72		
		$d_1^3$	9.16		
		$d_3$	1.19		
		$d_4'$	16.19		
		$d_{4o}$	6.11		
		$d_4$	15.41		

<sup>a</sup>LDA eigenvalues with respect to  $\Gamma_{15}^v$ .<sup>b</sup>FP, present full-potential calculation. Values of  $d_1$  and  $d_1^1$  are absolute, see text.<sup>c</sup>ASA and “warped” ASA, Brey, Christensen, and Cardona (Ref. 51).

the two regions and near the interface. The overlap of the spheres does not significantly change from that in the bulk calculations.

As a test of this calculation procedure, we first applied it to Si. We obtained  $a_v = dE_v/d\ln\Omega = 2.3$  eV for the  $\langle 110 \rangle$  direction, in excellent agreement with the value 2.2 eV obtained by Resta, Colombo, and Baroni.<sup>56</sup> On the other hand, Van de Walle and Martin<sup>55</sup> reported  $0.4 \pm \sim 1$  eV for the  $\langle 110 \rangle$  direction. Resta, Colombo, and Baroni<sup>56</sup> derived an analytic expression for the orientation dependence,

$$a_v = a_v^0 + a_v^1 f(\hat{n}), \quad (20)$$

with

$$f(\hat{n}) = 3 \left( 1 - \sum_i n_i^4 \right) / 2, \quad (21)$$

where  $n_i$  are the direction cosines. The function  $f(\hat{n})$  varies between 0 and 1, its values for the  $\langle 001 \rangle$  and  $\langle 111 \rangle$  directions respectively, and has the intermediate value  $\frac{3}{4}$  for the  $\langle 110 \rangle$  direction. This is not the case in Van de Walle and Martin's calculation,<sup>55</sup> whose values for  $\langle 001 \rangle$  and  $\langle 111 \rangle$  are in good agreement with those of Resta, Colombo, and Baroni.<sup>56</sup> There thus seems to be a prob-

lem with Van de Walle and Martin's value for the  $\langle 110 \rangle$  direction. We note that in order to obtain an accuracy of 1 eV in the deformation potentials, one needs the band offset with an accuracy of 0.01 eV for a 1% strain. This is fairly demanding.

For SiC, we obtain  $a_v = 4.3$  eV. In Resta, Colombo, and Baroni's analysis of the problem, the functional form of the orientation dependence can be worked out analytically for the case of nonpolar materials. The maximum magnitude of the angular variation is found numerically to be  $a_v^1 = 1.5$  eV for Si. For a polar material like SiC, this analysis does not apply. However, orientation effects on similar isovalent heterojunction band offsets have been found to be quite small (of the order of 0.02 eV at most).<sup>58</sup> This indicates that the orientation effect on the absolute deformation potential is probably of the order of magnitude of a few eV.

We have also tested the dielectric midgap approach of Cardona and Christensen<sup>54</sup> for the calculation of  $a_v$ . For Si, they obtain a value of -1.6 eV and for SiC we obtain -1.0 eV. The error in this approach which is of the order of several eV may seem to be very large. However, it is consistent with an uncertainty of the order of a few 0.1 eV in the band offsets, which is a reasonable estimate of the accuracy of this type of model.



For consistency of notation, we have written the hydrostatic deformation potential of the  $\Gamma_{15}^v$  valence-band maximum as  $d_1 = \sqrt{3}a_v$  in Table III. The absolute values of  $d_1$  and  $d_1^1$  in Table III for the other states are obtained from a full-potential calculation for the *relative* shifts with respect to the valence-band maximum and the *absolute* shift of the valence-band maximum discussed here.

## VI. CONCLUSIONS

In conclusion, we have calculated the elastic constants and the deformation potentials of important critical point eigenvalues of 3C-SiC. The agreement between the results found by experiment and by previous high-quality first-principles calculations and our calculated results for properties such as the transverse-optic-phonon frequency and its mode Grüneisen parameter, the lattice constant, the bulk modulus and its pressure derivative demonstrates the high accuracy of the present calculations. We have shown that our calculated elastic constants are consistent with known experimental values for hexagonal and polycrystalline SiC and 3C-SiC whiskers. The discrepancies are typically  $\sim 10\%$ . In view of the experimental difficulties (somewhat impure and slightly porous samples) and the intrinsic uncertainties associated with a comparison between 6H- or polycrystalline and 3C-SiC, this degree of agreement should be considered very good. Of course, a more direct comparison between a calculation for 6H and the measurements for 6H would, in principle, be preferable to the comparison between calculated 3C and measured 6H. This is in principle possible although the calculations would be significantly more time-consuming since the 6H cell contains 12 atoms. From Heine and co-workers' work,<sup>32,33</sup> it is known that the energy differences between the polytypes are extremely small, of the order of meV/atom. To investigate the intrinsic differences between the elastic constants of the polytypes, that is, of the second derivatives with respect to strain of these already very small energy differences, is a formidably challenging problem. Helbig, Karmann, and Stein's experimental study<sup>23</sup> did not reveal any significant difference between the 4H and 6H polytypes. Conceivably some changes could occur due to the varying nonideality of the  $c/a$  ratio in the polytypes. Cheng, Heine, and Needs<sup>33(d)</sup> investigated the effects of atomic relaxation and deviations from the ideal  $c/a$  ratio on the energies of the polytypes and found the relaxation energies to be of order 1 meV/pair of atoms. A measure of the expected deviations between, on the one hand, the cubic and rhombohedral (trigonal) polytypes and, on the other hand, the hexagonal polytypes of SiC, is the mag-

nitude of  $C_{14}$  which is zero by symmetry in the latter but not in the former. Its value is here found to be 66 GPa for the transformed 3C which is fairly small, but not negligible. The comparison between our present estimates of the transformed cubic elastic constants and the hexagonal measurements corrected for porosity indicate that the expected changes on the other elastic constants are smaller than this (of order 30 GPa). The hexagonal polytype with the smallest unit cell where this symmetry effect could be investigated is the 2H polytype which has the wurtzite structure with four atoms per cell. A calculation of the elastic constants of 2H-SiC would be feasible and interesting from this point of view.

Using an estimate of the surface energy based on our calculated cohesive energy, we have also calculated the theoretical cleavage strength according to Orowan's expression and obtained a value 25% larger than the experimental strength, which is to be considered fair agreement for this quantity. Further experimental work on the elastic constants of high-quality crystals of 6H and 3C SiC is clearly desirable. This is especially so in view of the recent improvements in the crystal growth of 6H SiC.

The complete set of deformation potentials of the upper valence and lower conduction bands at  $\Gamma$  and  $X$  was here calculated for the first time. The rather poor agreement with previous more approximate calculations of  $d_{\frac{1}{2}}$  and  $d_{5_0}$  of the valence-band maximum illustrates the difficulty of calculating these deformation potentials. Our value for the absolute deformation potential of Si along the  $\langle 110 \rangle$  direction was shown to be in excellent agreement with previous first-principles calculations and should thus give some credibility to our values obtained for SiC. To our knowledge, there are no experimental values available for the deformation potentials in 3C-SiC. In view of their importance for transport and optical properties, we hope that the present theoretical results will stimulate further experimental work in this area.

*Note added in proof.* Recently, Tersoff [J. Tersoff, Phys. Rev. B **39**, 5566 (1989)] computed the elastic constants of SiC using a semiempirical interatomic potential and obtained the values:  $C_{11} = 420$ ,  $C_{12} = 120$ , and  $C_{44} = 260$  GPa, in close agreement with our calculations.

## ACKNOWLEDGMENTS

The work at CWRU was supported by NASA (Grant No. NCC-3-25) and DARPA-ONR (Grant No. N00013-86-K-0773). M.v.S. was supported by ONR (Grant No. N00014-89-K-0132). The computations were performed at the OSC (PDS-145). We wish to thank Dr. J. A. DiCarlo for bringing some of the experimental literature on SiC elastic constants to our attention.

<sup>1</sup>See, e.g., *Amorphous and Crystalline Silicon Carbide and Related Materials*, Vol. 34 of *Proceedings in Physics*, edited by G. L. Harris and C. Y.-W. Yang (Springer, Berlin, 1989), and references therein.

<sup>2</sup>M. Methfessel, Phys. Rev. B **38**, 1537 (1988); M. Methfessel, C. O. Rodriguez, and O. K. Andersen, *ibid.* **40**, 2009

(1989); H. M. Polatoglou and M. Methfessel, *ibid.* **41**, 5898 (1990); M. Methfessel and M. van Schilfgaarde (unpublished).

<sup>3</sup>O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

<sup>4</sup>P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

- <sup>5</sup>U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).
- <sup>6</sup>J. F. Nye, *Physical Properties of Crystals* (Clarendon, Oxford, 1957), Chap. VIII.
- <sup>7</sup>Z. C. Feng, W. J. Choyke, J. A. Powell, *J. Appl. Phys.* **64**, 6827 (1988).
- <sup>8</sup>J. A. Lely, *Ber. Dtsch. Keram. Ges.* **32**, 229 (1955).
- <sup>9</sup>Y. M. Tairov and V. F. Tsvetkov, *J. Cryst. Growth* **43**, 209 (1978).
- <sup>10</sup>S. Nishino, J. A. Powell, and H. A. Will, *Appl. Phys. Lett.* **42**, 460 (1983).
- <sup>11</sup>J. A. Powell, D. J. Larkin, L. G. Matus, W. J. Choyke, J. L. Bradshaw, L. Henderson, M. Yoganathan, J. Yang, and P. Pirouz, *Appl. Phys. Lett.* **56**, 1353 (1990).
- <sup>12</sup>D. P. H. Hasselman and H. D. Batha, *Appl. Phys. Lett.* **2**, 111 (1963).
- <sup>13</sup>G. A. Slack, *J. Appl. Phys.* **35**, 3460 (1964).
- <sup>14</sup>W. A. Brantley, *J. Appl. Phys.* **44**, 534 (1973).
- <sup>15</sup>J. B. Wachtman, Jr. and D. G. Lam, *J. Am. Ceram. Soc.* **42**, 254 (1959).
- <sup>16</sup>S. M. Lang, *Properties of High-Temperature Ceramics and Cermets—Elasticity and Density at Room Temperature*, Natl. Bur. Std. (U.S.) Circ. No. 6 (U.S. GPO, Washington, DC, 1960).
- <sup>17</sup>E. Schreiber and N. Soga, *J. Am. Ceram. Soc.* **49**, 342 (1966).
- <sup>18</sup>R. D. Carnahan, *J. Am. Ceram. Soc.* **51**, 223 (1968).
- <sup>19</sup>P. T. B. Shaffer and C. K. Jun, *Mater. Res. Bull.* **7**, 63 (1972).
- <sup>20</sup>K. D. McHenry and R. E. Tressler, *J. Am. Ceram. Soc.* **63**, 152 (1980).
- <sup>21</sup>D. H. Yean and J. R. Riter, Jr., *J. Phys. Chem. Solids* **32**, 653 (1971).
- <sup>22</sup>G. Arlt and G. R. Schodder, *J. Acoust. Soc. Am.* **37**, 384 (1965).
- <sup>23</sup>R. Helbig, S. Karmann, and R. A. Stein, *Extended Abstracts of The Electrochemical Society* (Electrochemical Society, Hollywood, FL, 1989), p. 718.
- <sup>24</sup>Z. Li and R. C. Bradt, *J. Mater. Sci.* **22**, 2557 (1987).
- <sup>25</sup>J. J. Petrovic, J. V. Milewski, D. L. Rohr, and F. D. Gac, *J. Mater. Sci.* **20**, 1167 (1985).
- <sup>26</sup>D. W. Feldman, J. H. Parker, Jr., J. W. Choyke, and L. Patrick, *Phys. Rev.* **173**, 787 (1968).
- <sup>27</sup>B. P. Pandey and B. Dayal, *Phys. Status Solidi B* **58**, K53 (1973).
- <sup>28</sup>K. B. Tolpygo, *Fiz. Tverd. Tela (Leningrad)* **2**, 2655 (1960) [*Sov. Phys.—Solid State* **2**, 2367 (1961)].
- <sup>29</sup>K. Kunc, M. Balkanski, and M. A. Nusimovici, *Phys. Status Solidi B* **72**, 229 (1975).
- <sup>30</sup>D. H. Lee and J. D. Joannopoulos, *Phys. Rev. Lett.* **48**, 1846 (1982).
- <sup>31</sup>*Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, New Series, Group III, Vol. 17a (Springer, Berlin, 1982), p. 49.
- <sup>32</sup>N. Churcher, K. Kunc, and V. Heine, *J. Phys. C* **19**, 4413 (1986).
- <sup>33</sup>(a) C. Cheng, R. J. Needs, and V. Heine, *J. Phys. C* **21**, 1049 (1988); (b) J. J. A. Shaw and V. Heine, *J. Phys. Condens. Matter* **2**, 4351 (1990); (c) C. Cheng, V. Heine, and I. L. Jones, *ibid.* **2**, 5097 (1990); (d) C. Cheng, V. Heine, and R. J. Needs, *ibid.* **2**, 5115 (1990).
- <sup>34</sup>D. Olego and M. Cardona, *Phys. Rev. B* **25**, 1151 (1982).
- <sup>35</sup>J. H. Rose, J. R. Smith, F. Guinea, and J. Ferrante, *Phys. Rev. B* **29**, 2963 (1984).
- <sup>36</sup>L. Kleinman, *Phys. Rev.* **128**, 2614 (1962).
- <sup>37</sup>O. H. Nielsen and R. M. Martin, *Phys. Rev. B* **32**, 3792 (1985).
- <sup>38</sup>O. H. Nielsen and R. M. Martin, *Phys. Rev. B* **32**, 3780 (1985).
- <sup>39</sup>D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Baily, and R. H. Shumm, *Selected Values of Chemical Thermodynamics Properties, Tables for the First Thirty-Four Elements in the Standard Order of Arrangement*, Natl. Bur. Std. (U.S.) Tech. Note No. 270-3 (U.S. GPO, Washington, DC, 1968).
- <sup>40</sup>W. R. L. Lambrecht and B. Segall, *Phys. Rev. B* **42** (1991); **43**, 7070 (1991).
- <sup>41</sup>O. H. Nielsen, *Phys. Rev. B* **34**, 5808 (1986).
- <sup>42</sup>A. Reuss, *Z. Angew. Math. Mech.* **9**, 55 (1929).
- <sup>43</sup>H. B. Huntington, in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 7, pp. 213–351, in particular p. 317.
- <sup>44</sup>W. Voigt, *Lehrbuch der Kristallphysik* (Teubner, Leipzig, 1928).
- <sup>45</sup>R. Hill, *Proc. Phys. Soc. London Sect. A* **65**, 349 (1952).
- <sup>46</sup>Z. Li and R. C. Bradt, in *Ceramic Transactions, SiC 1987*, edited by J. D. Cawley and G. E. Semeler (American Ceramic Society, Westerville, OH, 1989), Vol. 2, p. 313.
- <sup>47</sup>A. Kelly, *Strong Solids*, 2nd ed. (Clarendon, Oxford, 1973), Appendix A.
- <sup>48</sup>E. O. Kane, *Phys. Rev.* **178**, 1368 (1969).
- <sup>49</sup>W. Pötz and P. Vogl, *Phys. Rev. B* **24**, 2025 (1981).
- <sup>50</sup>G. E. Pikus and G. L. Bir, *Fiz. Tverd. Tela (Leningrad)* **1**, 1642 (1959) [*Sov. Phys.—Solid State* **1**, 1502 (1959)].
- <sup>51</sup>L. Brey, N. E. Christensen, and M. Cardona, *Phys. Rev. B* **36**, 2638 (1988).
- <sup>52</sup>L. Kleinman, *Phys. Rev. B* **24**, 7412 (1981).
- <sup>53</sup>P. Lawaetz, *Phys. Rev.* **183**, 730 (1969).
- <sup>54</sup>M. Cardona and N. E. Christensen, *Phys. Rev. B* **35**, 6182 (1987).
- <sup>55</sup>C. G. Van de Walle and R. M. Martin, *Phys. Rev. Lett.* **62**, 2028 (1989).
- <sup>56</sup>R. Resta, L. Colombo, and S. Baroni, *Phys. Rev. B* **41**, 12 358 (1990).
- <sup>57</sup>W. R. L. Lambrecht, B. Segall, and O. K. Andersen, *Phys. Rev. B* **41**, 2813 (1990).
- <sup>58</sup>W. R. L. Lambrecht and B. Segall, *Phys. Rev. B* **41**, 8353 (1990).